Pressure as a parameter in the study of dilute magnetic alloys

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Abstract

A large body of data is reviewed, which illustrates how the high pressure technique can be used to gain information about the magnetic and electronic state of dilute magnetic alloys. Values for the pressure dependence of the elementary effective exchange interaction between a magnetic impurity spin and the conduction electron sea are extracted from the data and tabulated for a number of extremely dilute alloys containing both transition metal and rare earth impurities. Results of experiments on host alloy series employing 'lattice pressure' are compared to the present 'external pressure' results and critically analysed; it is shown how such a comparison can be used to give information about the extent of the electronic screening around an impurity potential. The effect of pressure on impurity–impurity interactions in spin glasses is also examined; a comparison of the pressure studies on extremely dilute alloys to those on spin glasses allows an estimate of the nature of the interaction mechanisms important in the latter case. Evidence for a pressure-induced spin glass to Kondo transition in LaCe is also presented. It is suggested that the present results fit into a larger picture that magnetism, when present, tends to be weakened when high pressure is applied.

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§ 1. INTRODUCTION

In recent years the high pressure technique has come to be recognized as a particularly valuable tool for studying the electronic and magnetic properties of solids. Owing to rapid advances in technology, it is now possible to employ under high pressure conditions almost every solid state diagnostic tool normally used at ambient pressure. The high pressure technique is perhaps best known for its capability to bring about transformations from one solid state to another such as insulator-to-metal, magnetic-to-non-magnetic, or crystal-structure transitions. A further, although less dramatic, capability of this technique is easily overlooked, namely, the ability to generate an often small but well-controlled continuous variation of the pertinent solid state parameters such as the density of states, exchange interactions, or electron–phonon coupling, allowing a critical evaluation of the volume dependences predicted by a particular theoretical model. Indeed, the interatomic distance, whose change under pressure can be directly measured, is a basic parameter in all theories of condensed matter. Varying solid state parameters by adjusting the chemical composition of a system can effect relatively large changes in the properties, but has the distinct disadvantage that these changes are less well defined than in analogous pressure studies. The former method is often very useful for quickly establishing the general trends of a particular physical phenomenon, subsequent pressure experiments allowing then an exacting comparison with theory. A particularly elegant example of the usefulness of the pressure technique is provided by high precision measurements of the pressure dependence of the Fermi surface to test the accuracy of band structure theory [1].

Before turning to the topics of central interest to this paper, let us first consider, in a general way, how magnetism changes with increasing atomic density. In magnetism, high pressures can cause changes in the exchange interactions, bandwidths, crystal field splittings, anisotropy parameters, and magnetic moments, to name a few [2]. It is well known that the majority of free atoms possess a magnetic moment which is often lost when the atoms condense to form a liquid or solid. This overall tendency for magnetism to weaken with increasing atomic density is also operative in solids under pressure. In local moment systems, such as Ce or SmS, pressures of only a few kilobars (1 bar = 0.987 atm = 10^5 Pa) are sufficient to at least partially squeeze out a magnetic 4f-electron [3]. With sufficiently high pressures it should be possible to completely squeeze out one or more inner electrons in any local
moment system; a transition from local moment to itinerant magnetism is also conceivable. In an itinerant or band ferromagnet the condition for the occurrence of magnetism at $T = 0$ K, the so-called Stoner criterion, is that $IN(E_f) > 1$, where $I$ is the exchange energy and $N(E_f)$ the density of states. For a free-electron gas with sample volume $V$, Bloch [4] has shown that $I \propto V^{-1/3}$ and $N(E_f) \propto V^{+2/3}$, so that one has $IN(E_f) \propto V^{+1/3}$, which decreases with pressure. For a free-electron gas, therefore, the high density or high pressure state is non-magnetic [5]. An analogous conclusion is reached for the more relevant case of a d-band ferromagnet where the density of states, which here in a certain approximation is proportional to $V^{+5/3}$, is believed to decrease faster with pressure than the exchange interaction $I$ increases [6]. Even the weak Pauli paramagnetism $\chi_p \propto N(E_f)$ and the atomic diamagnetism $\chi_{dia} \propto \langle r^2 \rangle$ should, within certain limits, decrease in magnitude with pressure, as both $N(E_f)$ and the mean square radius of the electron orbitals $\langle r^2 \rangle$ decrease. A reduction in magnetism, when present, with increasing atomic density would thus appear to be a general result. On the other hand, as will be discussed in § 5, a given non-magnetic system could become magnetic if sufficient pressure were applied to remove inner shell electrons; magnetism thus should behave cyclically under pressure, rising and falling.

Magnetism’s path to the gallows is diverse and in most systems truly enormous pressures (in the Megabar range) are required for a proper execution; indeed, the reduction in the saturation magnetization of Fe, Ni, or Co with pressure is only about 0.02% per kilobar [7]. An exception are the so-called weak itinerant ferromagnets which according to the Stoner criterion are just barely magnetic and possess only a small fraction of a Bohr magneton per atom. In ZrZn$_2$, for example, Smith et al. [8] have shown that pressures of only a few kilobars are sufficient to drive the Curie temperature $T_0$ to zero. A rather general expression for the pressure dependence of the Curie temperature, $dT_0/dP = AT_0 - B/T_0$, where $A$ and $B$ are positive constants, have been derived by Wohlfarth [9]. It follows that for systems with relatively small $T_0$, like ZrZn$_2$ with $T_0 (0) = 16.9$ K, $dT_0/dP$ should be negative, whereas for larger values of the Curie temperature, $dT_0/dP$ eventually goes through zero and becomes positive. These and other predictions of theory have received striking verification by experiment [10]. In addition, from $T_0(P)$ one can extract the value of the constant $B$ which is proportional to the ratio $I_{eff}/I_b$ of the exchange energy including correlation corrections to the ‘bare’ exchange energy [6]. High pressure experiments can thus give direct information about the importance of many-body correlation effects and have shown them to be appreciable [6]. Such studies are also an example of how the high pressure technique can be used to help decide whether an itinerant or local moment picture is more appropriate for a particular magnetic system. The behaviour of dilute local moment systems under pressure is the main topic of this paper.

The scope of the present review will be restricted for the most part to the use of high pressure as a parameter in dilute magnetic alloys containing at most a few percent of magnetic impurities statistically distributed within a non-magnetic host. The object of paramount interest in these studies is the interaction of a magnetic impurity with its surroundings, which are composed of other magnetic impurities and host conduction electrons, and how this interaction depends on pressure or, equivalently, molar volume $V$. The local moment picture is found to give a good description of the observed phenomena for a large class of systems. In a magnetic alloy of extreme dilution, like Au–5 p.p.m. Fe, the interaction $J$ of the impurity spin...
with the conduction electron spins of the host matrix leads, especially if $J$ is negative, to clear anomalies in the physical properties. In this concentration range impurity–impurity interactions are unimportant. Although the basic types of mechanisms contributing to $J$ are believed to be known, the actual calculation of $J$ from first principles is a very difficult problem [11]. The application of pressure causes $J$ to change and allows a determination of the volume dependence $J(V)$ which should be easier to calculate accurately than the absolute magnitude of $J$ itself. In the absence of a good theory of the exchange interaction, searching for trends in the behaviour of $J(V)$ for a large number of systems could be useful in helping to decide which approximations are appropriate when setting up a suitable theoretical model. In § 3 the results of a large number of relevant experiments on very dilute magnetic alloys under pressure, both by the author and others, are analysed in a consistent manner. The derived values of $J(V)$ are then collected and critically compared. Of particular interest is a comparison of the present ‘external pressure’ experiments with those on alloy series where ‘lattice pressure’ plays an important role; such a comparison reveals to what extent the properties of such alloy series depend merely on the lattice parameter or on other alloy variables such as the average number of valence electrons, the ionic radii of the host atoms, etc.

As the concentration of magnetic impurities is increased from the very dilute limit, interactions between the impurity spins gain in importance, leading frequently to magnetic ordering at a temperature $T_0$. Not only the ordering temperature $T_0$ but also the nature of this ordering (spin glass, ferromagnetic, etc.) and the kind of relevant interaction mechanism can depend on the concentration. A determination of the relative importance of the various possible interaction mechanisms over the entire concentration range is essential for an understanding of the magnetism of such systems on a microscopic level. Pressure studies are especially well suited for this purpose because each interaction mechanism (direct exchange, super-exchange, RKKY-exchange, dipole–dipole interaction, etc.) has its own characteristic pressure dependence which is mirrored in the way $T_0$ changes with pressure. In the case of the RKKY-mechanism a comparison of the pressure dependences of the parameters in the dilute and concentrated limits can give information about which angular momentum components of $J$ are predominant. In addition, in those cases where the relevant interaction mechanism and its pressure dependence are known, a pressure experiment allows a direct check of the functional dependence of a particular theory on the interaction parameters. The results of extensive pressure studies on metallic spin glasses are collected in § 4.

Finally, it will be shown that pressure can be used to study a particularly exotic type of magnetic phase transition, namely, that from an ordered (spin glass) state to a single-impurity (Kondo) state. This transition is but a specific example of the general trend from magnetism to non-magnetism with increasing pressure. Such experiments are useful for testing theoretical models of this transition such as those developed by Larsen [12] or Doniach [13]. Systematic studies of the effect of pressure on the magnetic state of both ordered and very dilute single-impurity systems, and transitions between the two, should, by extrapolation, be useful in understanding the even more complicated but quite widespread phenomenon of valency fluctuations in more concentrated magnetic systems.

In the next section some aspects of modern high pressure techniques are discussed with the emphasis on those techniques used by the author. A brief discussion of the measurement techniques for high accuracy electrical resistivity
measurements from 1–300 K is also included. The electrical resistivity, which can be measured to very high precision under high pressure conditions, is the physical property which is perhaps best suited for a quantitative study of the pressure dependence of the magnetic state in extremely dilute alloys.

§ 2. Experimental methods

2.1. Generation of high pressures

The highest pressures achieved under controlled laboratory conditions to date lie near 10 Mbar and are generated using either shock-wave or magnetic compression high pressure techniques. Employing the latter technique, Hawke et al. [14] have recently found strong evidence that hydrogen becomes metallic at a pressure of approximately 2 Mbar, neon remaining insulating to an estimated pressure of more than 5 Mbar. In such 'dynamic' pressure techniques the measuring time is only of the order of microseconds. A 'static' pressure technique, where the measuring time is arbitrarily long, is certainly better suited for carefully controlled studies of the effect of pressure on solid state properties over a wide temperature range. The generation of static pressures as large as ~ 1.3 Mbar has, in fact, been claimed by Mao and Bell [15]. The static pressure techniques can be subdivided into two major types, quasi-hydrostatic and hydrostatic, depending on whether a solid or a liquid (or gas) respectively, is used as the pressure transmitting medium. A review of static pressure techniques suitable for low temperature studies has recently been given by Paureau [16].

2.1.1. Quasi-hydrostatic pressure

A cross section of the type of pressure cell developed by Schilling et al. [17] is shown in fig. 1. Two samples are connected in series with a Pb-manometer whose superconducting transition temperature $T_c$ is a sensitive function of pressure. The $T_c$ versus pressure scale used here is somewhat revised from that of Eichler and Wittig [18] and includes recently re-determined pressure fixed points of Bi and Pb [19, 20]: 7.20 K—0 kbar, 6.21 K—25 kbar, 4.70 K—74 kbar, 3.60 K—130 kbar. Six electrical leads are introduced into the cell to allow high accuracy four-point electrical resistivity measurements on both samples. The samples themselves are located between two epoxy discs which serve as the pressure transmitting medium. Even such relatively soft solids as epoxy resin, NaCl, AgCl, and soapstone can support sizeable shear stress components [21] which can lead to the build-up of pressure inhomogeneities and local shear strains in the sample. The width of the superconducting transition $\Delta T_c$ of the Pb-manometer gives a measure of the pressure inhomogeneity in the pressure cell. Typical values of the pressure inhomogeneity over a given sample as estimated from $\Delta T_c$ lie between 2 and 7% of the measured pressure. The annular pyrophyllite gasket serves to contain the inner cell and restricts the outward extrusion of the epoxy discs and samples. As seen in fig. 1 (b), the pressure cell is mounted in a steel belt which gives it radial support. An epoxy outer gasket positions the pyrophyllite ring with the steel belt, providing further support to the sample and reducing the steepness of the pressure gradient. Pressure is applied to the cell by two opposing Al$_2$O$_3$ or B$_4$C anvils mounted in CuBe support rings. Application of force to the anvils drives them together, compressing the pressure cell and leading to a build-up of pressure on the samples. The rate of increase of pressure with applied force depends on the detailed past history of the pressure cell.
Fig. 1

(a) Top view of quasi-hydrostatic pressure cell of Schilling et al. [17]. Samples are sandwiched between two epoxy discs within a pyrophyllite gasket. (b) Side view of same pressure cell mounted in steel belt. Opposing anvils squeeze cell generating high pressures. (c) Side view of six-bolt high pressure clamp suitable for quasi-hydrostatic cell (fig. 1 (a) and (b)) or hydrostatic cell (fig. 2). Force generated by torquing bolts is transmitted through steel ball and guide-piston to opposing anvils. Numbers designate: 1 steel ball, 2 CuBe pressure clamp, 3 heater, 4 guide-piston, 5 hardened steel plate, 6 tungsten-carbide anvils, 7 thermometer, 8 copper block thermal sink, 9 clamp support-tube holder, 10 guide-piece for 16, 11 CuBe nuts, 12 hardened steel spring supports, 13 plate-springs, 14 ball bearing, 15 CuBe bolt (18 mm diameter thread), 16 bolt torque-tube, 17 strain gauges.

but usually lies between 1–2 kbar/ton. The incorporation of a Pb-manometer in the pressure cell is thus essential for an accurate determination of the pressure at low temperatures.

Applying or removing pressure from the pressure cell was found to lead to a certain amount of cold-working of the samples, resulting in a moderate alteration of the sample dimensions and an increase of the defect scattering in the resistivity. The magnitude of these unwanted changes depends on the pressures involved and on the past history of the pressure cell. Owing to the nature of the present investigations, it is essential to minimize any changes in the length/area factor $\alpha$ of the samples. One way to estimate changes in $\alpha$ is to include within the pressure cell an additional sample whose resistivity has a very low intrinsic pressure dependence. This is the case for a Au–0.5at.% V alloy where at room temperature we estimate that $-(\Delta \rho/\rho \Delta P) < +0.04\%/\text{kbar}$ [22]. In order to minimize both changes in $\alpha$ and variations in the amount of defect scattering in measurements at different pressures,
the pressure cell was initially preloaded to 90 kbar and then unloaded to zero pressure before commencing with high pressure measurements. The success of this procedure will be evident from the results of experiments presented in the next section. The change in $\alpha$ upon reloading to 100 kbar is estimated to be less than a few per cent. Related types of quasi-hydrostatic pressure cells suitable for small variation in $\alpha$ have been developed by Klein [23], Olijnyk and Crone [24], and Willer and Crone [25]. A 'beltless' pressure cell suitable for pressures to 160 kbar was introduced some time ago by Wittig [26], Bundy has recently used compax-tipped anvils to extend the pressure region to 500 kbar [19]. In the latter two cells the value of $\alpha$ cannot be controlled as well as in the present cell (fig. 1).

To compress the pressure cell a force of up to 30 t is generated and applied to the anvils by a 15 kg CuBe six-bolt high-pressure clamp shown in fig. 1 (c) adapted by Zimmer and Schilling [27] from a design of Eichler and Wittig [18]. Tightening two opposing bolts simultaneously, one with left-handed the other with right-handed thread, results in negligible net torque on the thin-walled clamp support tube and generates force through the large steel ball onto the guide-piston which presses the anvils together. The force can be monitored continuously by strain gauges mounted on the piston. Upon cooling from room temperature to liquid helium temperatures the force increases by about 30%. The force between the anvils can be changed at any temperature with the clamp mounted in the cryostat by lowering two stainless steel tubes with nuts on the lower end onto the clamp bolt heads. However, measurements are normally carried out at fixed pressure with variable temperature, the applied pressure being changed at room temperature after each low temperature run. It is essential that the force be only changed at room temperature because the increased hardness of the epoxy discs at low temperatures would lead to sizeable pressure gradients across the samples. For experiments where it is necessary to store forces larger than 30 t, the present clamp can be used in conjunction with a hydraulic press. A standard Chester-Jones type clamp is also available which can store 60 t of force and permits reaching pressures of approximately 100 kbar with the present cell.

2.1.2. Hydrostatic pressure

In a conventional hydrostatic pressure cell the sample is placed in a sealed Teflon bucket filled with alcohol which is then inserted into a cylindrical high pressure chamber and compressed on either side by two opposing pistons [16]. This type of cell is normally limited to pressures less than $\sim$30 kbar owing to the yield strength of presently available high pressure materials. Fasol and Schilling [28] have recently developed a new hydrostatic pressure cell for precise electrical measurements at low temperatures to pressures as high as 90 kbar. A cross-section of this pressure cell is shown in fig. 2. This cell is an extension of the diamond-anvil cell [16] to allow the generation of high hydrostatic pressures in a relatively large volume (\(\sim 3 \text{ mm}^2\)) into which six or more electrical leads can be introduced. Two supported WC-anvils are pressed into a hardened CuBe or steel gasket. A bore in the centre of the gasket contains the pressure-transmitting fluid and the sample arrangement. The volume of the bore decreases upon application of force to the anvils, generating hydrostatic pressure in the liquid. As a pressure transmitting fluid 4 : 1 methanol–ethanol is used. Viscosity measurements by Piermarini et al. [29] have shown that the relaxation time of this mixture at room temperature is negligible for our purposes up to 90 kbar and that non-hydrostatic stresses do not occur below 100 kbar [21]. The volume reduction of the alcohol mixture at atmospheric pressure upon cooling from 300 to...
Side view of hydrostatic pressure cell of Fasol and Schilling [28]. Two tungsten-carbide anvils press into a hardened CuBe or steel gasket. Six wires are embedded in radial grooves; the samples, mounted on a plastic disc, and the pressure-transmitting fluid are contained in a 2 mm diameter bore in the centre of the gasket.

80 K is approximately 30%. Electrical leads are introduced into the 2 mm diameter pressure chamber through shallow grooves milled into the metal gasket. The grooves are filled with epoxy resin which insures electrical insulation as well as sealing off the pressure chamber. The two samples, one of which is a Pb-manometer, are located on either side of a 1 mm diameter plastic disc. All leads to and between the samples pass through holes in this disc which thus provides not only electrical insulation but also mechanical rigidity. Two current and four voltage leads to the two samples are necessary for a precise four-terminal resistivity measurement. To date, accurate four-point resistivity measurements have been carried out on two samples simultaneously to pressures as high as 90 kbar at room temperature and 45 kbar at liquid helium temperature in separate pressure cells. Higher pressures at low temperatures are currently being attempted. Fasol et al. [30] have recently used this new pressure cell to study superconductivity and phase transitions in non-transforming V₃Si single crystals.

2.2. Measurement of electrical resistivity

The cryostat used in the high-pressure measurements is of standard design. A separate exchange gas tank between the liquid N₂ reservoir and He dewar allows slow, controlled cooling of the clamp to 80 K. Temperatures above 40 K are measured with a Platinum-resistor and below 40 K with a calibrated Germanium-resistor. Both sensors are located adjacent to the samples in an anvil support ring as shown in fig. 1 (c). The relative accuracy of the temperature measurement below 4:2 K is at least 0.03 K and better than 0.5% at any temperature. All critical electrical leads are thermally anchored to a copper block attached directly onto the massive high pressure clamp and pass out of the cryostat through the clamp support tube. All leads are thermocouple quality copper wire and are electrically shielded over their entire length resulting in low thermal voltages and low noise.

Resistivity measurements are carried out using the standard four-terminal technique. The current source from North Hills Electronics is constant to better than 1:10⁵ during the 10 hours needed to make a 300–1 K temperature run. The sample
potentials are first amplified by a temperature stabilized Amplispot galvanometric
cell amplifier and then displayed on a Solatron LM 1490 5½-digit digital-
voltmeter using an integration time of 2 s. The relative accuracy of the measurement
is better than $1 \times 10^4$ and the resolution better than 1 nV.

The resistivity measurements at atmospheric pressure are carried out in a
separate cryostat on samples with known dimensions. The absolute accuracy of the
resistivity is limited to ~1% by uncertainties in the length/area determination.
Small splinters are taken from the $P = 0$ sample to be used in the high pressure
experiment. Although a reliable determination of the dimensions of the samples used
in the high pressure cell is not possible, a comparison of the zero-pressure and high
pressure data allows a definition of the absolute resistivity scale for all data.

2.3. Sample preparation

Because of the variety of systems discussed in the present paper, no comprehen-
sive discussion of sample preparation procedures is attempted here. The reader
should consult the original papers for details of the sample preparation and
annealing procedures appropriate for each alloy.

§3. Very dilute magnetic alloys under pressure

The development of a general microscopic theory of magnetism in metals has
proved to be one of the most difficult problems in solid state physics. In an attempt to
simplify the problem at hand, concentrated magnetic systems can be diluted so
heavily with non-magnetic components that the strength of the interactions
between the magnetic moments becomes negligible, allowing a study of the magnetic
state of a single magnetic impurity in a non-magnetic metallic environment. The
nature of the magnetism in such magnetic alloys of extreme dilution has proved to be
of interest in its own right. However, the hoped for simplification did not occur, the
exact solution of the single magnetic impurity or Kondo problem providing
formidable theoretical difficulties [31, 32]. Lacking an accurate theory which relates
explicitly the basic parameters to various physical properties, it has not been
possible to extract from the data the detailed information about the values of the
essential parameters that is needed [33]. Application of pressure changes the values
of the parameters in a reversible well-controlled way on a single sample; the amount
a parameter changes can often be determined to much higher accuracy than its
absolute value, as will be illustrated in the present studies. Pressure studies thus not
only have the potential to provide valuable information about the volume
dependences of the parameters, but also to allow a test of the functional dependence
of a particular theory on these parameters.

3.1. Results of experiment

One of the quantities of principal interest in the present paper is $J(V)$, the volume
dependence of the effective exchange interaction between a given single magnetic
impurity and the conduction electrons. It is well known that negative values of $J$
lead to sizeable anomalies in many solid state properties [33]. In particular, the
temperature dependence of the electrical resistivity goes through a minimum,
exhibiting a large negative-slope anomaly at lower temperatures. Such behaviour is
found for both transition metal and rare earth impurity systems as seen in the data of
the author and co-workers in figs. 3–5. The measured resistivity can be understood as
(a) Total measured resistivity of CuFe per at.\% Fe versus temperature for different pressures. Dots are data from Schilling et al. [22], crosses are data from Loram et al. [34]. Solid lines are drawn for clarity. Curves resemble fig. 7 (b); pressure of 72 kbar doubles value of $T_K$.

(b) Total measured resistivity of Cu–110 p.p.m. Fe from (a) minus resistivity of Cu host, per at.\% Fe concentration, plotted versus reduced temperature. Curves for three pressures overlap well for temperatures below that of resistivity minimum, confirming universal behaviour in eqn. (8).

Fig. 4

Total measured resistivity of Y–0.5 at.\% Ce versus temperature for different pressures. Dots are data from Zimmer and Schilling [35]; solid lines are drawn for clarity. Shift of $\rho_{\text{spin}}(T)$ with pressure resembles that for CuFe in fig. 3 (a), but is more rapid.
Fig. 5

Total measured resistivity of Au–5 p.p.m. Fe versus temperature for different pressures. Dots are data from Crone and Schilling [36]. Solid lines are drawn for clarity. Pressure increases slope of $\rho_{\text{spin}}(T)$; comparison to fig. 7(c) indicates $T_K$ increases with pressure.

being made up of two components, a negative-slope impurity spin-scattering resistivity $\rho_{\text{spin}}(T)$ with characteristic temperature $T_K$ and a positive-slope phonon resistivity from the host matrix $\rho_{\text{phonon}}(T)$. Theory [31] predicts that the impurity resistivity is a universal function of $T_K$, i.e., $\rho_{\text{spin}} = \rho_{\text{spin}}(T/T_K)$. Inspection of the data in figs. 3–5 reveals that a sizeable shift in $\rho_{\text{spin}}(T)$ occurs under pressure. Although the nature of this shift may appear now to be different in the three sets of data presented, it will be shown in the following subsections that the behaviour of these and all other known resistivity data on negative-$J$ systems under pressure can be understood as a shift of $\rho_{\text{spin}}(T)$ to higher temperatures as $T_K$ increases. From this it follows, as will be seen presently, that in Kondo systems $J$ universally increases in magnitude with pressure; this is one of the main results of the present paper. The increase of $|J|$ with pressure is found to be quite appreciable, being between two to five times larger than the corresponding volume decrease. The data on CuFe in fig. 3(a, b) by Schilling and Holzapfel [22] are of particular importance because they confirm the correctness of the universal law $\rho_{\text{spin}} = \rho_{\text{spin}}(T/T_K)$ and thus lay the foundation for a general method, which is independent of the accuracy of a particular theoretical expression, of determining $T_K(P)$, and thus $J(V)$, from the high pressure data.

After this brief discussion of the experimental results, we now proceed with a review of relevant theory followed by a detailed analysis of the high pressure data. The discussion of theory in the present paper will be restricted to those aspects which are important for an understanding of the present experiments and their ramifications.

3.2. Results of theory

In a very dilute magnetic alloy the principal interaction of interest to us is that between a magnetic impurity with spin $S$ located at the origin and the sea of conduction electrons of the host metal with spin density $s(r)$. We describe this interaction by the hamiltonian [32]

$$\mathcal{H} = -j(r)S \cdot s(r) + v(r).$$

(1)
where \(j(r)\) gives the spatially dependent exchange interaction and \(v(r)\) the potential scattering. The spatial dependence of \(j(r)\) and \(v(r)\) leads to a wave-vector dependence in their Fourier transforms \(J(k, k')\) and \(v(k, k')\). For simplicity, we initially make the usual assumption that both \(j(r)\) and \(v(r)\) are isotropic zero-range delta-function potentials so that both \(J(k, k')\) and \(v(k, k')\) become constants, \(J\) and \(v\), respectively. Two assumptions implicitly contained in Eqn. (1) are: (1) the existence of a well-defined impurity spin \(S\); (2) the neglect of orbital angular momentum, i.e. \(L = 0\). The implications of the above simplifications in the present context will be discussed in detail in §§3.3.1 and 3.5. We mention now that it is clear that since pressure can precipitate a magnetic-to-non-magnetic transition, changing the value of \(S\), the above hamiltonian can only be valid over a restricted pressure range.

For negative values of the effective exchange parameter \(J\) a delicately balanced many body resonance is set up in the conduction electron system as the temperature is lowered through a characteristic temperature \(T_K\), the so-called Kondo temperature, given by the standard expression [37]

\[
T_K \approx T_f \exp \left[ \frac{1}{J_K N(E_f) \cos^2 \delta_v} \right],
\]

where \(T_f\) is the Fermi temperature, \(N(E_f)\) is the density of states at the Fermi energy, \(\delta_v\) is the potential scattering phase shift, and, as will be discussed fully in § 3.5, \(J_K\) is that component of the effective exchange parameter \(J\) which is responsible for the Kondo effect and is, therefore, appropriate for eqn. (2). The resulting anomalies in most solid-state properties can extend over many decades in temperature. Applying pressure shifts the location of these anomalies on the temperature scale, allowing an estimate of \(T_K(P)\) from which \(J_K(V)\) can be derived. Note that \(T_K\) increases if \(J_K\) increases in magnitude, assuming the other parameters in eqn. (2) stay constant. An accurate solution of eqn. (1) for negative \(J_K\), which is sometimes termed the ‘Kondo problem’, has remained an elusive object for many years [31, 32]. Recent use of renormalization-group techniques by Wilson et al. [38] have led to an accurate calculation of the magnetic susceptibility \(\chi\). These calculations show that as \(T \to 0\), \(\chi\) approaches a finite value, implying that the ground state of an \(S = 1/2\) local spin plus conduction electron system is a singlet, in agreement with the prediction by Mattis [39].

The physical property perhaps best suited for a study of the pressure dependence of the Kondo state is the electrical resistivity. Not only can this quantity be measured to very high precision under high pressure conditions, but also the build-up of the Kondo resonance as the temperature drops below \(T_K\) drives the spin-scattering of the conduction electrons to its maximum possible value, allowing a very accurate determination of \(\rho_{\text{spin}}(T)\), even at extreme dilution. Unfortunately, as yet no accurate renormalization-group calculation of the resistivity has been carried out. However, a number of approximate expressions have been derived [31, 32], the following being from Hamann [40] with the unitarity limit value given by Schrieffer [41] and generalized by Fischer [32, 37], Kondo [42], Nagaoka [43] and Schotte [44] to include potential scattering:

\[
\rho_{\text{spin}}(T) = \rho_0 \left\{ 1 - \cos 2\delta_v \frac{\ln T/T_K}{[\ln^2 T/T_K + \pi^2 S(S+1)]^{1/2}} \right\},
\]

where the s-wave unitarity limit resistivity is given by [41]

\[
\rho_0 = mc/ne^2\hbar N(E_f),
\]
and $m$ and $e$ are the electron mass and charge, respectively, $c$ is the impurity concentration, and $n$ is the free electron volume density. The unitarity limit value of the resistivity is approached for temperatures $T \ll T_K$ and has the value from eqn. 3

$$\rho_{\text{spin}}(T=0 \text{ K}) = 2S\rho_0 \cos^2 \delta_v. \hspace{1cm} (5)$$

The factor $2S$ serves to count the singly occupied magnetic quantum levels on the impurity [41]. The magnitude of $\rho_{\text{spin}}$ is reduced if the potential scattering increases. The temperature dependence of the spin-scattering resistivity given by eqn. 3 for $S=1/2$ is illustrated in fig. 6 and compared with a more accurate calculation by Larsen [12] which also takes into account interactions between impurities,

$$\rho_{\text{spin}}(T) = \frac{2S\rho_0 C(S)f_s P(T/\Delta)}{\left[ \ln \frac{2\pi T}{T_K} + \psi \left( \frac{1}{2} + \frac{\Delta}{2\pi T} \right) \right]^2 + f_s P(T/\Delta)}, \hspace{1cm} (6)$$

where $C(S) = 4/(2S + 1)$, $f_s = \frac{3}{2}(2S + 1)S(S + 1)$, $P$ is an integral defined by eqn. 38 in [45], $\psi$ is the digamma function, and $\Delta$ is defined by

$$\Delta - \Delta_c = \frac{1}{2} S(S + 1) \Delta - \frac{\pi T}{\Delta} + \psi \left( \frac{1}{2} + \frac{\Delta}{2\pi T} \right) - \psi \left( 1 + \frac{\Delta}{2\pi T} \right) \left[ \ln \frac{2\pi T}{T_K} + \psi \left( \frac{1}{2} + \frac{\Delta}{2\pi T} \right) \right]^2, \hspace{1cm} (7)$$

where $\Delta_c$ is the root-mean-square (r.m.s.) interaction strength between impurities [45]. Larsen’s curve in fig. 6 is appropriate for the extreme dilution limit of eqns. (6) and (7) where the interactions between impurities are neglected, i.e. $\Delta_c = 0$. Although

**Fig. 6**

Spin-resistivity versus reduced temperature according to Hamann (eqn. (3)) and Larsen (eqns. (6) and (7)).
eqn. 6 does not include potential scattering, $\rho_{\text{spin}}(T)$ is expected [46], at least for small $\delta_v$, to be bounded above and below by the same limits as Hamann’s curve (see fig. 6). Although sizeable deviations between Hamann’s and Larsen’s curves are apparent, both show the same general qualitative features: log $T$ dependence for $T >> T_K$, rise of resistivity with decreasing temperature, approach to the saturation or unitarity limit value for $T \ll T_K$. The inflection point in $\rho_{\text{spin}}$ versus log $T$ defines $T_K$ in Hamann’s expression, but occurs at $\sim 2T_K$ in Larsen’s curve. The quantitative differences between the various expressions for the Kondo resistivity are not of great importance in the present investigations because, as will be seen shortly, our principal method of estimating $T_K(P)$ is independent of which theoretical expression is used.

One feature characteristic of all non-divergent solutions of eqn. (1) is that the measurable properties, for example the resistivity, are all universal functions of $T/T_K$ [31, 47],

$$\rho_{\text{spin}} = \rho_{\text{spin}}(T/T_K).$$

(8)

This means that the Kondo temperature $T_K$ merely serves to define the temperature scale of the spin scattering. Such a universal behaviour is evident in fig. 6. Relevant to the case at hand, the universal behaviour in eqn. (8) means that if pressure were to cause $T_K$, for example, to increase, with $S, \delta_v$, and $\rho_0$ remaining constant, then the resistivity curve $\rho_{\text{spin}}$ should shift on a logarithmic temperature scale to higher temperatures without any change in shape. If this holds, then the change of $T_K$ under pressure can be obtained simply by shifting the experimental data at different pressures on the logarithmic temperature scale until the data overlap. As can be seen in fig. 6, a change in either $S, \delta_v$, or $\rho_0$ as $T_K$ varies would cause the resistivity curve to both shift and change its shape; the low temperature saturation value of the resistivity $\rho_{\text{spin}}(T = 0K)$ would also change.

In a given measurement it is possible to measure only a portion of the entire resistivity curve shown in fig. 6 which spans four decades of temperature variation. The temperature range where $\rho_{\text{spin}}$ can be determined accurately is limited in an actual experiment on the high temperature side by the phonon scattering of the host lattice, which usually obscures $\rho_{\text{spin}}$ for $T \gtrsim 10–20$ K, and on the low temperature side by either the limitations of the experimental apparatus, the influence of interactions between magnetic impurities, or the occurrence of superconductivity. In an actual experiment, therefore, one observes $\rho_{\text{spin}}(T)$ through a relatively narrow ‘temperature window’; if $T_K$ is changed by applying pressure, then $\rho_{\text{spin}}$ shifts past this temperature window, revealing only a portion of itself at any given pressure. Figure 7 is intended to represent what one would expect to observe assuming one views the resistivity curve through a temperature window about 30 K wide for temperatures located below, at, and above $T_K$. In each regime $\rho_{\text{spin}}$ is shown for two values of $T_K$ differing only by a factor of two, simulating a relatively small shift under pressure, the other parameters $S, \delta_v$, and $\rho_0$ being held constant. The manifestation in the total resistivity of an increase of $T_K$ is quite different in the three regimes! The shift of $\rho_{\text{spin}}$ when $T_K$ is doubled is perhaps most clearly seen in fig. 7 (b) where $T \approx T_K$; in addition, for these curves $\rho_{\text{spin}}(T = 0K)$ can be accurately determined from the known $\rho_{\text{spin}} \propto [1 - (\pi^2/2S + 3)](T/T_K)^2$ dependence [12] at low temperatures where $T \ll T_K$.

For these reasons the ideal candidate for an initial pressure investigation would be a system, like CuFe ($T_K \approx 30$ K), whose Kondo temperature lies within or very near the experimental temperature window.
3.3. Analysis of experiment—external pressure

3.3.1. Transition metal impurities

The results of the electrical resistivity measurements of Schilling and Holzapfel [22] under pressure on a Cu-110 p.p.m. Fe alloy are shown in fig. 3 (a); related work was carried out by Summers et al. [48]. The similarity of the data in fig. 3 (a) to the calculated curves in fig. 7 (b) is apparent. It is clear without detailed analysis that pressure shifts $\rho_{\text{spin}}(T)$ to successively higher temperatures, 72 kbar sufficient to double the value of $T_K$. In fig. 3 (b) some of the data, with the Cu host resistivity subtracted out, are plotted versus the reduced temperature $T/T_K$ and are seen to accurately overlap within experimental accuracy over the entire range of temperature below that of the resistivity minimum. The overlap for the other pressures is similarly accurate. Thus, over the pressure and temperature range considered here, these experiments confirm the existence of a universal resistivity curve for CuFe, $\rho_{\text{spin}} = \rho_{\text{spin}}(T/T_K)$. This is fortunate because it allows us to extract the pressure dependence of $T_K$ directly from the raw data, independent of any particular theoretical model or the $P=0$ value chosen for $T_K$. To derive $T_K(P)$ using this so-called ‘$\rho$-shift’ method, the data at different pressures are shifted on a logarithmic temperature scale until they overlap. The change in the value of $\rho_{\text{spin}}(T=0 \text{ K})$ under pressure in the data in fig. 3 is less than the experimental uncertainty [49], indicating that $S$, $\rho_0$, and $\delta_0$ are essentially pressure independent. Clearly for a ‘good moment’ system, one of the assumptions behind eqn. (1), one expects $dS/dP = 0$. In addition, from eqn. (4), and assuming a free electron dependence for $N(E_f)$, the anticipated pressure dependence of $\rho_0$ is only about +1% for 72 kbar.
Other changes with increasing pressure seen in fig. 3(a) are that the resistivity minimum fills up and the temperature of this minimum $T(\rho_{\text{min}})$ increases slightly. The former effect, as can be seen in fig. 7 (b), is due to the shifting of the spin-scattering curve to higher temperatures, whereas the latter effect follows from the reduction of the phonon scattering with increasing pressure due to the increase of the Debye temperature [22]. The fact that the data in fig. 3 (b) still show a resistivity minimum, even though the Cu host resistivity has been subtracted out, is due to large deviations from Matthiessen’s rule $\Delta_{\text{DMR}}$ which can be, in fact, larger than the phonon scattering itself. The present measurements can be used to determine these deviations and it is found that $\Delta_{\text{DMR}}(T) \approx 1.3 \rho_{\text{phonon}}(T)$. These supplementary effects are discussed in detail in [22]. Here we are principally interested in the effect of pressure on the spin-scattering resistivity. From the above it is clear that an accurate determination of the spin-scattering resistivity is only possible at low enough temperatures, $T < T(\rho_{\text{min}}) \approx 20$ K, where $\rho_{\text{phonon}}(T)$ and $\Delta_{\text{DMR}}(T)$ are negligible compared to $\rho_{\text{spin}}(T)$.

From the pressure dependence of $T_K(P)$ determined in the above manner for CuFe, the volume versus pressure relationship for Cu given by [50] $\Delta V/V_0 = -6.9 \times 10^{-4} P(\text{bar}) + 1.3 \times 10^{-6} [P(\text{bar})]^2$, and the volume dependence of $N(E_F)$, one can use Eqn. (2) to extract the sought after volume dependence of the effective exchange parameter $J_K(V)$ [51]. We use here the free electron value of the volume dependence of $N(E_F)$, $d \ln N(E_F)/d \ln V = +0.07$; this small value agrees reasonably well with the results of thermal expansion measurements on Cu by Carr et al. [52] (+0.63 ± 0.06) and band structure calculations by Davis et al. [53] (+0.43). The free electron value is used throughout this review unless stated otherwise. For CuFe a pressure of 72 kbar reduces the volume by 4.3%, doubles the Kondo temperature $T_K$, reduces $N(E_F)$ by 2.9%, and increases $J_K$ in magnitude by 11.2%. The logarithmic volume derivative of the effective exchange parameter is found to be $d \ln |J_K|/d \ln V \approx -2.6$ [54], which means that for a 1% volume decrease, $J_K$ increases in magnitude by 2.6%. The volume dependence of $J_K$ is far larger than that of $N(E_F)$ and thus is clearly responsible for the observed rapid increase of $T_K$ with pressure.

We would now like to extend the preceding studies on CuFe to other very dilute magnetic systems such as AuV, AuFe, CuCr, AgMn, etc. to see to what extent the results for CuFe can be generalized. The results of these and further experiments on very dilute magnetic alloys under pressure are summarized in table 1. We consider first systems with relatively high $T_K$ values. High pressure measurements by Schilling and Crone [55] on a Au-0.5 at.\% V alloy with $T_K \approx 300$ K resemble rather closely the curves shown in fig. 7 (a). In particular, to 70 kbar pressure causes $\rho_{\text{spin}}(T)$ to shift to higher temperatures with no change in shape. This result, plus the pressure independence of $\rho_{\text{spin}}(T = 0)$, point to the constancy of $S$, $\delta_\nu$, and $\rho_0$ under pressure. The results on AuV thus fully corroborate those on CuFe. For completeness we also include in table 1 the results of pressure measurements on the high-$T_K$ system AlMn [56].

For most recognized Kondo systems, $T_K$ lies below 1 K. In the measurements by Crone and Schilling [36] on the low-$T_K$ ($T_K \approx 0.2$ K) system Au-5 p.p.m. Fe shown in fig. 5, the spin resistivity $\rho_{\text{spin}}(T)$ shifts vertically and increases in slope when pressure is applied. This is exactly what is expected, according to fig. 7 (c), for a low-$T_K$ system when $T_K$ increases with pressure. Because $T_K$ lies below our temperature range, an accurate estimate of $\rho_{\text{spin}}(T = 0)$ for AuFe and other low-$T_K$ systems is not possible. Guided by the observed pressure independence of $S$, $\rho_0$, and $\delta_\nu$, found for
Table 1. Summary of high pressure results for very dilute magnetic alloys. $P = 0$ or $x = 0$ values of the Kondo temperature $T_K$, density of states at the Fermi energy for both spin directions $N(E_f)$, and effective exchange parameter $J_K$ are listed on the left. The volume dependences of the parameters for external pressure are shown on upper right, for lattice pressure on lower right. As explained in § 3.5, for 3d-impurities $J_K = J_2$, for 4f-impurities $J_K = J_3$. $P_m$ or $x_m$ is maximum pressure or concentration, respectively, used in determining volume dependences. $\nu = (V_0 - V)/V_0$, where $V_0$ is atomic volume at $P = 0$ and $V$ is atomic volume at a given pressure. All data were re-analysed in a consistent way. For method of determining logarithmic volume derivatives, see [54]. Details are given in references which are listed in same order as that of parameters. Letters mean: (a)—See § 3.3.2 for a discussion of LaCe including estimated best values of the parameters; (b)—For LaGd, $J_K$ in table heading should be replaced by $J$ where $J$ is here exchange parameter appropriate for ‘pair weakening’ in superconductivity (see § 3.3.2.); (c)—$\nu$-shift method (see § 3.3.1); (d)—$\nu$-slope method (see § 3.3.1); (e)—$T_s$ suppression method (see text): (f)—$\nu$-slope method with Larsen's curve in fig. 6, (see § 3.3.2).

| Dilute Alloys | $T_K(0)$ (K) | $N(E_f)(0)$ states/eV-atom | $J_K(0)$ (eV) | References | $P_m$ (kbar) | $\nu(P_m)$ or $\nu(x_m)$ | $d \ln T_K / d \ln V$ | $d \ln N(E_f) / d \ln V$ | $d \ln |J_K| / d \ln V$ | References |
|---------------|--------------|-----------------------------|---------------|-------------|-------------|---------------------------|-------------------|-------------------|-------------------|-------------|
| Cu-110 p.p.m. Fe | 24 | 0.294 | −0.408 | 34,61,62 | 82 | − | +0.048 | −15 | +0.67 | −26 | 22,50 (c, 83, 84) |
| Cu-50 p.p.m. Mn | 0.012 | 0.294 | −0.213 | 63,61,62 | 76 | − | +0.045 | −32 | +0.67 | −29 | 85,50 (d, 83, 84) |
| Au-5,20,32 p.p.m. Fe | 0.24 | 0.308 | −0.251 | 34,61,62 | 81 | − | +0.040 | −17 | +0.67 | −21 | 36,85 (e, d, 83, 84) |
| Au-24,50,80 p.p.m. Mn | 10⁻¹ | 0.308 | −0.157 | 65,61,62 | 70 | − | +0.035 | −46 | +0.67 | −29 | 36,85 (d, 83, 84) |
| Au-24,50,80 p.p.m. Mn | 10⁻¹ | 0.308 | −0.088 | 66,61,62 | 70 | − | +0.035 | −84 | +0.67 | −27 | 36,85 (d, 83, 84) |
| Au-20 p.p.m. Cr | 10⁻³ | 0.308 | −0.176 | 63,61,62 | 81 | − | +0.040 | −19 | +0.67 | −17 | 87,85 (c, d, 84) |
| Au-0.5 at.% V | 0.0 | 0.308 | −0.559 | 67,68,61,62 | 53 | − | +0.028 | −17 | +0.67 | −41 | 55,86 (c, 83, 84) |
| Ag-20 p.p.m. Mn | 10⁻⁴ | 0.262 | −0.184 | 65,61,62 | 61 | − | +0.058 | −28 | +0.67 | −19 | 24,60 (d, 83, 84) |
| Ag-20 p.p.m. Mn | 10⁻⁴ | 0.262 | −0.079 | 69,61,62 | 61 | − | +0.058 | −70 | +0.67 | −20 | 24,60 (d, 83, 84) |
| Al-0.13 at.% Mn | 530 | 0.571 | −0.316 | 56,61,62 | 21 | − | +0.026 | −8 | +0.67 | −24 | 56,88 (c, 83, 84) |
| La-3% Ce (d.h.c.p.) | 0.017 | 0.3 | −0.217 | 70,71,72,62 | 18 | − | +0.064 | −95 | +0.67 | −86 | 70,89 (c, 83, 84) |
| La-3% Ce (d.h.c.p.) | 3 × 10⁻⁴ | 0.3 | −0.172 | 73,71,72,62 | 17 | − | +0.063 | −134 | +0.67 | −99 | 73,89 (c, 83, 84) |
| La-2% Ce (f.c.c) | 0.12 | 0.3 | −0.249 | 73,71,72,62 | 19 | − | +0.067 | −69 | +0.67 | −70 | 73,89 (c, 83, 84) |
| La-3% Ce (f.c.c) | 0.04 | 0.3 | −0.273 | 73,74,72,62 | 15 | − | +0.054 | −42 | +0.67 | −45 | 73,89 (f, 83, 84) |
| La-2% Ce (f.c.c) | 0.04 | 0.3 | −0.273 | 73,74,72,62 | 15 | − | +0.054 | −42 | +0.67 | −45 | 73,89 (f, 83, 84) |
| Y-0.5 at.% Ce | 40 | 0.3 | −0.442 | 75,72,62 | 23 | − | +0.054 | −38 | +0.67 | −63 | 35,88 (c, 83, 84) |
| Y-1.0 at.% Ce | 40 | 0.3 | −0.442 | 75,72,62 | 25 | − | +0.059 | −29 | +0.67 | −51 | 90,88 (c, 83, 84) |
| La-0.6,0.8,1.0 | 11 | 0.3 | +0.110 | −72,76,77 | 11 | − | +0.041 | − | +0.67 | +9 | 76,89 (e, 83, 84) |
| 1.2 at.% Gd(b) | 1.1 | 248 | +0.038 | −78,76,77 | 11 | − | +0.041 | − | +4.5 | +3 | 76,89 (e, 83, 84) |

| La₁₋ₓTh₁₋ₓ% Ce | 1.1 | 248 | +0.036 | 82,78,62 | 11 | − | +0.041 | − | +4.5 | +3 | 76,89 (e, 83, 84) |
CuFe and AuV, we make the assumption that this is also the case for low-$T_K$ systems—i.e. we assume that, in general, $\rho_{\text{spin}}(T)$, for a given system, is part of one universal resistivity curve at all pressures. An estimate of $T_K(P)$ is thus obtained, as with CuFe and AuV, by shifting the $\rho_{\text{spin}}$ curves along the logarithmic temperature scale until they join up ($\rho$-shift technique). Because of the relatively low slope of $\rho_{\text{spin}}(T)$ for low-$T_K$ systems, the overlap region is rather small and, therefore, the quality of the overlap is not, as was the case for CuFe and AuV, a good test of the universality prediction of eqn. (8). However, as will be seen below, an independent method of estimating $T_K(P)$ agrees well with the present estimate.

For systems with extremely low values of $T_K$ ($\leq 10^{-3}$ K) the negative slope of $\rho_{\text{spin}}(T)$, as seen in fig. 6, is extremely small in our temperature range from 1 to 10 K. For this reason inevitable small shifts in the background defect resistivity as pressure is varied [22] impair the accuracy of the $T_K(P)$ determination if the $\rho$-shift technique is used. In the $T \gg T_K$ limit, therefore, it would be desirable to have an independent method of determining $T_K(P)$ which is insensitive to changes in background scattering, like the change in slope ($d\rho_{\text{spin}}/d \log T$) with pressure (see fig. 7(c)). $T_K(P)$ can be obtained by comparing the measured slope increase with that expected from eqns. (3) or (6) [57]. The pressure dependence of $T_K$ determined by using this so-called $\rho$-slope technique depends somewhat on the value of the spin $S$. The use of Kondo's [58] second Born approximation expression $d\rho_{\text{spin}}/d \log T \propto J_K^2$, which is spin independent, to determine $T_K(P)$ from the slope change is only justified for extremely small values of $T_K$, i.e. where $\ln T/\rho \gg \pi \sqrt{1/2} S(S+1)$ [46] or

![Fig. 8](image)

Effective exchange parameter $J_K$ for various systems in table I as a function of average atomic volume of sample, $V(P)$, relative to that of Cu at $P=0$, $V_{Cu}(0)$. $J_K$ always increases in magnitude with pressure. $P=0$ values of $T_K$ for AuMn and AgMn are taken as $10^{-11}$ K and $10^{-16}$ K, respectively. For $Cu_{1-x}Al_xFe$, $V(P)$ is defined to be the average atomic volume per host alloy valence electron, where the number of valence electrons is given by $N=3x+1(1-x)$. 
Pressure effects in dilute magnetic alloys

$T_K \lesssim 10^{-12}$ K for $T \simeq 1$ K and $S \gtrsim 1/2$. Application of the $\rho$-slope technique to the Au–5 p.p.m. Fe data results in the same values of $T_K(P)$ as obtained with the $\rho$-shift technique if a spin value $S = 1/2$ is assumed. The fact that this value of the spin lies somewhat lower than the value $S = 3/2$ derived for CuFe [59], which is probably generally appropriate for Fe impurities in noble metals, is not particularly disturbing in view of the abnormal values of $S$ often required to obtain the best fits of theoretical expressions for the resistivity to the data [34]. The good agreement in $T_K(P)$ using the independent $\rho$-slope and $\rho$-shift techniques for AuFe gives confidence when applying the former method to alloys like AgMn and AuMn with much lower values of $T_K$. The results of the measurements of Crone and Schilling [36] on AuMn and Olijnyk et al. [24, 60] on AgMn, and further studies are given in table 1. For AuMn and AgMn the parameters are calculated for two different initial values of $T_K$, reflecting the uncertainty in the values of the Kondo temperature for these systems. It should be noted that the value of the quantity of principal interest to us, namely $d \ln J_K/d \ln V$, is hardly changed, even when the initial value of $T_K$ assumed is varied by many orders of magnitude. The results of the high pressure studies on transition metal impurity systems are summarized in fig. 8 and table 1. The present ‘external pressure’ studies are also compared to those on alloy series using ‘lattice pressure’; a full discussion of these effects follows in §3-4.

3.3.2. Rare earth impurities

Negative $J$

Alloys combining trivalent Ce impurities with La, LaAl$_2$, and Y host metals display the typical negative resistance slope anomalies characteristic for negative values of $J$. In the crystalline field of the above hosts, the Ce Hund’s rule multiplet is split into a ground state doublet separated by roughly $\sim 100$ K from the nearest excited states [97, 98]. In the low-temperature range ($T \lesssim 20$ K), where information about the magnetic state of the Ce impurity can be gained from studies of $\rho_{\text{spin}}(T)$ and the suppression of the superconducting transition temperature $T_c$, the magnetic state can thus be treated as if it had an effective spin $S_{\text{eff}} = 1/2$.

A comparison of the high pressure resistivity measurements on Y–0.5 at.\% Ce by Zimmer and Schilling [35] in fig. 4 to those on Cu–110 p.p.m. Fe in fig. 3 reveals strong similarities in the two sets of data. Not only do both systems have approximately the same value for the Kondo temperature, $T_K \simeq 30$ K at $P = 0$ (see table 1), but also an analogous behaviour under pressure. The pressure shift of $T_K$ to higher temperatures in YCe is particularly rapid and can be estimated, as with CuFe, using the $\rho$-shift method. Our results in fig. 4 are in good agreement with previous studies by Dietrich et al. [90], and Maple and Wittig [99]. The rapid shift of the $\rho_{\text{spin}}$-curve to higher temperatures with pressure is particularly clear in the data of Dietrich et al. [90], where the phonon resistivity of the Y host is substracted off. Their value of $T_K = 17$ K is probably somewhat too low due to their neglect of deviations from Matthiessen’s rule; we feel the $T_K = 40$ K estimated by Sugawara and Yoshida [75] is more accurate.

There is some uncertainty in what values of the density of states are appropriate for determining $J_K$ from $T_K$ using eqn. (2) in systems with La, LaAl$_2$, and Y hosts. The bare densities of state estimated from specific heat measurements corrected for the electron–phonon mass enhancement lie near $N(E_f) \simeq 2-5$ states/eV-atom for both spin directions [78, 100]. In addition, the volume dependence of $N(E_f)$ is quite large, for La $d \ln N(E_f)/d \ln V \simeq -2$ and $-4.5$ from thermal expansion [101] and critical
magnetic field results [91], respectively. These large values of \( N(E_f) \) and its volume
dependence originate predominantly from the d-bands of the above hosts [102] and
are roughly an order of magnitude larger than typical free electron values used for
the noble metals, \( N(E_f) \approx 0.3 \text{ states/eV-atom} \) [61] and \( d \ln N(E_f)/d \ln V \approx +0.67 \) [83].
On the other hand, as emphasized by Schrieffer [41], it is the f-character in the
conduction band, not the d-character, which contributes in the case of rare earth
impurities to \( J_K \) resulting in the 'Kondo' spin-scattering in the electrical resistivity.
For La, LaAl\(_2\), and Y hosts it would thus seem more appropriate in an analysis of the
resistivity data to use the above free electron values of the density of states and its
volume dependence, in order to be consistent with the treatment of 3d-impurities in
noble metal hosts. Owing to these uncertainties, however, it is clear that the values of
the parameters in table 1 for these rare earth systems are not as reliable as those for
the noble metal host systems where the character of the conduction electrons at the
Fermi surface is relatively simple.

The dependences of \( T_K \) and \( J_K \) on volume for YCe are given in table 1. \( d \ln |J_K|/d \ln V \) is seen to be approximately twice as large as for CuFe and most other
transition metal impurity systems. The extremely rapid increase of \( T_K \) with pressure
in YCe compared to transition metal impurity systems with high \( T_K \) is thus
apparently not only due to the fact that the Y host is about four times more
compressible than a noble metal host, but also to a larger intrinsic volume
dependence of \( J_K \). Certainly, to pressures of the order of 40 kbar, the resistivity data
are consistent with a continuous increase of \( T_K \) with pressure. The question of whether
at higher pressures the system is best characterized by a high \( T_K \) value, or undergoes
a magnetic-to-non-magnetic transition, is very difficult to answer on the basis of a
resistivity measurement alone; the reason for this is that when \( T_K \) is very high,
\( \rho_{\text{spin}}(T) \) can no longer be accurately determined over an appreciable temperature
range around \( T_K \) due to the large contributions from the phonon scattering and
deviations from Matthiessen's rule. Using the unitarity limit value of the resistivity
\( \rho_{\text{spin}}(T=0 \text{ K}) \), which according to eqn. (5) is proportional to the spin \( S \), to indicate
whether or not a magnetic-to-non-magnetic transition occurs [90], is of questionable
value because even in the non-magnetic state there would be a very large (\( \delta \approx 1/2 \))
resonance scattering contribution; only when the pressure becomes large enough to
push the demagnetized level well clear of the Fermi surface would the resistivity at
\( T=0 \text{ K} \) be expected to decrease dramatically [47].

Whereas the high-\( T_K \) system YCe is analogous to CuFe, the low-\( T_K \) system LaCe
is analogous to AuFe, as can be seen by comparing the La-3% Ce data in fig. 21 (a) of
Zimmer and Schilling [27, 70], which will be discussed in detail in § 4.5, to the AuFe
data in fig. 5. In both LaCe and AuFe, pressure increases the slope \( |d\rho_{\text{spin}}/d \log T| \) and the
value of the resistivity at a given temperature, indicating according to fig. 7 (c),
an increase of \( T_K \) with pressure. An exact study of the pressure dependence of \( T_K \) in
LaCe is difficult because the temperature region where the spin-scattering resistivity
of very dilute LaCe can be determined accurately is bounded above (~ 5 K) by the
enormous phonon scattering of the La host (\( 10^4 \) times larger at 10 K than for the
noble metals!) and below by the onset of superconductivity in the La host (pure f.c.c.-
La is superconducting below 6 K). This problem can be alleviated somewhat by
increasing the Ce concentration into the few-per-cent region which opens the
'temperature window' in both directions simultaneously. The price for this
'opening', however, is high because, as will be discussed in detail in § 4, at higher Ce
concentrations, interactions between the Ce impurities can markedly affect the
temperature dependence of $\rho_{\text{spin}}(T)$. Measurements on f.c.c.- and d.h.c.p.-LaCe under hydrostatic pressure by Kim and Maple [73] reveal that in both cases the slope $|d\rho_{\text{spin}}/d \log T|$ at 4 K goes through a maximum at $P \approx 15$ kbar, increasing by a factor of $\sim 2.5$ from the zero pressure value. Our data in fig. 21 (a) are consistent with this result. In fig. 6 it can be seen that for both theoretical curves the slope of the resistivity reaches a maximum value at a temperature approximately equal to the Kondo temperature, i.e. $T_K(15 \text{ kbar}) \approx 4 \text{ K}$. The value of $T_K$ at $P = 0$ can then be estimated from the hydrostatic data [73] by assuming $T_K(15 \text{ kbar}) \approx 4 \text{ K}$ and then employing either the $\rho$-shift or $\rho$-slope method, the former of which gives $T_K(0) \approx 0.1 \text{ K}$ for f.c.c.-LaCe. This value of $T_K(0)$ is in reasonable agreement with the results of several other experiments [103, 104]. The value $T_K \approx 0.3 \text{ mK}$ for d.h.c.p.-LaCe obtained using the $\rho$-shift method would appear to be anomalously low. A similar analysis of our quasi-hydrostatic pressure data on d.h.c.p.-LaCe in fig. 21 (a) gives $T_K(0) \approx 17 \text{ mK}$, which is also quite low. To investigate the reasons for the differences in the $T_K(0)$ values, it should be noted that a determination of $T_K(P)$ by the $\rho$-shift method is susceptible to two main sources of error, namely, (1) interactions between impurities and (2) an increase in the background defect-scattering due to the cold-working of the sample as the pressure is changed. An increase in the defect scattering with pressure exaggerates the separation of the individual resistivity curves which thus require larger shifts on the temperature axis to come to overlap. The effect of impurity–impurity interactions, which is largest at $P = 0$, is both to reduce the resistivity slope and to introduce a negative curvature and even a resistivity maximum at sufficiently high concentrations (see figs. 16 and 21). If the experiment is carried out with increasing pressure, both effects will lead to an overestimate of the pressure dependence of $T_K(P)$. The much larger increase of the resistivity at a given temperature for d.h.c.p.-LaCe is notable in Kim and Maple’s data [73] and leads to the low value of $T_K(0)$ derived for d.h.c.p.-LaCe. However, the nearly identical change of slope $d\rho_{\text{spin}}/d \log T$ with pressure for both f.c.c.- and d.h.c.p.-LaCe [73] points to $T_K(0)$ being similar and $T_K(15 \text{ kbar}) \approx 4 \text{ K}$ in both phases. If, in addition, we assume $T_K(0) \approx 0.1 \text{ K}$ and $d \ln N(E_F)/d \ln V = +0.67$ [83], we obtain $d \ln |J_K|/d \ln V \approx -7.9$. This value is somewhat larger than what was found for YCe ($d \ln |J_K|/d \ln V \approx -5$ to $-6$) where the $T_K(P)$ determination, due to the much higher value of $T_K(0)$, is far less susceptible to errors originating from the effects of interactions between impurities or the increase of background defect scattering. If we assume for LaCe, as for YCe, that $d \ln |J_K|/d \ln V = -5$, then it follows from $T_K(15 \text{ kbar}) = 4 \text{ K}$ that $T_K(0) \approx 0.2 \text{ K}$. It would be desirable to use a method to estimate $T_K(P)$, like the $\rho$-slope method, which is independent of defect scattering. The formula used previously [57] is only valid for $T > T_K$; for a system like LaCe, with a relatively high value of $T_K \approx 0.1 \text{ K}$, it is more accurate to use Larsen’s resistivity curve directly. If we apply the $\rho$-slope method to Kim and Maple’s data [73] and use Larsen’s calculated $S = 1/2$ curve in fig. 6, then we obtain $T_K(15 \text{ kbar}) \approx 10 T_K(0)$, or $T_K(0) \approx 0.4 \text{ K}$. The $\rho$-slope method is susceptible to errors arising from impurity interactions, but not from changes in the defect scattering. In summary, on the basis of the available normal state data, we estimate that for both f.c.c.- and d.h.c.p.-LaCe: $T_K(0)$ lies between $0.1 \text{ K}$ and $0.4 \text{ K}$, $T_K(15 \text{ kbar}) \approx 4 \text{ K}$, and $d \ln |J_K|/d \ln V \approx -5$ to $-7$. To improve the accuracy of these estimates, a quantitative analysis should be carried out employing theoretical expressions for the resistivity which include the effect of impurity–impurity interactions.
The pressure dependence of the suppression of the superconducting transition temperature $T_c$ caused by the addition of Ce impurities to La has also been used to estimate $T_K(P)$ or $J_K(V)$ [76, 91, 104-106]. The use of first Born approximation expressions (like eqn. (9)) in some of these analyses is clearly insufficient. A more accurate theory which includes temperature dependent pair breaking has been developed by Müller-Hartmann et al. [81]; Müller-Hartmann [107] has recently reviewed the current status of theory for superconducting Kondo systems. Experimentally it is found that the suppression of $T_c$ in LaCe is a maximum at $\sim 15$ kbar, the same pressure at which the normal resistivity slope reached its maximum value, indicating that $T_K(15 \text{kbar}) \approx 4 \text{K} \approx 0.5 T_{c0}$, where $T_{c0}$ is the transition temperature in pure La at 15 kbar. This is in disagreement with the expectation of theory [81] where $T_K = 12.9 T_{c0}$ for maximum $T_c$ suppression and where detailed comparison with experiment [82] has yielded $T_K(0) \approx 1.1 \text{K}$ (see table 1), a value which would seem to be too high to be consistent with the $T_K$ estimate from the normal state properties, even if the effects of impurity interactions are taken into account. In related experiments on La$_{3-x}$Ce$_x$In alloys [108], a maximum $T_c$-suppression was also observed at pressures near 20 kbar. Another factor associated with superconductivity in La and La-compounds which causes uncertainty when using superconductivity as a probe of the Ce magnetic state in the present context is the fact that in La the superconductivity is probably predominantly a property of the d-bands [109], whereas it is the 4f-character in the ‘free conduction band’ which leads to the negative value of $J_K$ and to the resonant exchange scattering seen in the normal state anomalies [41]. As a result, not only is there uncertainty in which value of the density of states is appropriate for the normal and superconducting regimes [105], but also, as Wollan and Finnemore [110] have pointed out, it may be necessary to consider two separate pair-breaking and normal-state spin scattering times. Although a two-band model [111] may be necessary, the fact that the normal state resistivity slope and the superconducting $T_c$-suppression both reach their maximum values at the same pressure, $\sim 15$ kbar, points to a common mechanism in both cases and to an intimate interconnection between the influence of the magnetic impurity on both superconducting and normal state properties.

Positive $J$

We have chosen to first discuss the pressure dependence of those very dilute systems which have negative values of the effective exchange parameter $J$ because in this case the anomalies in the normal state properties are particularly large, allowing accurate determinations of even very small shifts with pressure. For magnetic impurities with very long-lived magnetic moments, like Gd impurities in rare earth hosts, $J$ is positive and relatively undramatic effects are observed in the measurable properties: (1) a small positive slope in the spin-scattering resistivity observed, for instance, in LaGd [112], LaGdAl$_2$ [79, 113], and LuGd [114], and (2) a non-resonant suppression of $T_c$ [98]. Unfortunately, no measurements of the temperature dependence of the normal state resistivity under pressure have yet been carried out on the above systems. We must, therefore, rely on the pressure dependence of the suppression of the superconducting transition temperature $\Delta T_c$ alone to give us an estimate of $J_K(V)$. For very low magnetic impurity concentrations, $\Delta T_c$ is given by the Abrikosov–Gorkhov expression valid in the first Born approximation [115],

$$\Delta T_c/\Delta c = -(\pi^2/4k)N(E_F)S(S+1)J^2.$$ (9)
From the measured pressure dependence of $T_c$ in LaGd and La, Smith [76] obtained, using eqn. (9):

$$d \ln \Delta T_c / d \ln V \approx d \ln N(E_f) / d \ln V + 2d \ln |J| / d \ln V \approx +2.5.$$ 

Since the measured logarithmic volume dependence of the La host density of states lies between $-2$ and $-4.5$ [91, 101], we have $d \ln |J| / d \ln V \approx +2.2$ to $+3.5$, and thus for this positive $J$ system, $J$ decreases with increasing pressure. This result is in marked contrast to those on negative $J$ systems where $|J_K|$ is found universally to increase with pressure. As will be discussed in § 5, studies of the pressure dependence of the magnetic ordering temperature for a number of rare earths [117] are consistent with a decrease of $J$ with pressure for LaGd and indicate that this result may hold for other 'good spin' rare earth impurities.

### 3.4. Analysis of experiment—lattice pressure

The substitution of one noble metal host for another, as in the alloy series Cu$_{1-x}$Au$_x$Fe, where Cu is replaced by Au, can have the effect of reducing the lattice parameter and average atomic volume. We now want to investigate the question to what extent the reduction of average volume across such an alloy series is equivalent to a volume reduction by external pressure.

#### 3.4.1. Transition metal impurities

In fig. 8 the volume dependences of $J_K(V)$ derived from studies on various very dilute magnetic systems under external pressure are compared to those from investigations on the alloy series Cu$_{1-x}$Au$_x$Fe by Loram et al. [34] and Star [118] and on Cu$_{1-x}$Al$_x$Fe by Schilling and Crone [94]. The $J_K(V)$ dependences are in general disjoint and clearly do not lie on a universal curve, even for a given magnetic impurity in different hosts (the difficulty in accurately estimating $T_K$ at $P=0$ causes some uncertainty in the values of $J_K(0)$, but not enough to account for the disjointedness). A comparison of the dependence of $J_K$ on the average volume in CuFe under pressure and in the Cu$_{1-x}$Au$_x$Fe alloy series offers a clue to the problem. It is clear from fig. 8 that for relatively small Au concentrations, applying lattice pressure to the Fe impurities by changing the Au concentration is equivalent to applying external pressure. The ionic radius of Au is about 40% larger than that of Cu and thus adding Au to Cu expands the lattice, generating, in effect, a negative pressure. Indeed, from fig. 8 it appears that there is a tendency of single impurities in a Cu host to have larger values of $T_K$ (or $|J_K|$) than in a Au host, indicating that the smaller lattice parameter in the Cu host is an important factor. The $J_K(V)$ curve of AuFe, however, does not match up to that of Cu$_{1-x}$Au$_x$Fe or CuFe. In the simple lattice expansion model discussed until now we have included only the average atomic volume but have neglected any influence of the immediate local surroundings of the Fe impurities on $J_K$. In fact, the cage surrounding each Fe impurity is considerably smaller in Au than in Cu owing to Au having a 40% larger ionic radius; this would be expected partly to counteract the lattice expansion effect and to raise $T_K$ for AuFe above the value expected by an extrapolation of the $J_K(V)$ data for Cu$_{1-x}$Au$_x$Fe to larger atomic volumes. A similar result should also apply to CuMn and AuMn.

We would now like to go one step further and discuss a method introduced by Schilling and Crone [94] which indicates how pressure studies can be useful in gaining information about the electronic structure of ternary alloys at zero pressure. We
have, in fact, already done this in the Cu$_{1-x}$Au$_x$Fe alloy series where we used the Fe ion as a ‘Kondo-probe’ to tell us that for small Au concentrations the exchange interaction $J_K$ appears to be a function of the average atomic volume regardless of whether this volume has decreased under the influence of external pressure or has increased by the addition of Au to Cu. In the spirit of the free electron model we now make the assumption that $J_K$ is, in fact, not merely a function of $V$ alone, but rather of the free electron density $N/V$ of the host matrix. Under this assumption, then, increasing the electron density in the alloy system Cu$_{1-x}$Al$_x$Fe by substituting Al$^{3+}$ (three valence electrons per atom) for Cu$^+$ (one valence electron per atom) should be equivalent to increasing $N/V$ by applying external pressure which decreases $V$.

Investigations on Cu$_{1-x}$Al$_x$Fe by Schilling and Crone [94] show clearly that the addition of 10% Al to Cu does, in fact, increase $|J_K|$ by approximately the same amount as $\sim$ 100 kbar pressure, even though (see table 1) adding Al to Cu expands the lattice. It is thus clear that, even if the $J_K = J_K(N/V)$ functional dependence were not correct, increasing the number of free electrons works in the same direction as decreasing the volume by pressure. In fig. 8 the dependence of $J_K$ on the relative volume per conduction electron is plotted for Cu$_{1-x}$Al$_x$Fe under the assumption that each Al atom contributes all three of its valence electrons to a free conduction band, i.e. $N = (1-x) + 3x$. The $J_K(V)$-dependence for Cu$_{1-x}$Al$_x$Fe is seen to be too small to match onto the CuFe high pressure data. It is as if the dependence of $N$ on $x$ given by the above formula were too large! Good agreement between the two sets of $J_K(V)$-dependences is, however, obtained if one assumes that each Al atom contributes only approximately half its three valence electrons to the conduction band. The remaining electrons presumably remain localized close to the Al$^{3+}$ ions as screening charge and are not ‘seen’ by most of the Fe Kondo-probes. Mößbauer isomer shift studies can also be used to estimate the degree of localization of the impurity screening charge [119]. The present studies represent an attempt to develop a technique applicable to a wider class of systems than those accessible to the Mößbauer technique.

3.4.2. Rare earth impurities

We now consider a number of rare earth systems and compare external to lattice pressure. Consider first dilute LaCe and YCe alloys, where $T_K(0) \approx 0.1$ K and 40 K, respectively, as discussed in § 3.3.2. We first ask the question: is the higher value of $T_K$ for YCe relative to LaCe understandable in terms of lattice pressure? Comparing the molar volumes of the hexagonal phases of both hosts, we find $V_Y/V_{La} = 0.882$; from this ratio and the known pressure–volume relation for La [89], we estimate that the lattice pressure in Y corresponds to an external pressure applied to La of approximately 35 kbar. The most reliable information on the $T_K$ value of LaCe is probably that at 15 kbar, $T_K \approx 4$ K, as discussed in § 3.3.2. If we now extrapolate this value to a pressure of 35 kbar assuming the reasonable value (see table 1 and discussion in § 3.3.2) $d \ln |J_K|/d \ln V \approx -4.5$, we find that $T_K(0) \approx 80$ K for YCe, which is in reasonable agreement with the above result from experiment [75]. The expected lattice pressure not only gives the correct sign but also approximately the right magnitude for the $T_K$-shift from LaCe to YCe. Indeed, measurements of the specific heat and $T_c$-suppression of La$_{1-x}$Y$_x$Ce alloys [120] also reveal a gradual increase of $T_K$ with $x$ across the alloy series. Related work has been done on the [(La$_{1-x}$Y$_x$)$_{10.65}$Ce$_{0.15}$] Al$_3$ alloy series by Steglich et al. [79]. Re-analysing their resistivity curves using the $\rho$-shift technique, we obtain the values of the parameters given in table 1.
Pressure effects in dilute magnetic alloys

The volume dependence of $J_K(V)$, $d \ln |J_K|/d \ln V \simeq -6\cdot3$, is in reasonable agreement with the high pressure results on LaCe and YCe and thus in this system lattice pressure appears to be the dominant factor. These results lend credibility for these systems to the use of lattice pressure, instead of external pressure, as in our experiments, to generate a change in $J_K$. It is natural to ask why the concept of lattice pressure seems to work rather well across the entire La$_{1-x}$Y$_x$Ce alloy series, whereas the correlation for Cu$_{1-x}$Au$_x$Fe works well only for low Au concentrations. As explained in the previous subsection, the deviation at higher Au concentrations can be attributed to local environment effects arising from the markedly different (40%) ionic radii of Au and Cu. However, for La and Y the difference in ionic radii is only $\sim 10\%$, and local environment effects should, therefore, be smaller in La$_{1-x}$Y$_x$ than in Cu$_{1-x}$Au$_x$. If this is true, then if one wants to use lattice pressure to generate a continuous well-defined change of the parameters, one should choose an alloy series where the difference in the ionic radii of the host metal constituents is small; otherwise, ‘local pressure’ effects will certainly be present and could conceivably dominate the long-range lattice pressure effect.

The situation for the alloy series La$_{1-x}$Th$_x$Ce is apparently more complicated than for the above rare earth systems [82, 98, 121]. As shown in table 1 the increase of $T_K$ and $|J_K|$ with decreasing average atomic volume is extremely rapid, indicating that more than lattice pressure is involved. Indeed, the additional outer electron of Th compared to La should, analogous to the case Cu$_{1-x}$Au$_x$Fe, reinforce the increase of $(N/V)$ and cause enhancement of the increase of $T_K$ with $x$. It should also be noted that for this system $T_K(P)$ was determined solely from the superconducting properties; it would be desirable to complement these estimates with measurements of the normal state properties.

Lattice pressure has been used to advantage in La$_{1-x}$Y$_x$Ce [122] and La$_{1-x}$Th$_x$Ce [123] alloys to study the remarkable phenomenon of re-entrant superconductivity which had been previously only observed in La$_{1-x}$Ce$_x$Al$_2$ alloys at $P=0$ [124]. Re-entrant superconductivity, where the superconductor returns to the normal state at a temperature below $T_c$, can be understood in terms of a temperature-dependent pair-breaking parameter in Kondo superconductors which may have a pronounced maximum [81, 107], opening up the possibility of a return to the superconducting state at even lower temperatures. The existence of such a third transition temperature in La$_{1-x}$Y$_x$Ce has recently been confirmed by Winzer [122, 125]. High pressure measurements on La--2 at.\% Ce show evidence for re-entrant superconductivity at very low temperatures [126].

Further systems where lattice pressure is surely an important factor are Zn$_{1-x}$Al$_x$Mn [127] and Y$_{1-x}$Th$_x$Ce [128]. The success of the lattice pressure concept in some cases should not detract from the fact that for a quantitative analysis, as we are attempting here, a variation of the magnetic properties of a single simple binary system by the application of external pressure is always to be preferred over employing more complicated ternary and quaternary systems to generate lattice pressure. In such multicomponent host systems the presence of not only lattice pressure but also local pressure, whose relative importance changes with alloy concentration and homogeneity, prevent the extraction of real quantitative information about the nature and intrinsic volume dependence of the physical parameters responsible for the microscopic magnetic state of the impurity. In more concentrated systems, where interactions between impurities become important, the variation of the composition of a binary or ternary host not only influences the
strength of these interactions by changing $J$, but also by varying the amount of
defect scattering [129], severely complicating the interpretation.

3.5. Discussion of results

One of the primary goals of the preceding studies of very dilute magnetic alloys
under pressure was to derive values for the volume dependence of the effective
exchange interaction $J(V)$ between a local moment spin and the host conduction
electrons. The preceding section was devoted mainly to outlining the methods used
for extracting $J(V)$ from the data and tabulating the values obtained. The universal
increase of the magnitude of $J$ with pressure, when $J$ is negative, is particularly
noteworthy, and is, in all likelihood as we shall see, but another example of the
general tendency for magnetic systems to demagnetize under pressure. In the
present section we would like to examine the mechanisms contributing to $J$ in more
detail and try to ascertain some of the ramifications of the pressure results.

3.5.1. Wave-vector dependence of $J$

At the beginning of §3.1 the actual spatial dependence of the exchange
interaction between a local magnetic impurity and the conduction electrons $j(r)$,
given in eqn. (1), was replaced by a simple delta-function, resulting in a constant
value of the effective exchange parameter $J$ which was used in the preceding
discussion of the data. In reality, the spatial dependence of $j(r)$ leads to a wave-vector
dependence of the effective exchange parameter $J(k, k')$, which is the sum of two
terms, a positive direct exchange interaction $J_+(k, k')$ and a negative interband
mixing interaction $J_-(k, k')$ [130–133]. If $\Psi_k$ is the conduction electron wavefunction, $\Phi_i$ is a localized 3d (transition metal) or 4f (rare earth) impurity orbital, and $R_{12} = |r_1 - r_2|$, then we have [130, 132, 133]

$$J_+(k, k') = \int \Phi_i^*(r_2) \Psi_k^*(r_1) \frac{\delta^2}{R_{12}} \Phi_i(r_1) \Psi_k(r_2) dr_1 dr_2.$$  \hspace{1cm} (10)

This integral is always positive since it is the Coulomb interaction of an overlap
charge density with itself [132]. The negative interband mixing integral is given,
according to Schrieffer [41], by

$$J_-(k, k') \approx -\frac{V_{ki}V_{ki}^*}{S} \left[ \frac{U}{E(E-E)} \right],$$  \hspace{1cm} (11)

which is valid for $|k'| = |k| = k_f$ and where $E$ is the energy required to remove an
electron from the impurity orbital and place it at the Fermi level, $U$ is the screened
Coulomb interaction energy of two electrons located in orbitals of the magnetic
impurity, and $V_{ki}$ is the mixing matrix element given by [133, 134]

$$V_{ki} \approx \int \Phi_i(r) V(r) \Psi_k^*(r) dr,$$  \hspace{1cm} (12)

$V(r)$ being a one-electron Hartree–Fock atomic potential. The total effective
exchange interaction $J(k, k')$ is the sum of its positive and negative components
[130–133]

$$J(k, k') = J_+(k, k') + J_-(k, k').$$  \hspace{1cm} (13)

The sign of $J(k, k')$ depends on which of these two components is larger. In particular,
we see from eqn. (11) that $J_-(k, k')$ is especially large when the energy $E$ is small, i.e.
'when the virtual bound state approaches the Fermi level.'
For the following discussion it will be useful, following Watson et al. [130, 132], to expand \( J(k, k') \) into its angular momentum components

\[
J(k, k') = \sum_{L} (2L+1) J_L(|k|, |k'|) P_L(\cos \theta),
\]

where \( \theta \) is the angle between \( k \) and \( k' \); \( J_L(|k|, |k'|) \) is the exchange parameter associated with the \( L \)th partial wave, and \( P_L(\cos \theta) \) are the Legendre polynomials. Different experiments average over \( J(k, k') \) in different ways [69, 131, 133]. For instance, as pointed out by Davidov et al. [69, 131] E.P.R. measurements determine \( J(k= k', |k| = k_f) \) from the \( g \)-shift given by

\[
\Delta g = J(k= k') N(E_f) = (J_0 + 3J_1 + 5J_2 + \ldots) N(E_f),
\]

whereas in the electrical resistivity, for example, the pertinent average is over \( J^2(k, k') (1 - \cos \theta) \), where \( k \) and \( k' \) run over the Fermi surface. Because different experiments weigh the various \( L \)-components of \( J \) differently, it is possible to estimate the magnitude of each component individually by carrying out a number of experiments on the same system [69, 131]. From eqns. (13) and (14) it is seen that each \( L \)-term can be written \( J_L = J_{L+} + J_{L-} \). For 3d-impurities it is expected that \( J_{0+} > J_{1+} > J_{3+} \), where the value of \( J_{2+} \) may be somewhat enhanced by virtue of the Clebsch–Gordan coefficients [132]. Also, we have for the mixing interaction, \( |J_{2-}| > |J_{0-}| \), all other components being negligible [130, 131]. If the \( L = 2 \) mixing interaction is strong enough, then \( |J_{2-}| > J_{2+} \) and thus \( J_2 < 0 \), leading to the Kondo resonance. For a 3d-impurity all other \( J_L \)-components are positive.

In the present context we are mainly interested in the extent to which the various angular momentum components are contained in our estimates of \( J(V) \) in the preceding section. Davidov et al. [69, 132] have written down an expression for the electrical resistivity in the second Born approximation containing explicitly the relevant \( J_L \)s (i.e. \( J_0, J_1, J_2 \) for a 3d-impurity). The crucial point is that although the positive \( L \)-components may be larger in magnitude than a negative \( J_2 \) they do not lead to the large resonant exchange or Kondo scattering (see fig. 6) which dominates the temperature dependence of the electrical resistivity. In particular, as pointed out by Larsen [46], the only \( J_L \)s which appear in the expression for \( T_K \) in eqn. (2) are those which are negative, i.e. \( J = J_2 \) for 3d-impurities. Experiment itself supports these conclusions. The relative unimportance of the resistivity contribution from \( J_0 \) and \( J_1 \), compared to \( J_2 \), is shown by the fact that for CuFe, for instance, both the universal resistivity curve [22] as well as the expected dependence [12]

\[
\rho_{\text{spin}} \propto \left[ 1 - \frac{\pi^2}{2S+3} \left( \frac{T}{T_K} \right)^2 \right]
\]

dependence for \( T \ll T_K \) are observed [68]. In the present pressure investigations on Kondo systems with 3d-impurities, therefore, it is clear that we are determining the pressure dependence of the \( J_2 \)-component alone. The above discussion is directly applicable to rare earth impurities, when \( L = 3 \) is substituted for \( L = 2 \). In the following discussion the ‘Kondo’ \( J_K \) is therefore defined as \( J_K = J_2 \) for 3d-impurities and \( J_K = J_3 \) for 4f-impurities.

3.5.2. Pressure dependence of \( J (J < 0) \)

One of the principal results of the present section is the universal increase of \( |J_K| \) with pressure for negative \( J_K \). Although the physical mechanism responsible for this
behaviour is not yet completely clear, the universality of the result alone would point to a common mechanism for all dilute alloys. Unfortunately, calculations of exchange integrals, such as those in eqns. (10) and (11) are only of preliminary character, the values $J_+$ and $J_-$ depending, in general, on the exact character of the wavefunctions involved [11]. The pressure dependence of $J_{K+}$ is expected to be quite small [105], although no exact calculation of $J_{K+}(V)$ exists, to our knowledge. However, if we assume in zeroth order approximation that the relative amount of wavefunction overlap in eqn. (10) remains constant, then, since $R_{12} \propto V^{-1/3}$, the volume dependence of $J_{K+}$ would be given by $d \ln J_{K+}/d \ln V = -1/3$, a value much smaller than the values $d \ln |J_K|/d \ln V \approx -2$ to $-6$ given in table 1. Some insight into possible mechanisms for the present pressure increase of $|J_K|$ is provided by Schrieffer’s expression [41] in eqn. (11) which can be written in the approximation $U \gg E$ in the form

$$J_{K-} = J_K - J_{K+} = -\frac{|V_{kl}|^2}{SE}. \quad (15)$$

Using the result from §3.3.1 that $dS/dP=0$ and assuming $|J_{K-}| \gg J_{K+}$ and $dJ_+/dP \approx 0$, it follows from eqn. (15) that

$$d \ln |J_K|/d \ln V \approx d \ln |J_{K-}|/d \ln V \approx d \ln |V_{kl}|^2/d \ln V - d \ln E/d \ln V. \quad (16)$$

The observed increase of $|J_K|$ with pressure could thus either arise from an increase in the covalent admixture matrix element $|V_{kl}|^2$ or a decrease in the separation $E$ of the local magnetic level from the Fermi level $E_F$, or both. It would seem reasonable that $|V_{kl}|^2$ would increase somewhat with pressure, however no careful calculation of $d \ln |V_{kl}|^2/d \ln V$ is available. If we assume that a decrease in $E$ is mainly responsible for the increase in $|J_{K-}|$, then from eqn. (16) it follows that $d \ln |J_K|/d \ln V \approx d \ln E/d \ln V$. Setting $E = E_i - E_F$, where $E_i$ is the energy of the local impurity state, and assuming $d \ln E_i/d \ln V = 0$ and $d \ln E_F/d \ln V = -2/3$, as for a free electron gas in the latter case, then we find

$$d \ln |J_K|/d \ln V = -\frac{2}{3} \frac{E_i}{E}. \quad (17)$$

Using $E_F = 7$ eV for a Cu host and $E_F = 5.5$ eV for Au and Ag hosts, one can use eqn. (17) and the values of $d \ln |J_K|/d \ln V$ from table 1 to estimate that $E \approx 1.3$ to 1.8 eV for the 3d-impurity systems; values of $E$ about half this large are found for the 4f-impurities. These values are in reasonable agreement with other experiments [33], particularly noteworthy being optical [135] and photoemission [136] data on AgMn where it was estimated that $U = 5$ eV and $E = 2$ eV, compared to our value of $E = 1.8$ eV for the same system. One objection to the present analysis is that it is difficult to understand why $E$ should always decrease under pressure; it is certainly conceivable that in some systems pressure would shift the local state away from $E_F$, causing $E$ to increase. Hopefully the present work will help stimulate the development of a suitable theory for the magnitude and volume dependence of exchange interactions in dilute alloys.

### 3.5.3 Pressure dependence of $J$ ($J > 0$)

LaGd is one of the few dilute magnetic alloys with positive $J$ which has been studied under pressure. From the pressure dependence of the $T_c$-suppression it was inferred (see table 1 and §3.3.2) that $d \ln |J|/d \ln V > 0$, where $J$ here is an average
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exchange parameter appropriate for the superconducting properties. This decrease of \( J \) with pressure is somewhat surprising since, as discussed above, one would expect that a positive \( J \) should increase slightly. It can be hypothesized that the observed decrease of \( J = J_+ + J_- \) with pressure arises principally, in fact, from an increase in the magnitude of the negative \( J_3- \) component with pressure, the \( J_+ \)'s staying essentially constant, i.e. the same mechanism operative in the negative-\( J \) Kondo alloys. If this is true, then under sufficient pressure \( J_3 = J_3+ + J_3- \) should become negative after going through zero at an estimated pressure of several hundred kilobars—LaGd, a high pressure Kondo system! Such a behaviour would also be consistent with the general tendency for magnetic systems to demagnetize under pressure, as was discussed at length in the Introduction. A negative value of \( J \) is a warning signal that the magnetic impurity is preparing to demagnetize. This can be understood from eqn. (15) where \( J_K \) should always become increasingly negative as \( E \rightarrow 0 \). When \( E = 0 \) the impurity spin \( S \) is no longer well-defined and the simple hamiltonian in eqn. (1) is no longer applicable. At extremely high pressures Gd will presumably lose one of its 4f-electrons completely to the conduction band.

3.5.4. Orbital moment

One of the assumptions implicit in the basic hamiltonian in eqn. (1) is that the orbital angular momentum can be neglected, i.e. \( L = 0 \). This assumption is certainly not valid for many rare earth impurities; Hirst [137] has pointed out that the orbital moment of even 3d-impurities in the noble metals need not be quenched because of the high local symmetry in these hosts. Indeed, E.P.R. studies [138] of Fe in Cu show that \( L \neq 0 \) and more recent N.M.R. studies [59, 139] indicate strongly that Fe, Cr, Mn, and Co impurities in Cu are characterized by both well-defined spin and orbital quantum numbers, in agreement with Hirst's model [140]. The assignment to a magnetic impurity of orbital as well as spin degrees of freedom can be carried out in the context of a generalized s–d interaction model [140, 141]. Fortunately, as pointed out by Hirst [142], the generalized Kondo problem arising from this model is very similar in structure to that arising from the simple s–d hamiltonian of eqn. (1). It would therefore not be expected that consideration of the generalized model would change the methods used or the main conclusions reached in this paper. Clearly both orbital as well as spin moments can contribute to the value of the exchange interaction \( J(k, k') \) [142]. The present high pressure experiments were carried out on systems with both S-state (Mn) and non-S-state (Fe, Cr, V) impurities. However, inspection of table 1 indicates that the orbital state of the impurity does not seem to play a dominant role in the volume dependence of the exchange interaction \( J_K(V) \).

3.5.5. Functional dependence of \( T_K \) on \( J_K \)

The expression given in eqn. (2) for \( \delta_0 = 0 \) which relates the Kondo temperature \( T_K \) to the effective exchange parameter \( J_K \), i.e. \( T_K = T_\Gamma \exp [1/J_K N(E_\Gamma)] \), differs somewhat from that obtained in the renormalization-group calculation [38],
\[
T_K = T_\Gamma \left[ J_K N(E_\Gamma) \right]^{\frac{1}{2}} \exp [1/J_K N(E_\Gamma)],
\]
which is valid for \( |J_K| N(E_\Gamma) \ll 1 \). Although the inclusion of the prefactor \( \left[ J_K N(E_\Gamma) \right]^{\frac{1}{2}} \) will result in a somewhat larger value of \( |J_K| \) for a given value of \( T_K \), the accuracy of eqn. 2 is sufficient for an extraction of the volume dependence of \( J_K \) from the pressure dependence of \( T_K(P) \) due to the dominance of the exponential factor. For values of \( |J_K| N(E_\Gamma) \lesssim 1 \) a more complicated
relationship between $T_K$ and $J_K$ must be employed [38] when determining $J_K(V)$ in systems with very large values of $T_K$ which are approaching the magnetic–non-magnetic transition as $E \rightarrow 0$. In this region the impurity moment is no longer well defined and one must replace the simple s–d hamiltonian in eqn. (1) by a more general Anderson hamiltonian [134]; unfortunately, the relationship between the effective exchange parameter $J_K$ and measurable experimental properties is here poorly understood. It is apparent that to obtain accurate values of the volume dependences of $J_K(V)$, we should stay well within the 'good moment' region where the values of $T_K$ are relatively small. In particular, we have seen that estimating $T_K(P)$ depends heavily on the existence of a universal dependence of the physical properties (here resistivity) on $T/T_K$; such universal behaviour surely breaks down near the magnetic–non-magnetic transition.

In the next section we consider interactions between impurities in more concentrated magnetic systems. In the RKKY-type of interaction, the exchange interactions discussed above lead to an indirect interaction between impurities in which the average is over all non-zero $J_L$-components. A comparison of the volume dependence of the magnetic ordering temperature $T_0(V)$ in such systems with the value of $J_K(V)$ determined in Kondo systems should therefore give information not only about whether the RKKY-interaction is responsible for the magnetic ordering but also about the relative magnitudes of the various $J_L$-components.

§4. MORE CONCENTRATED ALLOYS (SPIN GLASSES) UNDER PRESSURE

The major part of the previous section was concerned with deriving values for the volume dependence of the effective exchange interaction $J_K(V)$ in very dilute magnetic alloys from resistivity studies under pressure. In these measurements care was taken to keep the magnetic impurity concentration as small as possible to minimize the effects of inter-impurity interactions in the experimental temperature range. In the present section we concern ourselves predominantly with more concentrated magnetic alloys where the interactions between impurities are relatively strong and dominate over such single impurity properties as the Kondo effect. One of the inter-impurity interaction mechanisms believed to be important in such alloys is the indirect Ruderman–Kittel–Kasuya–Yoshida (RKKY) interaction which uses the host conduction electrons as intermediaries. In the RKKY-interaction, the elementary interaction between a magnetic impurity and the sea of conduction electrons, given by the various angular momentum components $J_L$ as in eqn. (14), sets up a long-range spin density polarization which in turn interacts with all other magnetic impurities in the system. The effective RKKY-exchange parameter, in the asymptotic limit and for zero exchange enhancement, is given by the following average over the $J_L$-components [69, 131, 132, 143]

$$J_{\text{RKKY}} = J_0 - 3J_1 + 5J_2 - 7J_3 + \ldots,$$

where, as discussed in §3.5.1, for a 3d-impurity the $J_0$, $J_1$, and $J_2 = J_K$ terms and for a 4f-impurity the $J_0$, $J_1$, $J_2$, and $J_3 = J_K$ terms are important and must be included in eqn. (18). The pre-eminent importance of the $J_K$-component in very dilute Kondo alloys, where $J_K$ is negative, is due to the fact that only this angular momentum component is involved in the large Kondo resonance, as was discussed in §3.5.1. It is, however, not at all obvious from the outset which of the above components is dominant in the RKKY-interaction in eqn. (18), even though $J_K$ has the largest
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In light of the discussion in the previous section, it would seem reasonable to assume that $J_K$ would have the largest pressure dependence; by determining $J_{RKKY}(V)$ and comparing it to $J_K(V)$, it should be possible to gain some information about the relative magnitudes of the various angular momentum components contributing to $J_{RKKY}$. It is also an interesting question whether or not the $J_K$-interaction, which, when negative, leads to fluctuations in the $z$-component of the spin, if not in its magnitude [144], is at all able to contribute to those interactions between spins which can lead to magnetic ordering at low enough temperatures.

In addition to the indirect RKKY-interaction between magnetic impurities via the conduction electrons, several other interaction mechanisms have been proposed as being possibly operative in dilute magnetic alloys. One such mechanism is the direct exchange interaction arising from the overlap of impurity orbitals [145] and another is the magnetic dipolar coupling [146, 147]. A pressure experiment, in fact, can be used to help decide which interaction mechanism is dominant in a given system. Each of the above types of magnetic interaction has its own intrinsic or characteristic volume dependence which we assume, for the purposes of discussion, is known. Since the magnetic ordering temperature $T_0$ involves a sum over the individual interactions between pairs of spins, a comparison of the volume dependence of $T_0$ in a given system to that of each possible interaction mechanism helps us point to which interaction mechanism is responsible for the particular type of magnetic ordering in question. The guilty interaction mechanism will betray itself by how it behaves under pressure!

To illustrate the above, consider the extensively studied system AuFe. The concentration dependence of the magnetic ordering temperature $T_0$ for AuFe is shown in fig. 9 [148]. $T_0$ is seen to increase with Fe concentration in a reasonably linear fashion, the downward curvature for $c<15\text{at.\% Fe}$ being attributed by Larsen [129, 148], using the RKKY-model, to self-damping by the Fe impurities. In the low concentration regime, where $c$ is a few per cent, the type of magnetic ordering is believed to be of the spin glass variety whereby as the temperature drops below $T_0$...

![Fig. 9](image)

Dependence of magnetic ordering temperature $T_0$ and resistivity maximum temperature $T_m$ on Fe-concentration in AuFe alloys using data collected by Larsen [148]. Note that $T_m$ lies above $T_0$, a general result. For $c \gtrsim 15\text{at.\% Fe}$ the nature of the magnetic ordering changes from spin glass to ferromagnetic.
Temperature dependence for AuFe alloys of (a) low field a.c. magnetic susceptibility $\chi$ from [152] and (b) spin-resistivity $\Delta\rho = \rho_{\text{f}} - \rho_{\text{Au}}$ from [154]. Both the susceptibility cusp at $T_0$ and the resistivity maximum at $T_m$ shift to higher temperatures with increasing Fe-concentration; in general, $T_m$ lies above $T_0$ for a given concentration.

the paramagnet freezes into a magnetic state with only short-range order, the spins pointing in more or less random directions [149, 150]. At temperatures below $T_0$, time dependent magnetic remanence effects are also observed [147, 151]. The so-called spin glass freezing temperature $T_0$ is marked by a sharp cusp in the low field a.c. susceptibility, as shown in fig. 10 (a) [149, 152]. The electrical resistivity has in general no sharp break in slope at $T_0$ [153], but does go through a maximum at a temperature $T_m$ [154] located somewhat higher than $T_0$, as seen in figs. 9 and 10. Both $T_0$ and $T_m$ increase with increasing impurity concentration. The precise nature of the spin glass frozen state is a matter of controversy at the present time [149, 150].

In the so-called phase-transition model, each spin senses the presence of all other spins via the long-range oscillatory RKKY-interactions; as the temperature is lowered through $T_0$, the spin system is believed to condense into a frozen spin state [150]. In a completely different physical model, the spin freezing is attributed to the Néel spin-blocking mechanism [155] where at temperatures below $T_0$ spin clusters are locked into certain fixed directions by an anisotropy energy which is perhaps magnetic dipolar in origin, without the necessity of invoking the RKKY-interaction [146]. For completeness it should be mentioned that there are also hybrid models invoking both RKKY and anisotropic dipolar interactions leading to the formation of so-called ‘spin clouds’ [147]. For the sake of clarity, we will here restrict our attention initially to either the extreme phase transition or the spin-blocking models. As we will see, the interactions involved in these models are expected to have markedly different volume dependences. A determination of $T_0(P)$ by a high pressure experiment would help clarify which model is more appropriate.

As the impurity concentration in AuFe is increased beyond the few per cent range, a sudden upward break in the concentration dependence of $T_0$ is observed at $c \approx 15$ at.$\%$ Fe, as seen in fig. 9, which marks a change-over in the nature of the magnetic ordering from spin glass to long-range ferromagnetic. In the concentration
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range near and above 15% it is conceivable that direct exchange interactions between impurity d-orbitals have gained sufficiently in importance to be instrumental in the observed long-range ordering. Larsen [148] has suggested that a determination of the pressure dependence of $T_0$ could shed some light on whether or not at this critical concentration a change in the relevant interaction mechanism is present. Pure Fe is generally believed to be an almost strong itinerant ferromagnet. As the Fe concentration is increased, therefore, the system AuFe is shuttled through a variety of different types of magnetic behaviour, namely, from Kondo $\rightarrow$ spin glass $\rightarrow$ inhomogeneous ferromagnet $\rightarrow$ itinerant ferromagnet. The pressure dependence of the magnetic ordering temperature, in addition to the concentration dependence of $T_0$, contains valuable information about the nature of the appropriate interaction mechanism in each magnetic regime, a knowledge of which is essential to an understanding of the microscopic nature of the particular ordered magnetic state itself. In the next section we present the results of high pressure experiments on AuFe and other systems in the low concentration or spin glass regime.

4.1. Results of experiment

The most direct method to determine the pressure dependence of the magnetic ordering temperature $T_0(P)$ is by measuring the low-field magnetic susceptibility under pressure. However, it is very difficult experimentally to attain simultaneously the high sensitivity necessary to accurately measure the temperature dependence of the low-field susceptibility cusp and the high pressures necessary for an accurate determination of the volume dependences. In an electrical resistivity measurement, on the other hand, high sensitivity and high pressure are much more easily realized. There are also advantages in using the same technique as on the extremely dilute Kondo systems to study the changes which occur in the pressure dependence as the concentration increases. Although, as seen in fig. 10 for AuFe, there appears to be in general no sharp effect in the resistivity at $T_0$, the interactions between impurities do lead to a resistivity maximum in those spin glasses which are Kondo systems in the very dilute limit [149, 153]. The temperature of this resistivity maximum $T_m$ is generally located above $T_0$. In § 4.3 we will see that from the value of $T_m$ we can infer the mean r.m.s. interaction strength $\Delta$ which is related to $T_0$.

The first measurements on a spin glass under high pressure conditions were carried out by Schilling et al. [156] on the system AuFe. The results of these and subsequent measurements of the electrical resistivity on the spin glasses AuFe and CuMn by Schilling et al. [156–158] and AgMn by Olijnyk et al. [24, 60] are shown in fig. 11. The directions of the shifts in $T_m$ with pressure are seen to vary markedly: for AuFe $T_m$ decreases, for CuMn $T_m$ stays constant, and for AgMn $T_m$ increases under pressure. An almost identical decrease of $T_m$ with lattice pressure is also observed in $\text{Au}_{1-x}\text{Cu}_x\text{Fe}$ alloys with increasing Cu concentration [156, 159]. Also observed in fig. 11 is an increase with pressure in both the negative resistivity curvature $T_m$ and the value of the resistivity at an arbitrary temperature $T_s$ which lies below 10 K where $\rho_{\text{spin}}$ dominates the resistivity (see caption to fig. 11). Similar experiments have been carried out on the following spin glasses at various concentrations: AuMn by Schilling et al. [157], AuCr and CuCr by Willer et al. [25, 160], MoFe by Ford and Schilling [161], and LaCe by Zimmer and Schilling [70, 27]. The volume dependence of $T_m$ is shown in the upper half of fig. 12 for all systems studied. $T_m$ is seen to have manifold behaviour under pressure, the sign and magnitude of $dT_m/dP$ depending not only on the system studied but also in a given system on the concentration.
Total measured resistivity $\rho_0$ of Ag–0.15 at. % Mn [24, 60], Cu–0.15 at. % Mn [157], and Au–0.1 at. % Fe [156–158] as a function of $\log T$ at different pressures, the order of measurement being given by the direction of the vertical arrows. Solid lines connecting data points are drawn for clarity. Absolute resistivity scale applies to the $P = 0$ data. The high pressure data are shifted vertically for clarity with the relative scale the same for all data in a given graph. The values of $\rho_0$ at $T_m$ are given in the respective references. In all cases $\rho_0(T_m)$ increases with pressure, where $T_m$ is an arbitrary temperature below 10 K. Vertical lines give $T_m$ values at $P = 0$ (see table 2). For AgMn, $dT_m/dP > 0$; for CuMn, $dT_m/dP \approx 0$; for AuFe, $dT_m/dP < 0$.

Particularly notable is $T_m(P)$ for the systems CuMn and AuCr where $dT_m/dP$ actually changes sign at different concentrations! Inspection of fig. 12 reveals that in a given system $d\ln T_m/dP$ always becomes more positive with increasing concentration. The behaviour of $T_m$ under pressure is thus rather complicated. The question now is whether an increase or decrease in $T_m$ implies a similar behaviour for the mean interaction strength $\Delta_c$ or the spin glass freezing temperature $T_o$. It would seem unlikely that $\Delta_c$ or $T_o$ would behave radically different under pressure, as does $T_m$, when the impurity concentration is varied by only a factor of three. What is needed for a quantitative analysis of the data is an accurate theory of the resistivity maximum. Larsen has developed such a theory [12, 45, 162], deriving an explicit expression for $T_m$ as a function of both the r.m.s. interaction strength $\Delta_c$ and the Kondo temperature $T_K$. Using this theory, the volume dependence of $\Delta_c(v)$ is found to be indeed far more simple than that of $T_m(v)$, $\Delta_c$ always increasing with pressure, as seen in the lower half of fig. 12. The pressure dependence of $\Delta_c$ is seen to have at most a small concentration dependence, in contrast to $T_m$. A volume reduction of 5%, which corresponds to $\sim 80$ kbar pressure on a noble metal, causes $\Delta_c$ to increase by between 10 and 35%, depending on the particular system. From table 1 we see that the same pressure caused the quantity $J_0^2 N(E_f)$ to increase between about 13 and 26%, which is comparable to the $\Delta_c$ increase observed here, i.e. we have very roughly
Dependence of the resistivity maximum temperature $T_m(v)$ and the mean interaction strength $\Delta_\alpha(v)$ on the relative volume reduction $v = (V_0 - V)/V_0$ for a number of alloys, where $V$ is the atomic volume at a given pressure and $V_0$, $T_m(0)$, and $\Delta(0)$ are $P = 0$ values. $\Delta_\alpha(v)$ is derived from $T_m(v)$ and $T_K(v)$ using Larsen's theory [12, 45] for those systems where $T_K(v)$ is known with reasonable accuracy. Whereas the pressure dependence of $T_m$ is strongly system and concentration dependent, $\Delta_\alpha$ always increases with pressure, having little concentration dependence. For references to systems listed, see § 4.1 in text or table 2.

\[
d\Delta_\alpha/dP \approx d[J_K^2 N(E_f)]/dP.
\]
As will be discussed in the next section, for a RKKY-interaction it is expected that $\Delta_\alpha \propto J_{RKKY}^2 N(E_f)$, where $J_{RKKY}$ is given by eqn. (18). It would thus appear, and this will be confirmed by the detailed analysis to follow, that in the spin glass systems studied, the RKKY-interaction is the principal impurity–impurity interaction mechanism and that the negative angular momentum component $J_K$ makes the most important contribution to this interaction [157, 163].

We now summarize the principal aims of the present investigations of spin glasses under pressure:

1. Determination of the volume dependences of impurity–impurity interactions $\Delta_\alpha(V)$ in spin glasses.
(2) Use of $\Delta_c(V)$ to help determine which of several possible interaction mechanisms is operative in spin glasses.

(3) Determine what role $J_K$ (which leads to the Kondo resonance in very dilute systems) plays in impurity–impurity interactions.

(4) Critical test of Larsen’s theory of the resistivity of ‘Kondo’ spin glasses. A large body of resistivity data on such systems exists; a good theory is needed to extract out quantitative information.

(5) Test for existence of predicted spin glass to Kondo transition by applying pressure to increase $|J_K|$ and $T_K$. Study of the critical behaviour of this transition.

(6) Comparison of these results to those at higher impurity concentrations where different types of magnetic ordering and interaction mechanisms may become prevalent.

4.2. Volume dependence of magnetic interactions

4.2.1. Generalized RKKY-interaction

The exchange interaction between a local impurity spin $S$ at $r_i$ and the conduction electrons given by eqn. (1) sets up a spatially oscillatory spin density polarization which in turn interacts with a second spin at $r_j$. The general solution of this problem for an arbitrary magnetic impurity state and host conduction electron band structure is a problem of enormous complexity [11, 31, 69, 130–132, 143, 164, 165].

Davidov et al. [69] have derived the following expression within the free electron model for the radial dependence of the generalized RKKY-spin polarization in the approximation that the effective exchange coupling $J(\mathbf{k}, \mathbf{k'})$ given in eqn. (14) is only a function of $k-k' = q$:

$$\sigma_{\text{RKKY}}(2k_tR_{ij}) = \frac{C}{(2k_tR_{ij})^4} \sum_{L} [(-1)^L(2L+1)J_LF_L(2k_tR_{ij})] = \sum_{L} \sigma_L, \quad (19)$$

where $R_{ij} = |r_i - r_j|$, $k_t$ is the Fermi wave-vector, $C = \frac{9\pi z^2 S_z}{8}$, $z$ is the number of conduction electrons per atom, $J_L$ is the exchange parameter associated with the $L$th partial wave as in eqn. (14), and the oscillatory functions $F_L(2k_tR_{ij})$ are given in [69]. The first $F_L$ function, for $L = 0$, is given by

$$F_0(x) = (\sin x - x \cos x), \quad (20)$$

and will be recognized as the usual RKKY-term. The other $F_L$ functions are more complicated functions of $2k_tR_{ij}$; for instance,

$$F_2(x) = \left[\left(-x + \frac{4}{x} \frac{720}{x^3} \cos x + \left(10 - \frac{234}{x^2} + \frac{720}{x^4}\right) \sin x\right)\right]. \quad (21)$$

The corresponding dependences of the spin polarizations $\sigma_0$ and $\sigma_2$ on $2k_tR_{ij}$ are shown in fig. 13; the oscillatory character and rapid decay of the spin polarization in the conduction electron sea with increasing separation from the impurity spin is clearly visible.

In the present context we are mainly interested not in the absolute magnitude of the spin polarization $\sigma_{\text{RKKY}}$ but rather in how it changes with pressure. It is important to note that in the free electron model $k_t \propto V^{-1/3}$ and thus, since $R_{ij} \propto V^{+1/3}$ the product $k_tR_{ij}$ remains constant under pressure. This implies that in the
Partial RKKY-spin density polarization versus $2k_f R_{ij}$ for s-wave $\sigma_0$ and d-wave $\sigma_2$ components using eqns. (19–21) setting, for simplicity, $J_0 = J_2$. Value of $2k_f R_{ij} \approx 13.3$ is appropriate for a Au–10 at. % Fe alloy.

general expression in eqn. (19) for $\sigma_{\text{RKKY}}(2k_f R_{ij})$, pressure primarily serves to vary the $J_L$s, the oscillatory spatial functions $F_L(2k_f R_{ij})$ merely acting as pressure independent weighting factors. This result carries over to the more pertinent case of a magnetic alloy where a large number of magnetic impurities interact with one another via the generalized RKKY-interaction. For a relatively dilute magnetic system, the average separation between impurities can be a number of lattice spacings and we need only consider the long-range part of $\sigma_{\text{RKKY}}$. In this limit of large $2k_f R_{ij}$, all the $F_L$s become equal to $2k_f R_{ij} \cos 2k_f R_{ij}$, so that from eqn. (19) we have

$$\sigma_{\text{RKKY}}(2k_f R_{ij}) = C \left(2k_f R_{ij}\right)^3 [J_0 - 3J_1 + 5J_2 - 7J_3 + \ldots] \cos 2k_f R_{ij}$$

where $J_{\text{RKKY}}$ is the effective RKKY-interaction parameter previously defined in eqn. (18). Indeed, for AuFe alloys with concentrations less than 10 at. % Fe, as seen in fig. 13, the spin polarizations $\sigma_0$ and $\sigma_2$ already have a nearly identical $\cos 2k_f R_{ij}$ oscillatory dependence. From eqn. (22), therefore, $J_{\text{RKKY}}$ is the only factor in the spin density polarization expression which should have any appreciable pressure dependence. For a free electron gas, $d \ln C/d \ln V = -d \ln E_f/d \ln V = +2/3$, a weak dependence.

We now consider what effect a pressure-induced change in $J_{\text{RKKY}}$ would have on an observable quantity like the magnetic ordering temperature $T_0$. For a spin glass, Larsen [148] has shown that

$$T_0 \propto \Delta \propto \left[ \sum_{j \neq i} \mathcal{J}_{ij}^2 \right]^{1/2},$$

Fig. 13
where $\Delta_e$ is the root-mean-square (r.m.s.) interaction strength in the alloy and $J_{ij}$ is the effective interaction strength between spins $S_i$ and $S_j$. For a system with RKKY-interactions involving one angular momentum component of $J_L$, $J_{ij} \propto N(E_f) J^2_{\text{RKKY}}$ [133]. For the case when more than one $J_L$ component is important, Larsen has derived [46] an analogous expression

$$J_{ij} \propto N(E_f) J^2_{\text{RKKY}},$$

where $J_{\text{RKKY}}$ is defined in eqn. 18. From eqns. (23, 24) it follows for the volume dependence of the ordering temperature $T_0$, in the case of RKKY-interactions, that

$$d \ln T_0 / d \ln V = d \ln \Delta_{\text{RKKY}} / d \ln V = 2 d \ln |J_{\text{RKKY}}| / d \ln V + d \ln N(E_f) / d \ln V.$$

This result holds generally for magnetic ordering in systems with long-range RKKY-interactions and is not specific for the spin glass type of ordering [166]. In the previous section we listed in table 1 the volume dependence of the effective exchange parameter $J_2$ for a number of very dilute Kondo systems with transition-metal impurities. If in eqns. (18) or (22) the $J_2$ term makes the dominant contribution to $J_{\text{RKKY}}$, then we expect from eqn. (25) that

$$d \ln T_0 / d \ln V = d \ln \Delta_{\text{RKKY}} / d \ln V \approx 2 \ln |J_2| / d \ln V + d \ln N(E_f) / d \ln V.$$

Inserting the volume dependences of $J_2$ and $N(E_f)$ from table 1 into eqn. (26) we can make the prediction that, if the RKKY-interaction is responsible for the magnetic ordering and the $J_2$ wave-vector component is dominant, then

$$d \ln T_0 / d \ln V = d \ln \Delta_{\text{RKKY}} / d \ln V \approx -3 \text{ to } -5$$

for 3d-impurities in the noble metals. This predicted increase of $T_0$ or $\Delta_{\text{RKKY}}$ with pressure is quite rapid, i.e. if $T_0 \approx 10$ K, then 100 kbar should be sufficient to increase $T_0$ between about 2 and 3 K. Whether or not $J_2$ does, in fact, dominate over the other wave-vector components is certainly not clear at the outset and the expression in eqn. (26) is intended at present to be used as a basis for further discussion.

4.2.2. Dipolar anisotropy

Let us assume that the spin glass freezing process is due to the blocking of spin clusters in certain fixed directions by a magnetic dipolar anisotropy interaction given by the following expression

$$\Delta_{ij}^{\text{DA}} = R_{ij}^{-3} [\mathbf{m}_i \cdot \mathbf{m}_j - 3(\hat{r}_{ij} \cdot \mathbf{m}_i)(\hat{r}_{ij} \cdot \mathbf{m}_j)],$$

where $\hat{r}_{ij} = (\mathbf{r}_i - \mathbf{r}_j)/R_{ij}$ and $\mathbf{m}_i$ and $\mathbf{m}_j$ are the respective magnetic moment vectors. Since $\Delta_{ij}^{\text{DA}} \propto 1/R_{ij}^3 \propto V^{-1}$, this interaction is clearly inversely proportional to the sample volume for isotropic compression. Therefore, if dipolar anisotropy were the dominant mechanism responsible for the spin glass freezing at $T_0$, from eqn. (23) we would expect a measurement of the pressure dependence of $T_0$ to give

$$d \ln T_0 / d \ln V = d \ln \Delta_{\text{RKKY}}^{\text{DA}} / d \ln V = -1,$$

where $\Delta_{\text{DA}}$ is the r.m.s. interaction strength of the dipolar anisotropy interaction. This pressure dependence is relatively small and should be easily distinguishable from that of the RKKY-interaction which, according to the preceding subsection, is expected to be about four times larger.
4.2.3. Direct 3d–3d exchange

In a given magnetic alloy, in addition to the relatively long-ranged RKKY- or magnetic dipolar interactions, there also exists the possibility of direct exchange interactions between the magnetic impurities owing to the overlap of their 3d-orbitals. In fig. 14 we reproduce the well-known Bethe–Sommerfeld–Slater interaction curve [167] where the direct exchange interaction between two spins $J_{ij}^{DE}$ is considered to be a function of the ratio of the separation of the two spins $R_{ij}$ to the radius of their magnetic orbitals $R_d$. Since $R_{ij}/R_d$ decreases under pressure, the volume dependence of the Curie temperatures $d\ln T_C/d\ln V$ of Fe $(0\pm 0.05)$, Co $(0\pm 0.07)$, and Ni $(-1.1)$ [168] would qualitatively agree with what would be expected from this interaction curve if the three alloys were shifted a bit further to the right. However, calculations by Stuart and Marshall [169] of the magnitude of $J_{ij}^{DE}$ have given values approximately two orders of magnitude too weak to account for the measured ordering temperatures of the iron-group ferromagnets; later estimates by Watson et al. [170] even gave the wrong sign of the interaction. In fact, Fe, Co, and Ni are generally believed to be itinerant ferromagnets and not a collection of localized moments coupled by direct exchange. In the case of the ferromagnet Gd, measurements by McWhan and Stevens [171] have shown that its Curie temperature decreases with pressure, in contrast to an increase expected from fig. 14; this result is not surprising since it is widely accepted that the RKKY-mechanism, and not direct exchange, is important for interactions between rare-earth ions in metals.

As is seen in fig. 14, when the magnetic impurities are close together, the direct exchange mechanism is expected to vary strongly with the separation between impurities [167, 172] only being of real importance for nearest- or next-nearest-neighbour spins. For this reason, this mechanism can hardly be important for dilute magnetic alloys such as we are studying here, e.g. Au–0.1 at.\% Fe, where the mean inter-impurity separation is many lattice spacings. Such a dilute system would be
located well to the right of the maximum of the interaction curve in fig. 14 where $J_{ij}^{DE}$ is determined primarily by a normal positive exchange integral of the form

$$J_{ij}^{DE} = \int \int \Phi_i^*(r_2)\Phi_j^*(r_1)\left(\frac{e^2}{R_{12}}\right)\Phi_i(r_1)\Phi_j(r_2)dr_1dr_2,$$

where $\Phi_i$ and $\Phi_j$ are the impurity wave functions and $R_{12} = |r_1 - r_2|$. Owing to the $1/R_{12} \propto V^{-1/3}$ dependence in this integral, in a very crude zeroth order 'scaling approximation' [172] one would expect that

$$\frac{d \ln J_{ij}^{DE}}{d \ln V} = \frac{d \ln J_{ij}^{DE}}{d \ln V} = \frac{d \ln J_{ij}^{DE}}{d \ln V} = -1/3.$$  

(31)

This dependence is quite small, being three times weaker than the dipolar interaction and 10–15 times weaker than the RKKY-interaction. However, as Monro [172] has pointed out, in addition to the above scaling dependence, there is also a pressure dependence of $J_{ij}^{DE}$ arising from electronic screening and wave-function distortion effects, which can be appreciable. In fact, for Cr$^{3+}$ impurities in ruby he estimates that $d \ln J_{ij}^{DE}/d \ln V \approx -2$ [172]. At the present time there would appear to be considerable uncertainty in the values of $J_{ij}^{DE}$ and its volume dependence; further work on both the theoretical as well as on the experimental side are necessary to clarify the situation.

### 4.3. Results of theory

To fulfill the aims outlined at the end of §4.1 it is necessary that we carry out a quantitative analysis of the high pressure resistivity measurements presented in figs. 11 and 12. As seen in figs. 10 and 11 the spin-resistivity of 'Kondo' spin glasses, i.e. spin glasses which in the extreme dilution limit are Kondo systems ($J_K < 0$) with a negative resistivity slope, can go through a well-defined maximum. The origin of this resistivity maximum is indicated in fig. 15. In the extreme dilution 'Kondo' limit each impurity spin can scatter the conduction electron spins independent of all other impurity spins and the spin-resistivity follows $\rho_{\text{Kondo}}$. At high impurity concentrations, the effect of the interactions between impurities, which lead to the spin glass freezing at $T_0$, is to markedly disturb the build-up of the delicately balanced Kondo resonance, causing the resistivity to fall off, resulting in a resistivity maximum at a temperature $T_m$ which lies above $T_0$. The value of $T_m$ clearly depends both on the magnitude of the slope of the Kondo resistivity (which is a function of $T/T_K$, see fig. 6) as well as on $T_0$ or the r.m.s. impurity interaction strength $\Delta_e$ defined in eqn. (23). There is some evidence from experiment that $\Delta_e$ and $T_0$ are proportional [148]. If the functional dependence $T_m = T_m(\Delta_e, T_K)$ is known, then from the volume dependences $T_m(V)$ and $T_K(V)$ it should be possible to extract the volume dependence of the mean interaction strength $\Delta_e(V)$, the quantity of principal interest to us here. It should be pointed out that the resistivity maximum in the present context arises from a quenching of the Kondo resistivity by inter-impurity interactions and is not to be confused with the resistivity maximum originating from the critical scattering in long-range ordering systems at temperatures slightly above their ordering temperatures [173].

Recently Larsen has extended his accurate resistivity calculation [174] appropriate for the extreme dilution Kondo limit to include interactions between impurities which are important at higher impurity concentrations [12, 45, 162]. The results of this calculation are illustrated in fig. 16 where the normalized resistivity is plotted versus $\log T/T_K$ for a wide range of the parameters $T_m$, $\Delta_e$, and $T_K$ [12].
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Fig. 15

Schematic diagram of the resistivity of isolated impurities \( \rho_{\text{Kondo}} \) and interacting impurities \( \rho_{\text{spin glass}} \) as a function of log \( T \). Interactions between impurities give rise to a resistivity maximum at \( T_m \) and a susceptibility peak at \( T_o \).

The uppermost curve corresponds to the extreme dilution zero-interaction (\( \Delta_c = 0 \)) Kondo limit and is the same dependence as shown in fig. 6. As we turn on the interaction strength \( \Delta_c \), while keeping \( T_K \) constant, for instance by increasing the impurity concentration, the ratio \( \Delta_c/T_K \) increases and the unitarity limit value of the resistivity at the lowest temperature decreases. This behaviour is clearly seen in resistivity measurements to low temperatures on CuCr by Daybell and Yeo [175] and on CuFe by Silverman and Briscoe [176] shown in fig. 17. At higher concentrations for \( \Delta_c \geq T_K \) a clear resistivity maximum appears in fig. 16 and shifts to higher temperatures with increasing concentration, in qualitative agreement with the AuFe data shown in fig. 10. On the other hand, increasing \( T_K \), for instance by applying pressure, while keeping \( \Delta_c \) constant, would decrease the ratio \( \Delta_c/T_K \) and move one up the group of curves in fig. 16. A decrease of \( \Delta_c \) is thus equivalent to an increase of \( T_K \) because only the ratio \( \Delta_c/T_K \) determines which resistivity curve is appropriate. It should be noted that if the resistivity is plotted against log \( T \) instead of log \( (T/T_K) \), then the appropriate resistivity curve should also be shifted to higher temperatures when \( T_K \) increases.

We now focus our attention on the principal feature of the spin-resistivity of Kondo spin glasses, the resistivity maximum, and ask how its temperature \( T_m \) depends on \( \Delta_c \) and \( T_K \). For the purposes of illustration we assume for the moment that the RKKY-interaction is the principal interaction mechanism and that the negative Kondo-\( J_K \) is the principal angular momentum component in \( J_{\text{RKKY}} \), i.e. we assume \( \Delta_c \propto J_K^2 \) as in eqn. (26) (for 3d-impurities, \( J_K = J_2 \)). This quadratic dependence of \( \Delta_c \) on \( J_K \) is shown in the upper half of fig. 18 and compared to the much more...
rapid exponential dependence of $T_K$ on $J_K$, $T_K \propto \exp(1/J_K N(E_f))$, from eqn. (2). For sufficiently small values of $|J_K|$, then, $\Delta_i \gg T_K$ and inter-impurity interactions dominate over the Kondo effect; the system is in the spin glass regime. If we now increase $|J_K|$, for instance by applying pressure, $T_K$ will eventually become larger than $\Delta_i$; the system is in the Kondo regime. Under a sufficiently large pressure, therefore, every Kondo spin glass should become a fully-fledged, albeit interaction inhibited, Kondo system. An example for such a pressure-induced magnetic transition will be given in §4.5.

Fig. 16

Functional dependence of the resistivity per impurity on the relative temperature $T/T_K$ and on the relative interaction strength $\Delta_i/T_K$ according to Larsen [12]. The uppermost curve is for $\Delta_i = 0$, the single impurity limit (see fig. 6). For $\Delta_i > 0$ the low temperature resistivity plateau decreases, a pronounced resistivity maximum appearing for $\Delta_i/T_K \approx 1$.

Fig. 17

Total measured resistivity per impurity versus log $T$ for (a) CuCr alloys [175] and (b) CuFe quenched films [176]. The low temperature resistivity plateau is depressed as the impurity concentration increases, as expected from theory (fig. 16). However, the impurity concentration is not sufficient to cause a pronounced resistivity maximum.
The temperature of the resistivity maximum $T_m$ has been shown by Larsen [45, 157] to have the following explicit dependence on $\Delta_c$ and $T_K$ in the limit $\Delta_c \gg T_K$:

$$T_m = \Delta_c \left[ \frac{2(R_2 + R_1 x_0 + x_0^2)}{i_0(R_5 + R_4 x_0 + R_3 x_0^2 + x_0^3)} \right]^{-1},$$

(32)

where $x_0 = \ln \left( \frac{T_m}{T_K} \right)$, $i_0 = 1.0855$, $R_1 = 9.527$, $R_2 = 20.792$, $R_3 = 10.00$, $R_4 = 25.375$, and $R_5 = 24.610$. When $\Delta_c \gg T_K$ doesn’t hold, a more general, though less accurate, expression [177] can be used. The dependence of $T_m$ on $|J_K|$ shown in fig. 18 was derived using these expressions assuming the dependence of $T_K$ and $\Delta_c$ on $J_K$ given above for the RKKY-interaction case. The curves for $\Delta_c$ and $T_m$ in fig. 18 are drawn for a certain fixed impurity concentration and will shift if this concentration varies. In contrast to the monotonic increase of $T_K$ and $\Delta_c$ with $|J_K|$, $T_m$, the temperature of the resistivity maximum, goes through a pronounced maximum itself! This means...
that $T_m$ can either increase, stay constant, or decrease as $|J_K|$ increases with pressure, even though $\Delta_\epsilon$ always increases! The assumption sometimes made that $T_m \approx \Delta_\epsilon$ is thus clearly false. The behaviour of $T_m$ under pressure should thus depend heavily on the $P=0$ value of $J_K$. Further general predictions of Larsen’s theory in the spin glass regime $\Delta_\epsilon > T_K$ are:

1. The value of the resistivity at an arbitrary temperature $T_s$ increases with pressure (see fig. 16).
2. The negative resistivity curvature at $T_m$ increases in magnitude with pressure.
3. $d\ln T_m/dP$ becomes more positive in sign as the concentration increases, independent of its sign at $P=0$.

4.4. Analysis of experiment

The results of the electrical resistivity measurements under pressure on a number of spin glasses have been presented in figs. 11 and 12 and discussed in §4.1. The pressure dependence of the resistivity maximum temperature $T_m$ was seen to be quite complicated, $dT_m/dP$ depending in magnitude and sign not only on the system being investigated, but also on the concentration of magnetic impurities in a given system. The results of Larsen’s theory presented in the preceding section showed that indeed a varied dependence of $T_m$ on pressure should be expected, $dT_m/dP$ depending sensitively on the initial $P=0$ value of $J_K(0)$ or, equivalently, $T_K(0)$ for a given system. Using the values of $T_K(0)$ from table 1, a number of systems are drawn in fig. 18 according to their approximate values of $J_K(0)$. Owing to the limits of attainable pressure, in a given experiment one can trace out only a small portion of the entire $T_m(|J_K|)$ curve; the lengths of the arrows in fig. 18 correspond roughly to the change in $|J_K|$ for $\sim 100$ kbar. In general, therefore, under the assumption of RKKY-interactions with dominant $J_K$ angular momentum component, Larsen’s theory predicts that for small values of $|J_K|$ ($T_K \leq 10^{-6}$ K, e.g. AgMn), $T_m$ increases with pressure, for intermediate values of $|J_K|$ ($T_K \approx 10^{-2}$ K, e.g. CuMn), $T_m$ should be pressure independent, and for large values of $|J_K|$ ($T_K > 0.1$ K, but always $\Delta_\epsilon > T_K$, e.g. AuFe), $T_m$ should decrease with pressure. According to fig. 16, for even larger values of $|J_K|$ ($T_K > 10$ K, e.g. CuFe, AuV, or YCe, where $T_K > \Delta_\epsilon$) a well-pronounced resistivity maximum should no longer be observed; this expectation is confirmed experimentally (see figs. 3, 4 and 17). The above critical $T_K$-values are based on a transition-metal impurity concentration of roughly 0.1 at.-% in a noble metal.

A comparison of the above expectations from Larsen’s theory, outlined both in the present section and at the end of §4.3, with the experimental results in figs. 11 and 12 show that they are in excellent qualitative agreement. Particularly impressive is the good correlation between the value of $J_K$ or $T_K$ at $P=0$ for a given system and the sign and magnitude of $dT_m/dP$, as a comparison of fig. 18 with fig. 12 will substantiate. In fact, this correlation appears to be on such firm footing that it would seem possible to use the measured value of $dT_m/dP$ in a given spin glass system to estimate $T_K(0)$ itself: if $dT_m/dP > 0$, $T_K(0)$ is relatively low, whereas if $dT_m/dP < 0$, then $T_K(0)$ is relatively high. In addition, the good agreement between experiment and theory lends some support to the assumption, which was used to construct the $J_K$ dependences of $\Delta_\epsilon$ and $T_m$ in fig. 18, that the RKKY-interaction is important in spin glasses. To investigate this question on a more quantitative basis we use the measured values of $T_m(V)$ and $T_K(V)$ to calculate, using eqn. (32), the volume...
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dependence of the r.m.s. interaction strength $\Delta_c(V)$ for those systems where $T_K(V)$ is known to sufficient accuracy. The results are shown graphically in the lower half of fig. 12 and numerically in table 2. In all cases the interaction strength $\Delta_c$ increases with pressure, even though the pressure dependence of $T_m$ has different signs. The value of the volume dependence of $\Delta_c$, $d\ln \Delta_c/d\ln V$, is large and lies between $-2.1$ and $-7.5$ for 3d-impurity systems. The measured volume dependence of the interaction strength $\Delta_c(V)$ is clearly too large to be consistent with the value $d\ln \Delta_c^{PA}/d\ln V = -1$ expected for the magnetic dipolar interaction discussed in § 4.2.2. The present experiments thus indicate that the dipolar mechanism cannot be solely responsible for the inter-impurity interactions in spin glasses. As discussed in § 4.2.3, the anticipated pressure dependence of the direct 3d–3d exchange interaction $\Delta_c^{de}$ is not well known, but is probably less than the values of $d\ln \Delta_c/d\ln V$ found here. A further argument against the importance of direct exchange in the present studies is the strong dilution of the 3d-impurity systems studied, where $c \leq 0.35$ at.% Direct exchange may play a role at much high impurity concentrations, like $c > 15$ at.% in AuFe. If, on the other hand, the RKKY-interaction is operative here, then we expect as in eqn. (26) that $d\ln \Delta_c/d\ln V = 2d\ln |J_{RKKY}|/d\ln V + d\ln N(E_f)/d\ln V \approx 2d\ln |J_2|/d\ln V + d\ln N(E_f)/d\ln V$, assuming $J_2$ is the dominant angular momentum component in the exchange interaction given in eqn. (18), i.e. $J_{RKKY} \approx 5J_2$. In table 2 we compare values of $d\ln \Delta_c/d\ln V$ from the present high pressure measurements on spin glasses with the values of $2d\ln |J_2|/d\ln V + d\ln N(E_f)/d\ln V$ obtained from table 1 which were derived from the results of very dilute Kondo alloys in § 3.3. The agreement in all cases is reasonably good. As discussed in § 4.2.1 with reference to eqns. (25, 27) the present results are not only consistent with the dominance of RKKY-interactions in dilute spin glasses, but also indicate that the same $J_2$ or interband mixing interaction which leads to the Kondo effect in very dilute alloys with transition metal impurities is also predominantly responsible for the magnitude of the RKKY-interaction between these same impurities at higher concentrations.

The prevalence of RKKY-interactions in the spin glasses AuFe [129, 148] and CuMn [46] is also indicated by studies of the concentration dependence of $T_0$ which bends over with increasing concentration to $c \approx 15\%$, as shown in fig. 9. In the RKKY-interaction model one expects a linear concentration dependence of $T_0$ in the absence of any damping of the RKKY-spin density amplitude due to scattering centres such as the magnetic impurities themselves [129, 148]. Estimating this damping from the magnitude of the electrical resistivity at $T \approx T_0$, leads to good agreement with the observed concentration dependence of $T_0$ and thus implies that the same electrons which are scattered, giving the increase in the resistivity, are responsible for the interactions between impurities, i.e. the RKKY-interaction mechanism. For AuFe this damped RKKY-model seems to work well all the way up to the percolation limit of $\sim 15\%$ Fe in Au [129, 148]. Because the dipolar interaction is not transmitted by electrons and thus cannot be damped by electron mean free path effects, it would not, for instance, be able to account for the observed concentration dependence of $T_0$ [46].

Therefore, both pieces of evidence, the present high pressure experiments and the analysis of the concentration dependence of $T_0$, refute the applicability of the extreme magnetic dipolar anisotropy model [146] of spin glass freezing. However, it should be pointed out at this time that these two sets of experiments cannot, unfortunately, clearly distinguish between the pure RKKY phase-transition model.
Table 2. Summary of high pressure results for more concentrated magnetic systems. \( P = 0 \) values of temperature of resistivity maximum \( T_m \), Kondo temperature \( T_K \), and r.m.s. interaction strength \( \Delta \) are listed on the left. The volume dependences of \( \Delta \) and \( T_m \) for external pressure are shown on the right. \( \Delta \) is obtained from \( T_K \) and \( T_m \) using eqn. (32) when \( \Delta \gg T_K \), otherwise using Larsen's expression in [177]. The magnetic ordering temperatures \( T_O \) and their volume dependences for Gd, Fe, Co, Ni, Cr, and Mn are listed under \( \Delta \) and \( d \ln \Delta \)/\( d \ln V \), respectively. \( P_m \) is maximum pressure used in determining volume dependences, \( \nu = ( V_0 - V)/V_0 \), where \( V \) is atomic volume at given pressure and \( V_0 \) is atomic volume at \( P = 0 \). Values of \( T_K(0) \) and \( \frac{d \ln \langle |J_K| \rangle}{d \ln V} + \frac{d \ln N(E_f)}{d \ln V} \) are taken from table 1, the latter quantity for Gd, \( \alpha \)-Fe, Cr, and \( \alpha \)-Mn being obtained using results on very dilute LaGd, AuFe, AuCr, and AgMn or CuMn, respectively. For the method of determining logarithmic derivatives, see [54]. Letters mean: (a)—For CuCr and MoFe, \( T_K(V) \) is not known accurately enough to estimate \( \Delta(V) \); (b)—\( T_K(0) \) increases with Ce concentration owing to contraction of the lattice (see [27] and [70]). Values of parameters used here taken from table 1, \( d \ln \langle |J_K| \rangle/d \ln V = -4.5 \), \( d \ln N(E_f)/d \ln V = +0.67 \), \( T_K(0) = 0.4 \) K, \( N(E_f)(0) = 0.3 \) states/eV-atom, \( D = 75,000 \) K, Larsen's theory for \( S = 1/2 \), [12] and [177], is used to extract \( \Delta(V) \) from \( T_K(V) \) and \( T_m(V) \); (c)—In this case \( J_K \) represents an average over the Js appropriate for the superconducting properties (see text).

| System               | \( T_m(0) \) (K) | \( T_k(0) \) (K) | \( \Delta(0) \) (K) | \( P_m \) (kbar) | \( \nu(P_m) \) | \( d \ln \Delta \)/\( d \ln V \) | \( \frac{2 \ln \langle |J_K| \rangle}{d \ln V} + \frac{d \ln N(E_f)}{d \ln V} \) | \( d \ln T_m \)/\( d \ln V \) | References |
|----------------------|------------------|------------------|-------------------|------------------|----------------|-------------------|-------------------|-------------------|----------------|
| Au-0.10 at.\% Fe     | 2.38             | 0.24             | 1.43              | 40               | +0.021         | -30               | -3.5              | +3.8              | 157            |
| Au-0.13 at.\% Fe     | 3.48             | 0.24             | 1.87              | 60               | +0.031         | -3.1              | -3.5              | +3.1              | 156            |
| Au-0.10 at.\% Cr     | 3.00             | \( 10^{-3} \)    | 0.645             | 102              | +0.049         | -2.1              | -2.7              | +0.13             | 25,160         |
| Au-0.15 at.\% Cr     | 4.73             | \( 10^{-3} \)    | 0.966             | 102              | +0.049         | -2.2              | -2.7              | +0.13             | 25,160         |
| Au-0.20 at.\% Cr     | 10.2             | \( 10^{-3} \)    | 1.91              | 108              | +0.051         | -2.5              | -3.0              | +0.3              | 25,160         |
| Au-0.10 at.\% Mn     | 2.53             | \( 10^{-4} \)    | 0.43              | 96               | +0.046         | -0.5              | -1.5              | -1.5              | 157            |
| Au-0.10 at.\% Mn     | 2.53             | \( 10^{-11} \)   | 0.174             | 96               | +0.046         | -0.5              | -1.5              | -1.5              | 157            |
| Au-0.15 at.\% Mn     | 3.32             | \( 10^{-4} \)    | 0.56              | 40               | +0.021         | -5.9              | -1.5              | -1.5              | 157            |
| Au-0.15 at.\% Mn     | 3.32             | \( 10^{-5} \)    | 0.23              | 40               | +0.021         | -4.5              | -1.5              | -1.5              | 157            |
| Ag-0.15 at.\% Mn     | 4.07             | \( 10^{-4} \)    | 0.67              | 60               | +0.057         | -4.8              | -3.1              | -2.3              | 24,60          |
| Ag-0.10 at.\% Mn     | 4.07             | \( 10^{-16} \)   | 0.19              | 60               | +0.057         | -4.7              | -3.3              | -2.3              | 24,60          |
| Ag-0.10 at.\% Mn     | 3.00             | \( 10^{-4} \)    | 0.51              | 60               | +0.057         | -4.1              | -3.3              | -1.5              | 24,60          |
| Ag-0.15 at.\% Mn     | 3.00             | \( 10^{-16} \)   | 0.14              | 60               | +0.057         | -3.3              | -3.3              | -1.5              | 24,60          |
| Cu-0.15 at.\% Mn     | 2.40             | 0.012            | 0.75              | 96               | +0.034         | -7.5              | -5.1              | -1.4              | 157            |
| Cu-0.35 at.\% Mn     | 9.1              | 0.012            | 2.32              | 67               | +0.040         | -8.5              | -5.1              | +0.15             | 157            |
| Cu-0.35 at.\% Cr (a) | 2.91             | 29               | 2.45              | 61               | +0.038         | —                   | —                   | —                   | —              |
| Cu-0.40 at.\% Cr (a) | 5.42             | 29               | 4.10              | 65               | +0.041         | —                   | —                   | —                   | —              |
| Cu-0.60 at.\% Cr (a) | 7.7              | 29               | 5.30              | 65               | +0.041         | —                   | —                   | —                   | —              |
| Mo-0.10 at.\% Fe     | 3.34             | 1                | 2.47              | 35               | +0.012         | —                   | —                   | —                   | 157            |
| La-10\% Ce (b)       | 3.23             | \( 0.49 \)       | 2.08              | 10               | +0.058         | -8.6              | -8.3              | -9.1              | 27.70          |
| La-20\% Ce (b)       | 5.02             | \( 0.72 \)       | 3.28              | 16               | +0.058         | -9.2              | -8.3              | -7.7              | 27.70          |
| La-40\% Ce (b)       | 9.86             | 1.33             | 5.39              | 16               | +0.058         | -8.5              | -8.3              | -7.0              | 27.70          |
| Gd                   | —                | —                | 2.32              | 50               | +0.091         | 2.9               | +2.5(c)           | —                   | 76,117         |
| z-Fe                 | —                | —                | 1043              | 18               | +0.010         | 0.005              | -3.5              | —                   | 168            |
| Ni                   | —                | —                | 631               | 160              | +0.007         | -1.1              | —                   | 168.178          |
| Co                   | —                | —                | 1400              | 60               | +0.029         | 0.007              | —                   | —                   | 168            |
| Cr                   | —                | —                | 312               | 70               | +0.035         | 2.7               | -2.7              | —                   | 116            |
| z-Mn                 | —                | —                | 95                | 8                | +0.008         | +18                | -3.5              | —                   | 179            |
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[150] and the hybrid ‘spin cloud’ model [147], discussed at the beginning of § 4, the latter of which employs both RKKY- and magnetic dipolar anisotropy interactions. The reason for this inability is that in the spin cloud model the size of a ‘spin cloud’, which together with the dipolar energy determines the magnitude of the anisotropy energy barrier which is related to the value of $T_0$, depends on the strength of the RKKY-interaction, which varies with pressure or damping. It turns out that the pressure or damping dependence expected for $T_0$ or $\Delta_c$ is the same both in the phase-transition and ‘spin cloud’ models, making them indistinguishable with either technique.

4.5. Spin glass to Kondo transition

Changing the effective exchange parameter $J_K$ with pressure, in addition to varying the magnetic ordering temperature $T_0$, can also precipitate a phase transition from one magnetic regime to another. A second-order transition from an antiferromagnetic to a Kondo spin-compensated ground state is predicted by Doniach [13] for a one-dimensional system as $J_K$ is increased in magnitude to a critical value $J_c$. Similarly, Larsen [12] finds a sharp transition at $T = 0$ K signalling a transition from a spin glass ($\Delta_c > T_K$) to a Kondo ($T_K > \Delta_c$) phase as $|J_K|$ increases beyond a critical value where $\Delta_c = T_K$. That such a transition should always occur in Kondo spin glasses when sufficient pressure is applied is evident from fig. 18 where it is seen that no matter how small $T_K$ or $J_K$ at $P = 0$, because of its exponential dependence on $J_K$, $T_K$ will eventually pass up $\Delta_c^\text{RKKY} \propto J_K^2$, precipitating a spin glass to single-impurity transition. For $T_K << \Delta_c$, $T_0(P)$ should initially increase with pressure as $|J_K|$ increases. As $T_K$, however, approaches $\Delta_c$ from below, Kondo fluctuations should begin interfering with the spin glass ordering process, causing $T_0(P)$ to pass through a maximum and eventually fall to zero, as indicated in the upper half of fig. 18. A determination of the critical behaviour of $T_0(P)$ at this transition is interesting in its own right and would provide an important test of theories of this phenomena. As was shown in the last section, the electrical resistivity is a particularly sensitive function of both $T_K$ and the strength of the interactions $\Delta_c$, which lead to the spin glass freezing phenomena at $T_0$, and as such is a useful technique for determining when the system in question has passed through the critical value of the parameters $T_K = \Delta_c$. The question now is, how does the resistivity behave when the transition is crossed? In fig. 19 we plot the resistivity versus temperature using the results of Larsen’s theory shown in fig. 16 for values of the parameters which would roughly correspond to an experiment under pressure, setting the interaction strength $\Delta_c = 1$ K and letting $T_K$ increase from 0.1 K to 10 K with pressure. For the purposes of discussion we ignore for the moment the relatively small increase of $\Delta_c \propto J_K^2$ with pressure. The critical value of the parameters for the spin glass to Kondo transition is obtained for $T_K = \Delta_c = 1$ K. Inspection of fig. 19 reveals the following characteristic changes in the resistivity which are to be expected as the magnetic phase transition is crossed by applying pressure:

1. $dT_m/dP < 0$, as is true for all ‘high-$T_K$’ systems.
2. The resistivity becomes increasingly asymmetric about $T_m$, the low temperature side lifting up rapidly.
3. For $T_K \gg \Delta_c$ the resistivity maximum becomes very broad; the resistivity looks increasingly Kondo-like. The expected slight increase of $T_m$ at very high pressures seen in fig. 18 for $T_K > \Delta_c$ is in practice very difficult to observe.
Functional dependence of the spin-resistivity per impurity on $T$ and $T_K$ for a constant value of $\Delta_c = 1\, \text{K}$ using curves in fig. 16 from Larson's theory [12]. As $T_K$ increases with pressure, $T_m$ should decrease and $\rho(T_m)$ increase, the asymmetry of the resistivity around $T_m$ should increase for $T_K > \Delta_c$, curves becoming Kondo-like (fig. 6) for $T_K \gg \Delta_c$. Our temperature window restricts observation of these curves to 1–20 K temperature range.

Total measured resistivity $\rho_t$ of (a) Mo–1 at.% Fe [161] and (b) Cu–0.6 at.% Cr [25, 160] as a function of $\log T$ at different pressures. Absolute resistivity scale applies to the $P=0$ data. The high pressure data are shifted vertically for clarity with the relative scale the same for all data in a given graph. The values of $\rho_t$ at $T_m$ are given in the respective references. In all cases pressure causes $\rho_t(T_m)$ to increase and $T_m$ to decrease.
owing both to the extreme flatness of the resistivity maximum and the low temperatures at which $T_m$ occurs.

(4) $\frac{d\rho(T_s)}{dP} > 0$ for all values of $\Delta_c$ and $T_K$, where $T_s$ is an arbitrary temperature.

From fig. 18 suitable candidates for such a pressure-induced magnetic phase transition in our temperature and pressure range are MoFe, CuCr, and LaCe. In fig. 20 the results of high pressure experiments on MoFe by Ford and Schilling [161] and CuCr by Willer et al. [25, 160] are shown. Features (1), (2), and (4) listed above are clearly visible in the data, but the pressure available is not large enough to sweep $T_K$ from well below to well above $\Delta_c$ as would be desired for clear identification of the transition. For such studies the rare earth system LaCe, with its relatively high compressibility and the nearness of the 4f$^1$-level to the Fermi energy, is the ideal candidate. Indeed, the increase of $T_K$ with applied pressure in this system is very rapid, as was discussed in detail in § 3.2.2.

The results of the high pressure resistivity measurements on the alloys La–3% Ce, 10%, 20%, and 40% Ce are shown in fig. 21. As was previously discussed, and is seen in fig. 7 (c), the increase of the low temperature resistivity slope with pressure in La–3% Ce is due to the increase of the Kondo temperature $T_K$. At higher Ce concentrations a resistivity maximum is seen to appear which shifts to higher

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**Fig. 21**

![Graph](image)

Total measured resistivity $\rho$ of various LaCe alloys versus log $T$ at different pressures. Absolute resistivity scale applies to the $P=0$ data. The high pressure data are shifted vertically for clarity with the relative scale the same for all data in a given graph. The values of $\rho$ at a fixed temperature $T_s$ are given in [70]. In all cases $\rho(T_s)$ increases with pressure, where $T_s$ is an arbitrary temperature below 10 K, a temperature region where $\rho_{\text{spin}}(T)$ dominates the resistivity.
temperatures with increasing Ce concentration. For the La-40% Ce alloy the resistivity maximum is buried under the phonon scattering but appears if the La host resistivity is subtracted [27] or if pressure is applied. In all cases \( \frac{dp(T_s)}{dP} > 0 \) and the resistivity maximum is seen to shift to lower temperatures with pressure, becoming increasingly asymmetric about \( T_m \). The spin-resistivity also clearly becomes more Kondo-like with pressure; this is particularly clear in the La-10% Ce data at 17.9 and 26 kbar which look very much like the CuFe data in fig. 3. Particularly interesting are the measurements on La-40% Ce where the resistivity maximum is seen to appear from under the phonon scattering at 9.3 kbar, broaden markedly at 16.2 kbar, and probably shift to higher temperatures again at 23.5 kbar, in agreement with the \( T_m(P) \) dependence expected from fig. 18. The above observations are consistent according to the above criteria for a pressure-induced spin glass to Kondo transition in LaCe. The concentration range over which LaCe shows spin glass behaviour has not yet been clearly established; the presence of a resistivity maximum alone is not sufficient to prove the existence of the spin glass state. It is doubtful whether the La-40% Ce system with its high impurity concentration is a spin glass. It is, however, clear that the present measurements on La-3%, 10%, 20%, and 40% Ce alloys can be at least qualitatively accounted for by considering the spin-resistivity to be a function of only the temperature, an interaction strength parameter \( \Delta_c \), and the Kondo temperature \( T_K \). According to table 2, the volume dependence of \( \Delta_c \) is larger than for 3d-impurity systems; it is also seen that this volume dependence is in good agreement with the dominance of the RKKY-interaction mechanism in LaCe.

It is natural to ask whether the behaviour of pure Cerium metal can be understood with the same model as for LaCe alloys. It is interesting to note that the atomic volume of \( \gamma \)-Ce is about 8% less than for pure La which corresponds to a lattice pressure of about 23 kbar [89]. The Kondo temperature of \( \gamma \)-Ce should, therefore, lie near 12 K, assuming that for dilute LaCe \( T_K(0) = 0.4 \) K and \( \frac{d\ln J_3}{d\ln V} = -4.5 \). It is certainly conceivable that the Kondo spin fluctuations associated with this relatively high value of \( T_K \) could be partly responsible for the low Neel temperature \( T_N = 12.5 \) K of \( \beta \)-Ce [180] and the lack of magnetic order in the \( \alpha \)-Ce phase, both of which have about the same density as \( \gamma \)-Ce. It should, however, be noted that in d.h.c.p. La\(_{1-x}\)Ce\(_x\) alloys there is no sign of the concentration dependence \( T_0(x) \) bending over at the highest Ce concentrations which would be indicative of a suppression of \( T_0(x) \) by the increasing value of \( T_K \) [181] as the Ce concentration increases.

\$5. \textbf{Summary and Conclusions}$

In the present review we have attempted to bring together the results of most available high pressure measurements on dilute magnetic alloys and show how such investigations can be used both to give detailed information about the magnetic states of such alloys as well as to provide a critical test of theory. In particular, as discussed in §3, high pressure studies on extremely dilute Kondo alloys were successful, first in confirming the existence of the universal resistivity law \( \rho = \rho(T/T_K) \) predicted by theory, and then in using this law to derive the volume dependence of the negative effective exchange interaction \( J_K(V) \) between a local moment spin \( S \) and the conduction electron sea. Unfortunately, an accurate theory of this important exchange interaction is still lacking. Values of the relative change of \( J_K \) with volume, such as those given in table 1, should provide a more sensitive test.
for the correctness of the structure of a proposed theory than, say, the absolute magnitude of $J_K$ at $P = 0$ alone. Perhaps the single most important result in § 3 is the universal increase of the magnitude of $J_K$ with pressure in Kondo systems. Although the exact physical mechanism responsible for this behaviour is not yet clear, the universality of the result alone would point to a common mechanism in all cases. It is suggested that the increase of $|J_K|$ with pressure is connected with the approach of the magnetic impurity state to the Fermi level and thus constitutes another example of the general tendency for magnetic systems to eventually demagnetize under pressure, as discussed in the Introduction.

The phenomenon of lattice pressure in a number of ternary magnetic systems was discussed in § 3.4 and compared to similar investigations on binary alloys under external pressure. A reasonably good correlation is found for several systems, particularly in those cases where the difference in ionic radii of the host matrix components is small. However, we emphasize here that the application of external pressure is always to be preferred to lattice pressure, as a technique, when the object of the experiment is to extract well-defined volume dependences of the parameters from the data or make exacting comparisons with theory. On the other hand, combining external pressure and lattice pressure results on Cu$_{1-x}$Al$_x$-100 ppm Fe alloys, it was shown how the Fe-impurities could be used as ‘Kondo-probes’ to sense the local electron density. It was estimated that only about half of each Al$^{3+}$ ion’s three valence electrons go into a free band, the other half remaining localized as screening charge.

Whereas in very dilute magnetic alloys each magnetic impurity can interact with the surrounding sea of conduction electrons independently of the other impurities, at higher impurity concentrations interactions between impurities become important and can lead to a spin glass type of ordering. The various models of the spin glass freezing phenomenon [146, 147, 149, 150] rely, in part, on different relevant interaction mechanisms. Since each possible interaction mechanism has its own characteristic volume dependence, a high pressure experiment can, in principle, help to decide which mechanism is dominant in a given system. The present high pressure studies of the electrical resistivity of various dilute spin glass alloys (e.g., Au-0.1 at.\% Fe) are discussed in § 4.4 and indicate that the largest contribution to the interactions between impurities arises from the indirect RKKY-mechanism and the negative ‘Kondo’ angular momentum component $J_K$ makes the dominant contribution to this interaction $J_{RKKY}$. This dominance of the $J_K$ component is consistent with recent E.P.R. results by Davidov et al. [69] on very dilute AgMn where it is estimated that $J_0 \approx +0.13 \text{eV}$, $J_1 \approx +0.09 \text{eV}$, and $J_2 = J_K \approx -0.13 \text{eV}$. Using eqn. (18), we find $J_{RKKY} = J_0 - 3J_1 + 5J_2 - \ldots \approx +0.13 - 0.27 - 0.65 = -0.79 \text{eV}$, so that $J_{RKKY} \approx 5J_2$ because of the partial cancellation of the first two terms. Apparently, a similar result holds for other systems as well. It is interesting, and perhaps paradoxical, that the same interaction $J_K$, which is responsible for the Kondo spin fluctuations in very dilute systems, can also, in more concentrated systems, be mainly responsible for the spins freezing in place below $T_0$. The use of a single $J_K$ to give, depending on the magnitude of $J_K$, both magnetic ordering and Kondo behaviour has been proposed in theories of Larsen [12] and Doniach [13]. It should be noted, however, that for the systems discussed in the present context the values of $T_K$ or $|J_K|$ are rather low, i.e. $T_0 \approx T_K$. For systems with larger values of $T_K$ or $|J_K|$, where $T_0 \approx T_K$, the Kondo spin fluctuations should interfere with the spin freezing process and lower $T_0$ [12, 13]. Evidence for a pressure-induced spin glass to
Kondo transition in LaCe was discussed in § 4.5. Such a transition is anticipated in general for Kondo spin glasses because the increase of $T_K$ with pressure is far larger than that of $T_0$ or $\Delta_c$. In fact, the spin glass to Kondo transition is but another example of how a magnetic system can begin to demagnetize under pressure.

The present high pressure resistivity studies also provided a critical test for the correctness of Larsen’s theory for the resistivity of Kondo spin glasses [12, 45, 162] which was outlined in § 4.3. The excellent agreement between theory and experiment gives confidence when applying this theory to other problems, for instance to studies of the concentration dependence of the mean interaction strength $\Delta_c(c)$. Such studies on AuFe [129, 148] and CuMn [46], in fact, have revealed that $\Delta_c(c) \propto T_0(c)$ over an appreciable concentration range, supporting the close connection between these two quantities asserted by eqn. (23).

Further evidence for the importance of the RKKY-mechanism in spin glasses is provided by an analysis of the concentration dependence of $T_0$ in AuFe [129, 148] (see fig. 9) and CuMn [46] where the deviation of $T_0$ versus $c$ from linearity can be quantitatively accounted for by including the damping of the RKKY-oscillations. For AuFe this RKKY-damping model works well at concentrations all the way up to the percolation limit at 15% Fe, above which AuFe becomes a long-range inhomogeneous ferromagnet. The changeover in the type of magnetic ordering at 15% Fe is evident in the concentration dependence of $T_0$ shown in fig. 9 which shows a sharp break at $c \approx 15\%$ and a steeper slope for $c > 15\%$. Pure $\alpha$-Fe is widely believed to be an itinerant ferromagnet. Increasing the Fe concentration in Au from 0 to 100% thus causes a drastic change in the nature of the interaction mechanisms which lead to magnetic ordering, i.e. from local moments interacting via the indirect RKKY-interaction to band exchange in an itinerant ferromagnet. This difference is mirrored in the volume dependence of $\Delta_c$ and $T_0$: for Au-0.1 at. % Fe, $d \ln \Delta_c/d \ln V \approx -3$ and for $\alpha$-Fe, $d \ln T_0/d \ln V \approx 0 \pm 0.05$, as listed in table 2. Large differences are also evident in table 2 for AuMn and $\alpha$-Mn and for AuCr and Cr. A notable exception is formed by the spin glass LaGd [182] ($d \ln \Delta_c/d \ln V = d \ln N(E_F) J_z^2/d \ln V \approx +2.5$ from table 1) and the ferromagnet Gd ($d \ln T_0/d \ln V \approx +2.0$) which indicates that the same interaction mechanism (RKKY) is operable at both low and high Gd concentrations. The absence of marked structure in $T_0(c)$ in La$_{1-x}$Gd$_x$Al$_2$ [183], and d.h.c.p. La$_{1-x}$Ce$_x$ [181] alloys for all $x$ is also consistent with a dominance of the RKKY-interaction mechanism across the entire concentration region in these systems. Gd and Ce local moments are relatively well-localized and one expects neither itinerant magnetism nor any contribution from direct exchange in alloys with Gd, Ce, or other rare-earth impurities. The pressure and concentration dependence studies sketched here are thus consistent with the general picture that has evolved of the differences between magnetism in 3d- and 4f-alloys which arise from differences in the degree of localization of the magnetic orbitals.

In this review we have emphasized the general tendency of pressure to demagnetize a magnetic system and have given examples of this behaviour evidently present in the present results on dilute magnetic alloys, i.e. universal increase of $|J_K|$ with pressure, spin glass to Kondo transition in LaCe, etc. In fact, we predict that even a ‘good moment’ $J_K = J_z > 0$ system like LaGd will become a Kondo system under sufficiently high pressure. Carrying this idea further, we hypothesize that a spin glass system like La-5 at. % Gd will exhibit the following behaviour as pressure is successively increased from 1 atm to an arbitrarily high value which lies certainly in the multi-megabar pressure range:
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(1) Spin glass, $J_3 > 0$, $S = 7/2$, $L = 0$, $dT_0/dP < 0$ (because $J_3 = J_{3+} + J_{3-}$ decreases with pressure as $|J_{3-}|$ increases, see §3.3.2);
(2) Kondo spin glass, $J_3 < 0$, $dT_0/dP > 0$;
(3) Spin glass to Kondo transition, $T_0 \to 0$ K;
(4) Kondo system, $dT_K/dP > 0$, $T_K$ gets large;
(5) possible intermediate valency behaviour.
(6) Gd loses one 4f-electron, $S = 3$, singlet ground state;
(7) Gd loses second 4f-electron, $S = 5/2$, $L = 5$, spin glass, $J_3 > 0$, $dT_0/dP < 0$;
(8) Kondo spin glass, $J_3 < 0$, $dT_0/dP > 0$;
(9) Spin glass to Kondo transition, $T_0 \to 0$ K, and so forth! In pure Gd at some pressure the 4f–4f overlap may become sufficiently large that Gd becomes an itinerant ferromagnet; further pressure would then lead to weak itinerant ferromagnetism and finally paramagnetism.

The above behaviour is essentially a repeated fall and rise of magnetism as pressure is increased. It could thus be possible to magnetize a non-magnetic metal like Cu by applying enough pressure to squeeze an inner d-electron out into a free band. This rise and fall of atomic or band magnetism should continue with increasing pressure until all electrons have been squeezed out of their orbits, with only the bare nuclei left over. Of course, owing to the limitations of available pressure in the laboratory, only a very narrow section of the entire magnetism–pressure phase diagram can be mapped out in an experiment on a given system. Whether or not the above hypotheses prove to be true in detail, it is certainly clear that a rich variety of magnetic behaviour will be exhibited by a single system when it is subjected to sufficiently large pressures. The application of very high pressures can thus not only contribute to the understanding of known magnetic phenomena but can also create new ones.

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Note added in proof—Recent preliminary magnetic susceptibility measurements under high pressure carried out in our laboratory on a CuMn spin glass reveal that the spin glass freezing temperature $T_0$ increases with pressure, supporting the resistivity results given in the present review.

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impurities (see, for example: MEIER, J. S., CHRISTOFE, C. W., WORTMANN, G., and HOLZAPFEL, W. B., 1974, *Solid St. Commun.*, 15, 485, and references therein). In these giant moment systems $J$ is positive and is estimated to vary roughly inversely proportional to the sample volume, i.e. $d \ln J/d \ln V \approx -1$. This is in contrast to the apparent decrease of $J$ with pressure observed in LaGd, also a positive-$J$ system.

**References**


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[46] Larsen, U. (private communication).

[47] See also discussion of this point in [22].


[49] The actual change in $R(T=0K)$ was about +0.2% in our pressure range (see [22]).


[51] The pressure dependence of $T_f$, like that of $N(E_f)$, is small for all noble metal hosts and will be neglected since in eqn. (2) $T_f$ only appears as a prefactor and not in the exponent.


[54] Given a set of parameter values $X$ corresponding to the relative sample volume $V/V_0$, the logarithmic volume derivative $d \ln X/d \ln V$ was determined by the slope $B$ of the least squares fit to all data using the expression in $X = A + B \ln (V/V_0)$. In this review, we use $X = T_K, N(E_f), |J_K|, \Delta_{1/2}$, and $T_m$.


[57] The 'p-slope' values of $T_K(V)$ and $J_K(V)$ given in table 1 were derived using the following expression, equivalent to that in eqns. (6) and (7) for $\Delta = 0$ and $T \gg T_K$, obtained by Larsen (private communication): $p_{spin} = [2 S \rho_0 \pi^2 S(S+1)/4]/[(2 n T/T_K + \Psi(1/2))^2 + \pi^2 S(S+1)/16]$. Use of this expression or that in eqn. (3) causes little change in the extracted pressure dependences.


[60] Olijnyk, H., Caron, J., and Lüscher, E. (to be published).


[62] $J_K$ values derived from $T_K$ values using eqn. (2) and $T_f = 10^5 K$ for all Cu, Au, Ag, Cu$_{1-x}$Al$_x$, and Cu$_{1-x}$Au$_x$ host alloys. $T_f = 13.6 \times 10^4 K$ for AlMn [56], $T_f = 8 \times 10^4 K$ for La and LaAl$_2$ hosts. $T_f = 7.5 \times 10^4 K$ for Y hosts. It is assumed $\cos \delta = 1$ in all cases.


[71] It was assumed that $T_K(15 \text{ kbar}) = 4 \text{ K}$ and the $\rho$-shift method was used to arrive at the $T_K(0)$ value given here (see text).

[72] A value $N(E_f) = 0.3 \text{ states/eV-atom}$ is chosen as representative of a free $s$-$p$ band (see text).


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[125] Winzer, K. (private communication).


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