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Electrical behavior of Eu at very high pressures and low temperatures

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Normally Eu has a valence of two while its Periodic-Table neighbors Sm and Gd have valences of three. There is theoretical reason to believe that some densification of Eu by pressure would shift the balance of the $4f$ and $5d$ electrons to promote it to a valence of three and a different crystal structure. Some theoretical treatments suggest that the high-pressure form of Eu might be superconducting at sufficiently low temperatures. In our experiments, the electrical resistance of Eu specimens was observed to pressures above 400 kbar and temperature down to 2.3 K. In this range, no superconductivity was observed. Based upon reproducible discontinuities of dR/dT and of dR/dP, and the reported observations of others, a tentative P,T phase diagram is proposed. As the pressure is varied there is one phase below about 125 – 150 kbar and a different phase above. As the temperature is increased in the low-pressure phase there is a magnetic ordering transformation in the 90 – 75-K region, and in the high-pressure phase there is a change at about 150 K, the physical nature of which has not been established.

INTRODUCTION

The electronic structure of the lanthanide rare-earth metals is complex. The $4f$ and $5d$ electronic energy levels are quite close, and each of the levels is split by the crystal field. The fact that Eu is ordinarily divalent while its neighbors Pm, Sm, Gd, and Tb are trivalent illustrates the sensitivity of the electronic structure in this series. Decreasing the interatomic distance by application of high pressure causes different shifts of the $4f$ and the $5d$ energy levels resulting in changes of valence, structure, and properties. This was shown experimentally in 1964 by Stager and Drickamer[1] in electrical resistance experiments on 11 rare-earth elements up to pressures of about 250 kbar (modern 1975 scale) and temperatures ranging from 77 to about 300 K. There are also interesting magnetic ordering effects at lower temperatures, and compressibility effects, which have been observed experimentally by McWhan *et al.*,[2] and by Cohen *et al.*[3] in measurements on Eu. Different experimental studies[3,4] on Eu show agreement that a first-order phase transformation is coincident with magnetic ordering in the 90-K region.

In 1975, Johansson and Rosengren[5] worked out a "generalized" phase diagram on an empirical basis for the lanthanides. In this work, they point out that Eu and Yb, because of the tendency for the $4f$ shell to be half-filled or filled, are divalent in the solid state, whereas the others are trivalent. But, upon compression, both these elements should go over into trivalent metallic states more like the other members of the lanthanide series. They also point out that although the localized magnetic moments due to the $4f$ electrons prevent the formation of a superconducting phase in most of the rare earths, some of the nonmagnetic ones do show superconductivity. They suggest that when Eu takes on a trivalent state under pressure it could attain a $4f$ (Ref. 6) nonmagnetic configuration, and could then be superconducting. On the basis of a characterizing factor f, as applied to trivalent Eu, their analysis suggests that the critical temperature of superconduction, if it exists, might lie below 2 K.

Following the development in our laboratory of a sintered-diamond-tipped opposed-piston apparatus capable of operation to pressures up to about 600 kbar and temperatures down to 2.3 K (Ref. 6) we were encouraged by Matthias[7] to test the high-pressure forms of Eu for superconductivity. Using Eu that he provided for us from Bell Telephone Laboratories, we have carried out a number of experiments at pressures ranging from 55 to 420 kbar over the temperature range of 2.3 to 300 K.

Our results, in general, are in approximate agreement with those reported in Refs. 1 – 4 when pressure values are corrected to the currently accepted scales.[8,9] Based upon reproducible discontinuities of dR/dT, we observe the 90 K magnetic ordering change in the lower-pressure phase (up to about 150 kbar), while in the higher-pressure phase a different dR/dT discontinuity occurs in the 150-K region, the nature of which has not been established. In addition, for the high-pressure phase in the 60-K region, there is a broad bend in the $R(T)$ curves not characteristic of simple metals. We found no evidence of superconductivity in the temperature range we investigated. This need not be discouraging, however, as Johansson and Rosengren predict superconductivity would not be expected above about 2 K. A pressure-temperature phase diagram based on our observations, and those of others, is proposed.

The apparatus and procedures used are described in Ref. 6. Because of its ready reaction with oxygen or water, the Eu material had to be shaped to size and loaded into the pressure cell under the protection of white oil. The specimen dimensions were about 0.01-mm wide, and 0.6-mm long. Electrical connections to the ends of the specimen in most experiments consisted of gold foil electrodes which in turn were connected by fine tungsten wires to the conducting part of the pressure pistons which served as links to the external wiring system. To minimize possible oxidation the specimen was prepared as rapidly as possible and the pistons sealed down upon the cell promptly.

A few runs were made at room temperature to pressures as high as about 450 kbar to test for the resistance up-jump transition at about 125 kbar reported by Stager and Drickamer,[1] and by others. With our material and system the resistance jump was not as sharp as shown in Ref. 1, but it did take place, and could be seen to reverse upon unloading, as shown here in Fig. 1. Thus we believe that at the higher pressures in our experiments the Eu was in the high-pressure phase, presumably the trivalent form.

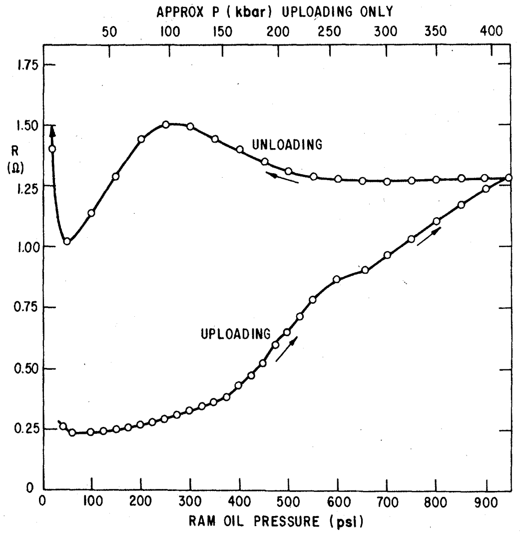

FIG. 1. Resistance versus loading at room temperature of Eu specimen.

In the cryogenic experiments the specimen in the apparatus was pressurized to the desired value at room temperature, clamped at that loading, transferred to the cryostat, cooled to liquid N_2 and then to liquid-He temperature. Then the temperature was lowered still more by reducing the pressure over the liquid He by pumping. During the very slow warm up, when the condition of the pressure apparatus closely approximated thermal equilibrium, the resistance of the specimen and the temperature were monitored carefully. The resistance of the specimen itself was obtained by subtracting the small, but known, electrode linkage resistance from the total resistance. These specimen resistances plotted against temperature were examined for discontinuities suggesting first-order phase changes, and for discontinuities of dR/dT suggesting second-order phase changes. A typical $R(T)$ plot is shown in Fig. 2 for an experiment at 55 kbar, where the change in slope at about 95 K due to magnetic ordering is quite evident.

Since it was not possible to make every specimen

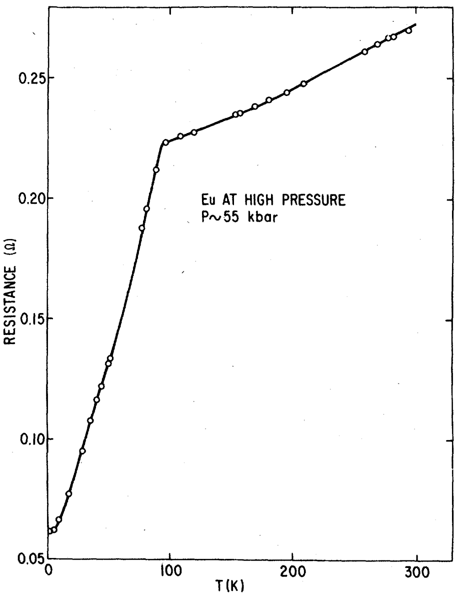

FIG. 2. Resistance versus temperature at 55 kbar for Eu specimen.

exactly the same size and chemical quality, comparisons between different runs were made on the basis of the ratios of resistance normalized to that of a common reference state of 55 kbar, 300 K, obtained in the initial room-temperature pressurization part of the run. Such a reference state was helpful in the analyses of the data, but could not be considered as strictly accurate because of possible changes in the chemical condition and the mechanical dimensions of the specimen during the remainder of the run involving temperature and loading excursions.

In order to examine fairly accurately the resistance of the Eu specimen itself at very low temperatures two of the earliest experiments were run with Nb electrodes and connecting wires to take advantage of the superconducting zero resistance of the Nb below about 8 K. The data obtained from one of these runs are shown in Fig. 3 as resistance against temperature at a cell pressure of about 330 kbar. The resistance behavior of the Nb electrode harness was determined by making a "blank run" under the same conditions but with no Eu specimen present. In this run corresponding to Fig. 3 the rounding of the $R(T)$ curve in the 60–70 K region, and the marked discontinuity of dR/dT at about 140 K, may be seen.

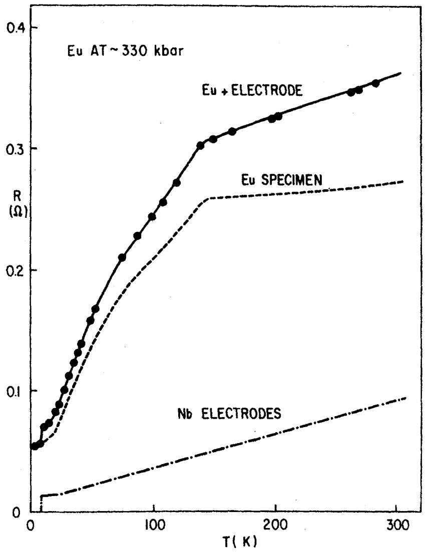

FIG. 3. Resistance versus temperature at about 330 kbar for Eu specimen (data derived from readings taken with Nb electrode harness).

EXPERIMENTAL RESULTS

Table I lists the experimental cryogenic temperature cycle runs and the conditions under which they were made. In two cases temperature cycles were run on the same specimen at two different pressures, and for one specimen data were taken at three different pressures.

Inspection of the R(55 kbar, 300 K) column in Table I brings out the variability of the specimen resistance from one setup to another. As mentioned earlier, this variability was probably a result of chemical quality as well as exact size differences of the individual specimens.

In the temperature cycle runs at fixed pressures

TABLE I. Listing of Eu runs made (in chronological order).

Apparatus	Electrodes	Connecting wires	Pressure for T cycle	Resistance (55 kbar, 300 K) Total	Eu specimen
Di-T[a]	Nb	Nb	330 kbar	0.19Ω	0.10Ω
Di-T	Nb	Nb	420	0.39	0.30
Di-T	Pt	W	(i) 155	0.35	0.18
			(ii) 260	0.37	0.20
Di-T	Au	W	400	0.26	0.12
WC	Au	None	55	0.272	0.272
WC	Au	None	(i) 75	0.48	0.48
			(ii) 110	0.51	0.51
WC	Au	None	(i) 90	0.203	0.203
			(ii) 108	0.212	0.212
			(iii) 125	0.228	0.228
Di-T	Au	W	160	0.75	0.58
Di-T	Au	W	170	0.28	0.11
WC	Au	None	125	0.58	0.58
Di-T	Au	W	400	0.43	0.26

[a] Di-T indicates sintered-diamond-tipped tungsten-carbide pistons; WC indicates tungsten-carbide pistons.

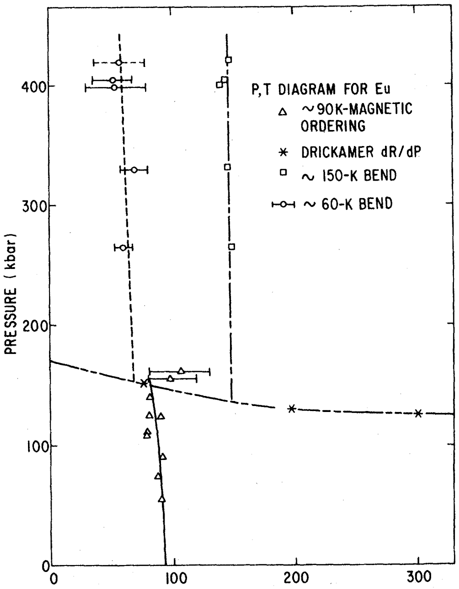

FIG. 4. Proposed P,T phase diagram for Eu.

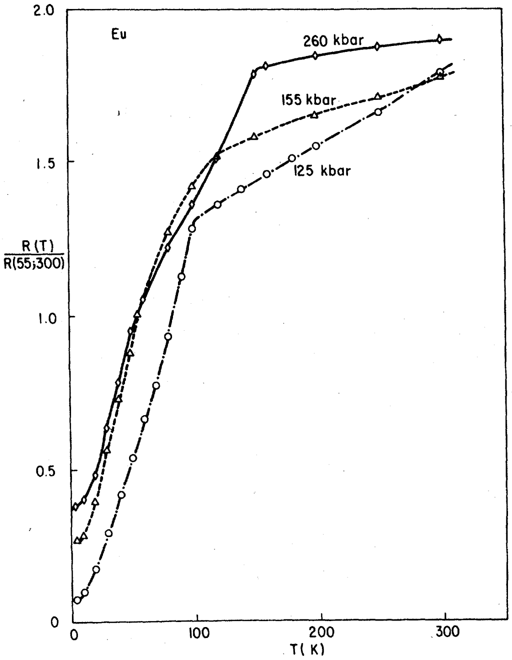

FIG. 5. Normalized resistance of Eu versus temperature in the transition region 125—260 kbar.

there were no instances of clean first-order resistance jumps with temperature, but there were a number of reproducible abrupt changes of dR/dT of particular character, such as those which appear in Figs. 2 and 3. Figure 4 presents a summary of these characteristic "bend" points on a pressure-temperature diagram. Also in the same diagram are plotted the resistance-jump points reported by Stager and Drickamer[1] in their $R(P)$ runs at temperatures of 77, 200, and 300 K (with their pressure values changed to the modern 1975 scale).

The considerable difference between the character of the $R(T)$ curves for pressures below about 125 kbar compared to those at pressures above about 250 kbar may be appreciated by comparing Figs. 2 and 3. The bend which occurs prominently at 90 to 75 K at the lower pressures persists weakly on up to about 150—180 kbar, but at a temperature in the range of 90—100 K. More striking, however, is the appearance at pressures above the Stager-Drickamer line of a new bend in the 150-K region. This sequence is illustrated in Fig. 5 which shows the progression of the $R(T)/R$(55 kbar, 300 K) curves as the pressure is increased from 125 to 260 kbar. As suggested by the plots in Fig. 4 the Stager-Drickamer line separates the low- and high-pressure phases, and the temperature transitions in these two phases are quite different. For the low-pressure phase the 90- to 75-K transition is known to be due to magnetic ordering,[2,3,4] but we have no direct experimental information as yet regarding the nature of the 150-K one in the high-pressure phase.

In the high-pressure phase the $R(T)$ curves also show characteristic rounded bends in the 60—70 K region which are unlike the behavior of a simple metal. This unusual effect may be caused by some kind of sluggish phase change, or a change in the electron scattering mechanism of conduction with temperature. Although our runs consisted mainly of temperature traverses at various constant pressures, plus a few pressure traverses at room temperature, it was possible to synthesize a family of isothermal pressure traverses by using the "normalized resistance," $R(T)/R$(55 kbar, 300 K), as mentioned earlier, and cross plotting the isotherms. The data assembled in this manner are shown in Fig. 6 which presents the "synthesized" $R(P)$ isotherms at various temperatures from 20 to 300 K. While there is considerable scatter of the points, especially at the higher temperatures, the general shapes of the curves resemble those for the room-temperature compressions. They are consistent with a phase boundary line in the 125-kbar region at all temperatures, and suggest another phase boundary line in the region of about 300 kbar.

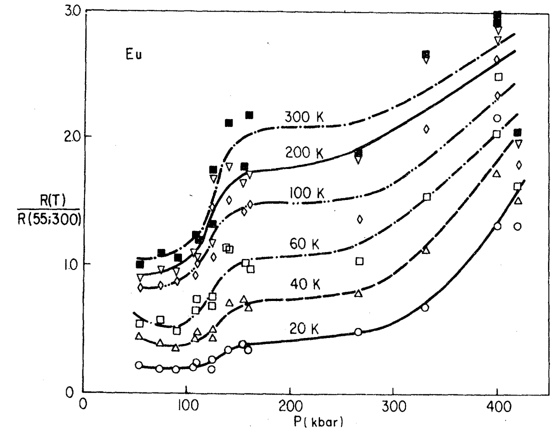

FIG. 6. "Synthesized" normalized $R(P)$ isotherms made by cross plotting the $R(T)$ isobar data.

DISCUSSION

This experimental work combining very high pressures and low temperatures has provided an idea of the behavior of Eu over a considerable range of conditions. The tentative P,T phase diagram which has been suggested by the data needs to be tested in more detail by x-ray diffraction and by magnetic measurements. The x-ray diffraction tests should be possible in a good diamond squeezer apparatus,[10] but magnetic measurements on such small specimens in appropriate ultrahigh-pressure apparatus are very difficult.

Since the experimental evidence strongly suggests that Eu is in a different phase at pressures above about 150 kbar and at low temperatures it would be worth considerable effort to test it at 200 or 300 kbar to temperatures well below 2 K looking for superconductivity.

As pointed out by Johansson and Rosengren,[5] in the progression from the heavier to the lighter lanthanides there is a structure sequence; hcp, samarium-type, dhcp, fcc. As discussed by McWhan[11] the reverse sequence of structure may be observed in the lighter lanthanides by compressing them to higher densities. The generalized phase diagram of Johansson and Rosengren is shown here (in light lines) in Fig. 7 to provide a background for some speculation about the behavior of Eu. Because Eu is divalent at lower pressures one would not expect it to fit into the diagram. However, if at pressures above about 125 kbar it does become trivalent it might be expected to fit from that pressure on up. Superposed on the Johansson and Rosengren diagram in Fig. 7 (in heavy lines) is a proposed diagram for Eu. In the divalent (low-pressure) phase it is known to be bcc,

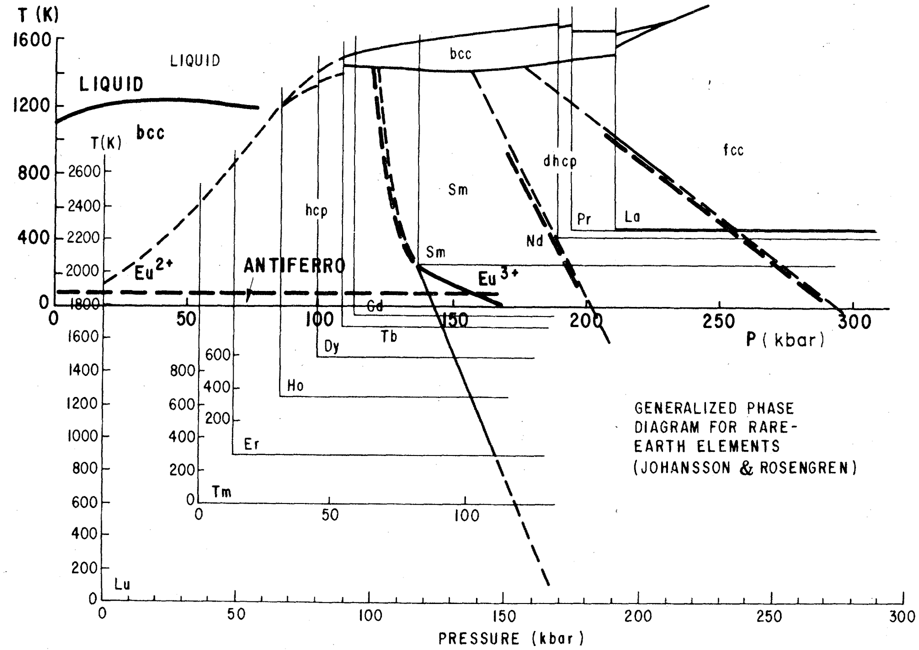

FIG. 7. Speculative strucural phase diagram for Eu based upon the generalized diagram of Johansson and Rosengren for the lanthanides.

and its melting temperature has a maximum of about 1260 K at 30 kbar according to Jayaraman.[12] In the range 130 — 170 kbar at temperatures of 300 to 70 K the present evidence suggests that it becomes trivalent and Sm-like. If this be true, then following the generalized diagram to higher pressures (densities) one might expect a sequence of transformations to dhcp to fcc at room temperature at about 180 and 280 kbar, respectively. In our room-temperature $R(P)$ data, Fig. 8, there does seem to be a reproducible but very small step in the resistance at about 180 kbar, and a much more pronounced one in the 280-kbar region. Such an interpretation of steps in the resistance curves regarding structure can be only speculative. Some good x-ray diffraction studies are indicated, as mentioned earlier.

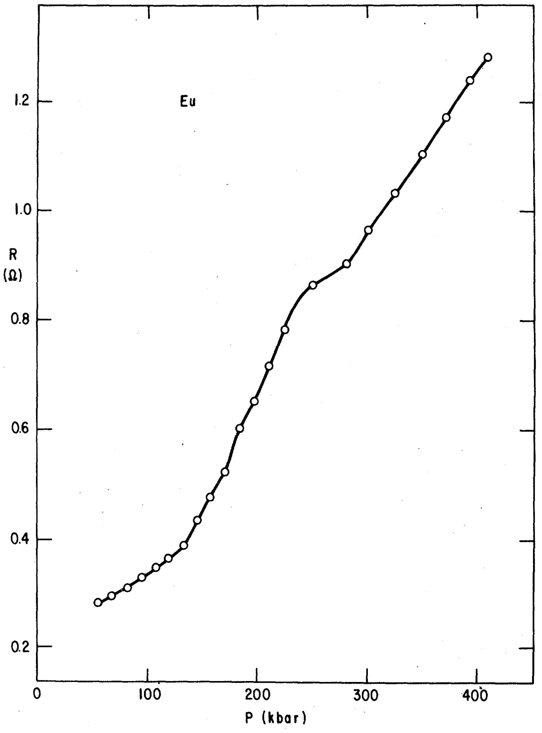

FIG. 8. Resistance versus pressure for an Eu specimen at room temperature.

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