

Pressure-induced superconductivity in europium metal

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Abstract. Of the 52 known elemental superconductors among the 92 naturally occurring elements in the periodic table, fully 22 only become superconducting under sufficiently high pressure. In the rare-earth metals, the strong local magnetic moments originating from the 4f shell suppress superconductivity. For Eu, however, Johansson and Rosengren have suggested that sufficiently high pressures should promote one of its 4f electrons into the conduction band, changing Eu from a strongly magnetic ($J=7/2$) $4f^7$ -state into a weak Van Vleck paramagnetic ($J=0$) $4f^6$ -state, thus opening the door for superconductivity, as in Am ($5f^6$). We report that Eu becomes superconducting above 1.8 K for pressures exceeding 80 GPa, T_c increasing linearly with pressure to 142 K at the rate +15 mK/GPa. Eu thus becomes the 53rd elemental superconductor in the periodic table. Synchrotron x-ray diffraction studies to 92 GPa at ambient temperature reveal four structural phase transitions.

1. Introduction

An important open question in condensed matter physics is whether the ground state of all nonmagnetic metals might be superconducting. For the elements, the known values of the superconducting transition temperature T_c vary over nearly six orders of magnitude from 325 μ K for Rh [1] to 160 K for the high- T_c superconductor $\text{HgBa}_2\text{Ca}_2\text{Cu}_3\text{O}_8$ at 30 GPa pressure [2]. However, we emphasize that there is no reason that the value of T_c for a particular material cannot be 10^{-20} K or even lower, a value far below that inaccessible to experiment. That such elements as the noble metals or some alkali metals are not listed as superconducting may simply be that experiments have not yet been carried out to sufficiently low temperatures. Superconductivity is a complex phenomenon. A reliable, accurate estimate from theory of the value of T_c for an arbitrary material is not yet possible. Since elemental metals contain only one atomic species, one would anticipate that a thorough understanding of their properties, including superconductivity, should be relatively easy to attain.

In Figure 1 we display the *Periodic Table of Superconductivity* where the 30 elements in yellow superconduct at ambient pressure and those (33) in light green are known to superconduct only if external pressure is applied. See the figure caption for further details. Of the 92 naturally occurring elements in the periodic table, fully 53 superconduct either at ambient or high pressure. The latest is the object of this paper, europium (Eu), an antiferromagnet, where we report superconductivity near 2 K for pressures exceeding 80 GPa [3].

Periodic Table of Superconductivity

(dedicated to the memory of Bernd Matthias)

30 elements superconduct at ambient pressure, 23 more superconduct at high pressure.

H		ambient pressure superconductor										high pressure superconductor										He	
		T_c (K) T_c^{max} (K) P(GPa)										T_c^{max} (K) P(GPa)											
	Li 0.0004 14 30	Be 0.026											B 11 250	C	N	O 0.6 100	F	Ne					
	Na	Mg											Al 1.14	Si 8.2 15.2	P 13 30	S 17.3 190	Cl	Ar					
K	Ca 25 161	Sc 19.6 106	Ti 0.39 3.35 56.0	V 5.38 16.5 120	Cr	Mn	Fe 2.1 21	Co	Ni	Cu	Zn 0.875	Ga 1.091 7 1.4	Ge 5.35 11.5	As 2.4 32	Se 8 150	Br 1.4 100	Kr						
Rb	Sr 7 50	Y 19.5 115	Zr 0.546 11 30	Nb 9.50 9.9 10	Mo 0.92	Tc 7.77	Ru 0.51	Rh .00033	Pd	Ag	Cd 0.56	In 3.404	Sn 3.722 5.3 11.3	Sb 3.9 25	Te 7.5 35	I 1.2 25	Xe						
Cs	Ba 1.3 12	insert La-Lu	Hf 0.12 8.6 62	Ta 4.483 4.5 43	W 0.012	Re 1.4	Os 0.655	Ir 0.14	Pt	Au	Hg- α 4.153	Tl 2.39	Pb 7.193	Bi 8.5 9.1	Po	At	Rn						
Fr	Ra	insert Ac-Lr	Rf	Ha																			
	La- <i>fcc</i> 6.00 13 15	Ce 1.7 5	Pr	Nd	Pm	Sm	Eu 2.75 142	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu 12.4 174								
	Ac	Th 1.368	Pa 1.4	U 0.8(β) 2.4(α) 1.2	Np	Pu	Am 0.79 2.2 6	Cm	Bk	Cf	Es	Fm	Md	No	Lr								

Figure 1. Periodic Table listing elements which superconduct at ambient pressure (yellow) or only under high pressure (light green). For each element the upper position gives the value of T_c (K) at ambient pressure; middle position gives maximum value T_c^{max} (K) in a high-pressure experiment at the pressure P(GPa) (lower position). If T_c decreases under pressure, only the ambient pressure value of T_c is given. Sources for T_c values are given in Ref. [4].

Why is superconductivity in Eu of particular interest? Because Eu is one of only two elemental metals in the periodic table where partially filled, highly localized orbitals may coexist with superconductivity, the other being Am. In all rare earths except La and Lu, strong local magnetic moments in the 4f shell prevent superconductivity from occurring at ambient pressure. In contrast to the other rare-earth metals, however, Eu and Yb are divalent and thus possess much larger atomic radii than their trivalent brothers. Under sufficient pressure one would expect Yb to become trivalent and thus magnetic as one 4f-electron is promoted into the conduction band $4f^{14}$ ($L = S = J = 0$) to $4f^{13}$ ($J = L+S = 3+1/2 = 7/2$). In contrast, under sufficient pressure divalent Eu, which is strongly magnetic with $4f^7$ ($J = S-L = 7/2$), would become trivalent with $4f^6$ where $J = L-S = 3-3 = 0$, a nonmagnetic ground state. Because of quantum mechanical mixing with the low-lying magnetic excited states, trivalent Eu should exhibit only Van Vleck paramagnetism, a very weak form of magnetism which, as we know from americium (Am), is able to coexist with superconductivity. For this reason Johansson and Rosengren [5] predicted many years ago that Eu would be expected to become superconducting under

sufficiently high pressure. In 1981 Bundy and Dunn [6] were unable to find superconductivity in Eu to pressures as high as 40 GPa in their experimental range above 2.3 K. In the present experiments a diamond-anvil cell was used to extend the experimental pressure and temperature ranges to 142 GPa and 1.5 K, respectively.

2. Experiment

For the ac susceptibility experiments on Eu a membrane-driven diamond-anvil cell [7] was used with 1/6-carat, type Ia diamond anvils with 0.18 mm culets beveled at 7° out to 0.35 mm. The disc-shaped metal gaskets were 250 μm thick and 2.8 mm diameter. The gaskets were preindented to 25-30 μm , and a 90 μm diameter hole was electrospark drilled through the center. The high-purity Eu sample (99.98% metals basis), obtained from the Materials Preparation Center of the Ames Laboratory [8], was packed into the gasket hole together with several tiny ruby spheres to allow the determination of the pressure *in situ* at 1.6 K from the R1 ruby fluorescence line with resolution 0.2 GPa using the revised pressure scale of Chijioke *et al* [9]. No pressure medium was used. The three highest pressures attained (127, 135, and 142 GPa) were determined from the shift in the diamond vibron [10] at the sample center since the ruby fluorescence could no longer be resolved at these extreme pressures.

The room-temperature synchrotron x-ray experiments on Eu were carried out up to 92 GPa at HPCAT, beamline 16ID-B, using a wavelength of 0.41493 \AA . A Mao-type symmetric cell was used with identical diamond anvils as above. Here the gaskets were made of Re rather than CuBe. Pt powder was included with the Eu sample in the gasket hole to serve as an internal manometer. Further details of the DAC techniques are given elsewhere [4,7,11].

3. Results of Experiment

Four-point electrical resistivity measurements to 91 GPa were carried out on Eu [3]; however, the failure of one of the four Pt leads made a quantitative analysis difficult. At 73, 81, and 91 GPa a sharp downturn is observed in the resistivity near 2 K which suggests a superconducting transition. However, the resistivity does not approach zero, presumably because of the failure of one of the Pt leads.

An ac magnetic susceptibility measurement, a far superior indicator of a superconducting transition, was attempted next, yielding the results shown in figure 2. Whereas at 76 GPa no evidence is seen for a superconducting transition down to nearly 1.5 K, for pressures of 84 GPa and above a large, sharp diamagnetic transition is observed first at 1.78 K which increases with pressure at the rate +18 mK/GPa, reaching 2.75 K at 142 GPa. The magnitude of this transition is consistent with full superconducting shielding. These values of T_c for Eu at pressures near 1 Mbar are much lower than those observed for the related trivalent *s,p,d*-electron metals Sc, Y, La, and Lu where T_c lies in the range 10 - 20 K [4]. Why is this? Perhaps Eu is not completely trivalent, but rather mixed-valent. Or it may be that the Van Vleck paramagnetism acts to suppress the value of T_c in Eu at these pressures.

To explore whether the appearance of superconductivity in Eu above 1.5 K at 84 GPa might be prompted by a structural phase transition, changes in crystal structure under pressure should be studied, preferably at low temperatures. Previous x-ray diffraction studies to 30 GPa at room temperature reveal a bcc to hcp transition in Eu near 12.5 GPa with a close-packed Eu_{III} phase appearing above 18 GPa [12]. Room temperature synchrotron x-ray measurements at the HPCAT beamline (Advanced Photon Source, Argonne National Labs) were carried out to 92 GPa. The results of the first run for increasing pressure are shown in figure 3 where the d-spacing is plotted versus pressure for all Eu diffraction peaks which could be identified. The bcc-to-hcp transition at 12 GPa and the hcp-to- Eu_{III} transition at 18 GPa are clearly seen. In addition, for pressures above 38 GPa a new Eu_{IV} phase is seen to appear. Not shown are data which reveal a Eu_{IV} -to- Eu_{V} transition at even higher pressures (60 GPa). The phases appearing above 18 GPa are currently under analysis, but appear to be neither bcc nor hcp, likely having orthorhombic or monoclinic symmetry. The full results of the extensive x-ray diffraction studies on Eu at ambient temperature will be reported elsewhere.

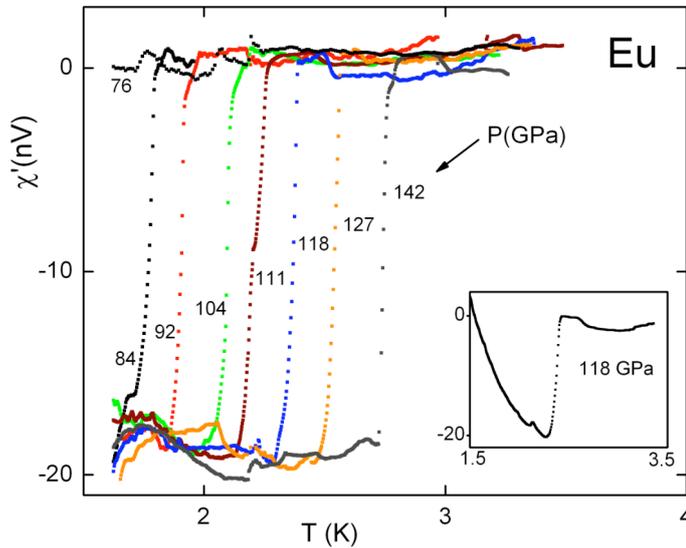


Figure 2. Real part of the ac susceptibility versus temperature for Eu metal as pressure is increased from 76 to 142 GPa. The superconducting transition appears at 84 GPa and shifts slowly under pressure to higher temperatures. T_c is determined from the temperature at the transition midpoint. The inset shows raw susceptibility data at 118 GPa. Figure from Ref. [3].

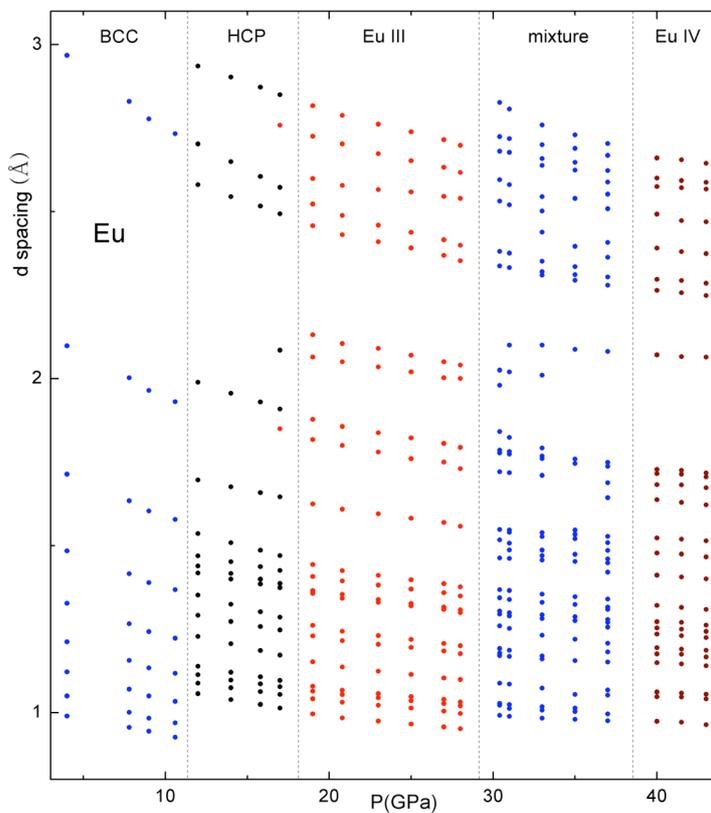


Figure 3. d-spacings for Eu versus pressure revealing three phase transitions to 43 GPa.

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