# Magnetic and Structural Properties of Europium Metal and Europium Monoxide at High Pressure

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The change of the Néel temperature of europium metal and of the Curie temperature of EuO with pressure has been measured up to 90 kbar by resistivity and initial-permeability methods, respectively. The compressibility of Eu and EuO has been determined relative to NaCl in the same range of pressure by powder x-ray diffraction methods. The compressibility is represented by the Birch equation; for Eu, $B_0 = 124$ kbar and $\xi = 0.9$ ($d\beta_0/dp = 2.8$) and the standard deviation is 1.8; for EuO, $B_0 = 1070$ kbar and $\xi$ was assumed to be zero and the standard deviation is 2.8. For Eu, $d \ln T_N/d \ln V \approx 0$ down to $V/V_0 = 0.8$. The initial slope for EuO is $d \ln T_c/d \ln V = -6 \pm 2$. The results are discussed in terms of the theories of exchange interaction in the heavy rare-earth metals and the europium chalcogenides.

## INTRODUCTION

$O$F the elements which exhibit antiferromagnetism or ferromagnetism, europium has the largest atomic volume (29 cm³/mole) and the largest compressibility ($8.5 \times 10^{-3}$ kbar⁻¹). The magnetic properties of europium do not fit a simple model of seven localized $4f$ electrons. The magnetic susceptibility cannot be explained on the basis of either a simple divalent ($4f^7$) or a trivalent ($4f^6$) model.[1] The magnetic moment as determined from neutron-diffraction studies is $5.9\,\mu_B$, whereas a divalent model would give a value of $7\,\mu_B$.[2]

Europium monoxide is one of the few oxides that shows true ferromagnetic coupling.[3] The magnetic properties of EuO and the other europium chalcogenides can be explained by the Heisenberg model and the molecular-field approximation.[4] The simple theoretical model indicates that the nearest-neighbor exchange ($J_1$) predominates over the next-nearest-neighbor exchange ($J_2$) so that the pressure variation of the Curie temperature gives a measure of $(dJ_1/dP)$.[4] As the magnetic properties result from well localized $4f$ electrons, the magnetic ordering must be via an indirect exchange mechanism. The large compressibility of europium makes it possible to study the variation of the magnetic ordering energy over a large range of volume within a reasonable range of pressure.

Several other properties of europium have been measured as a function of pressure. The compressibility has been reported by Spedding, Hanak, and Daane[5] to

12 kbar, by Monfort and Swenson[6] to 20 kbar and by Stephens[7] to 45 kbar. The electrical resistivity has been measured by Stromberg and Stephens[8] to ~150 kbar and by Stager and Drickamer[9] to ~700 kbar. The latter study covered the temperature range from 77 to 296°K. The electrical resistance exhibits a sharp rise at ~160 kbar which might reflect a transition. The melting curve of europium has been determined up to 65 kbar by Jayaraman, and it exhibits a maximum similar to that observed in barium.[10]

In this paper the change in the Néel temperature of europium and in the Curie temperature of EuO have been determined up to ~90 kbar, and the compressibilities have been measured relative to NaCl in the same pressure range.

## EXPERIMENTAL METHODS AND RESULTS

### Compressibility

The compressibility was determined in a high-pressure guinier-type focusing x-ray camera. The diluted sample is mounted in the center of a boron-diluted epoxy-resin disk. The disk is then pressed between tungsten carbide anvils. Mo $K\alpha$ radiation is used. The sample is mixed with NaCl as an internal standard, and the pressure is obtained by comparing the observed volume change in NaCl with Bridgman's[11] bulk-volume-compression data to 100 kbar. The details of the experimental methods are described in Refs. 12

[1] R. M. Bozorth and J. H. Van Vleck, Phys. Rev. **118**, 1493 (1960).
[2] N. G. Nereson, C. E. Olsen, and G. P. Arnold, Phys. Rev. **135**, A176 (1964).
[3] B. T. Matthias, R. M. Bozorth, and J. H. Van Vleck, Phys. Rev. Letters **7**, 160 (1961).
[4] T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, J. Appl. Phys. **34**, 1345 (1963).
[5] R. H. Spedding, J. J. Hanak, and A. H. Daane, Trans. AIME **212**, 379 (1958).

[6] C. E. Monfort, III, and C. A. Swenson, J. Phys. Chem. Solids **26**, 623 (1965).
[7] D. R. Stephens, J. Phys. Chem. Solids **25**, 423 (1964).
[8] H. D. Stromberg and D. R. Stephens, J. Phys. Chem. Solids **25**, 1015 (1964).
[9] R. A. Stager and H. G. Drickamer, Phys. Rev. **133**, A830 (1964).
[10] A. Jayaraman, Phys. Rev. **135**, A1056 (1964).
[11] P. W. Bridgman, Proc. Am. Acad. Arts Sci. **76**, 1 (1964).

TABLE I. Compressibility data for Eu and EuO relative to NaCl.

| Run 1 | | | Run 2 | | |
|---|---|---|---|---|---|
| NaCl | | Eu | NaCl | | Eu |
| $10^3 \, a/a_0$ | $P$ (kbar) | $10^3 \, a/a_0$ | $10^3 \, a/a_0$ | $P$ (kbar) | $10^3 \, a/a_0$ |
| 992 | 6.5 | 988 | 992 | 6.5 | 986 |
| 980 | 16.9 | 962 | 971 | 26.0 | 946 |
| 962 | 37.3 | 928 | 964 | 34.8 | 930 |
| 959 | 41.5 | 920 | 959 | 40.7 | 923 |
| 953 | 49.0 | 911 | 956 | 44.1 | 919 |
| 951 | 52.0 | 907 | 956 | 44.1 | 917 |
| 941 | 69.0 | 894 | 950 | 53.9 | 906 |
| 945 | 62 | 891 | 945 | 60.8 | 895 |
| 937 | 74.5 | 883 | 941 | 68.2 | 888 |
| 935 | 77.5 | 881 | 929 | 89.2 | 866 |
| 936 | 77.5 | 876 | 926 | 94.6 | 859 |
| 930 | 87.8 | 864 | | | |

| NaCl | | EuO |
|---|---|---|
| $10^3 \, a/a_0$ | $P$ (kbar) | $10^3 \, a/a_0$ |
| 996 | 3.3 | 998 |
| 988 | 9.7 | 997 |
| 981 | 15.5 | 995 |
| 976 | 21.0 | 994 |
| 962 | 37.5 | 990 |
| 954 | 48.5 | 987 |
| 950 | 54.8 | 985 |
| 947 | 59.2 | 987 |
| 943 | 66.5 | 981 |
| 934 | 79.5 | 977 |
| 931 | 85.0 | 975 |

and 13. The europium was purchased from American Potash and Chemical Corporation, and the stated purity was 99.9%. The EuO was given to us by Olsen,[14] and a guinier x-ray powder pattern showed only one phase present and gave a lattice parameter of $a = 5.145 \pm 0.003$ Å in agreement with the literature. The results are given in Table I.

Birch[15] has shown that the pressure-volume data of a large number of elements and compounds can be described by an equation of the form

$$P = (3B_0/2)(y^7 - y^5)[1 - \xi(y^2 - 1)],$$

with $y = (V_0/V)^{1/3} = a_0/a$. $B_0$ is the bulk modulus at $P = 0$ and $\xi = 3 - \frac{3}{4}(dB_0/dp)$ at $P = 0$. This equation is derived from Murnaghan's theory of finite strain. The data for europium were fitted graphically to the Birch equation, and the resulting parameters were $B_0 = 124$ kbar and $\xi = 0.9$. The standard deviation $(\sigma)$ was 1.8 kbar which is about the expected experimental error.

Our data can be compared with the measurements of Monfort and Swenson[6] who expressed their results to 20 kbar by an expansion of the form $V/V_0 = 1 - aP + bP^2$. From the relations $a = 1/B_0$ and $b = (1/2B_0^2)(5 - \frac{4}{3}\xi)$,[15] one calculates $a = 8.06 \times 10^{-3}$ kbar$^{-1}$ and $b = 1.3 \times 10^{-4}$ kbar$^{-2}$. These values are in good agreement with



FIG. 1. The compressibility of Eu and EuO. EuO □; Eu run 1 ●, run 2 ○; Stevens △, Monfort and Swenson – – – –, Birch equation ($B_0 = 124$ kbar and $\xi = 0.9$) ——.

$a = 8.45 \times 10^{-3}$ kbar$^{-1}$ and $b = 1.0 \times 10^{-4}$ kbar$^{-2}$ given by Monfort and Swenson.[6] The pressure derivative of the bulk modulus is quite small; $dB_0/dP = 4 - \frac{4}{3}\xi = 2.8$. In most materials such as K or Na $(dB_0/dP) \approx 4$, but a value of 2.8 has been reported for Cs.[16] The different sets of data are compared in Fig. 1. The smaller compressibility observed by Stephens[7] has been discussed by Monfort and Swenson.[6]

The electrical resistance studies of Stager and Drickamer show a large anomaly at ~160 kbar which might reflect a transition.[9] Attempts to obtain x-ray diffraction patterns above this pressure failed. The maximum pressure which can be reached in the Bridgman anvil, boron-epoxy disk geometry is a function of the compressibility of the sample. The largest reduction in lattice parameter of europium that was observed was $a/a_0 = 0.799$. Extrapolating via the Birch function indicates that this corresponds to a pressure of ~160±15 kbar. This sets a lower limit for the transition if it exists.

The compressibility of EuO is small and consequently no attempt was made to determine $\xi$ in the Birch equation. Setting $\xi = 0$ $(dB_0/dP = 4)$ the data give a value of $B_0 = 1070$ kbar $(\sigma = 2.8)$. The agreement between the data and the Birch equation is shown in Fig. 1.

## MAGNETIC MEASUREMENTS

### A. Eu

The pressure dependence of the Néel temperature can be determined by measuring among other things the electrical resistance or the initial permeability as a function of temperature at various pressures. The resistance measurements were made either in Bridgman anvils or in a small girdle die with silver chloride as

[12] D. B. McWhan and W. L. Bond, Rev. Sci. Instr. 35, 626 (1964).
[13] D. B. McWhan, J. Appl. Phys. 36, 664 (1965).
[14] J. F. Dillon, Jr., and C. E. Olsen, Phys. Rev. 135, A434 (1964).
[15] F. Birch, J. Geophys. Res. 57, 227 (1952).

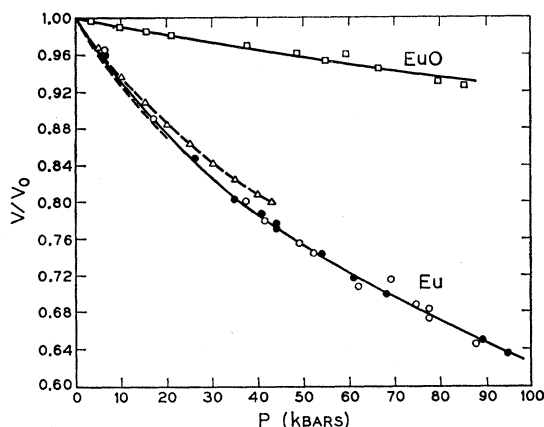[16] C. E. Monfort, III, and C. A. Swenson, J. Phys. Chem. Solids 26, 291 (1965).

the pressure transmitting medium. Details of the techniques can be found in Refs. 17, 18, and 19. The pressure calibration is relative to the transitions observed by resistance methods in Bi (25.4, 26.8, and 82 kbar), Tl(37), and Ba(59). In the girdle the Bi and Eu resistance were monitored simultaneously. The temperature was measured by either a copper-Constantan (with anvils) or a Chromel-Alumel (in girdle) thermocouple. The temperature range was from 77 to 298°K, and the pressure range was from 5 to 90 kbar (girdle) or 20 to 90 kbar (anvils). Typical $R$-versus-$T$ curves taken in the girdle are shown in Fig. 2(a). The heating and cooling rates varied from 1.5 to 5°K/min and temperature cycles were made over a 3- to 5-day period on each sample.

Attempts to measure the initial permeability by a transformer method which had been successful for Gd, Tb, Dy, and Ho failed.[19] Typical curves are shown in Fig. 2(b). Instead of a peak at the Néel temperature, a series of plateaus was observed. The pressure dependence of these was opposite in sign to that observed in the resistance measurements. Europium is very reactive chemically, and on the basis of the results of similar measurements on EuO it is believed that the antiferromagnetic transition in Eu was masked by a ferromagnetic transition in a small amount of a europium
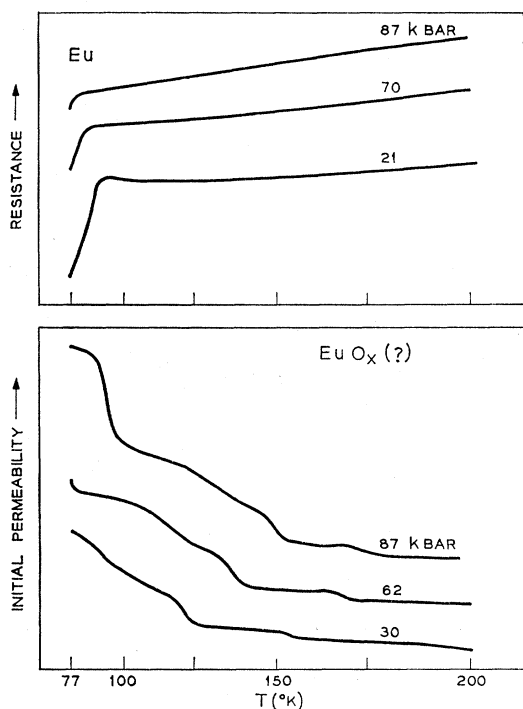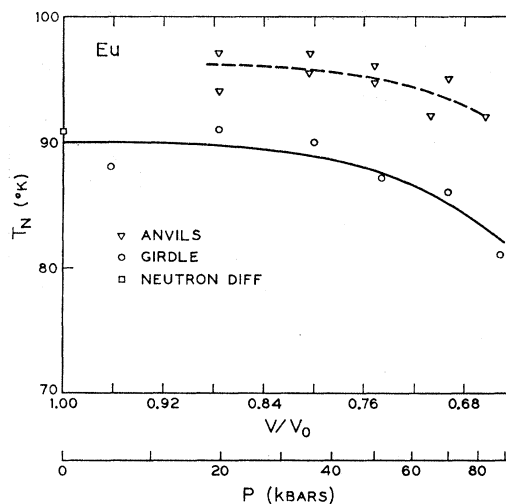


Fig. 3. Néel temperature of Eu versus volume.

suboxide. The series of plateaus suggests that a series of suboxides may exist. For the transition occuring at 120°K the data from four runs all fit a straight line with a slope of +0.37°K/kbar. This value was incorrectly reported as resulting from Eu instead of a europium suboxide by one of the authors.[20]

Combining the data on the Néel temperature of europium from the resistance measurements and the compressability data, a curve for $T_N$ versus relative volume can be drawn and this is shown in Fig. 3. The shape of the curves obtained in the anvils and the girdle die are similar, but there appears to be a systematic error in one or both sets of data. The origin of this error has not been found.

### B. EuO

The pressure dependence of the Curie temperature of EuO was measured by an ac method in which the sample forms the core of a small transformer as described in Ref. 19. The EuO was cast in epoxy resin and machined into a washer-shaped sample. Two coils of No. 44 wire were wound bifilarly to complete the transformer. The primary coil produced a field of $\sim$1 Oe with a frequency of 6 kc. At the Curie point the secondary voltage rises sharply, and the Curie temperature was obtained by extrapolating the curve to the temperature at which it intersects an extrapolation of the background. The results are combined with the compressibility measurements to give the curve of $T_c$ versus $V$ shown in Fig. 4. The Curie temperature could only be measured directly above 25 kbar where it rose far enough above 77°K to make a reasonable extrapolation. The points shown below 25 kbar were obtained by measuring the displacement of the rising curve along the temperature axis with increasing pressure. The experimental points of $T_c$ versus $V/V_0$ show



Fig. 2. (a) Relative resistance of Eu versus temperature. (b) Initial permeability of surface phases on Eu versus temperature.

[17] P. C. Souers and G. Jura, Science **140**, 481 (1963).
[18] P. C. Souers and G. Jura, Science **145**, 575 (1964).
[19] D. B. McWhan and A. L. Stevens, Phys. Rev. **139**, A682 (1965).

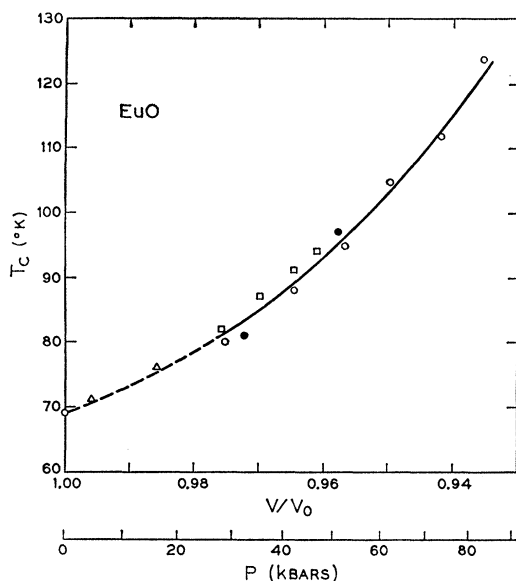[20] D. B. McWhan, Bull. Am. Phys. Soc. **10**, 591 (1965).

FIG. 4. Curie temperature of EuO versus volume.

definite curvature, but this effect will be overemphasized by the slight broadening of the transition with increasing pressure. As the temperature is measured relative to 77°K the observed $\Delta T_c$ will be larger by approximately the amount of broadening. This error is estimated to be $<5°K$ at 82 kbar. The initial slope is $dT_c/dP$ $=+0.37\pm0.10°K/kbar$ ($d \ln T_c/d \ln V = -6\pm2$). A value of $+0.4\pm0.1$ has been reported by Sokolova et al., in studies up to 12 kbar.[21]

## DISCUSSION

### A. Eu Metal

The data for europium metal show that a 40% reduction in volume only produces a 10°K decrease in the Néel temperature. As high as 460 kbar, the curves of resistance versus temperature given by Stager and Drickamer[4] could be interpreted in terms of a magnetic ordering temperature of the order of 120°K. This apparent insensitivity of the magnetic energy in europium to large changes in volume is remarkable. By comparison, in the heavy rare-earth metals, Gd, Tb, Dy, and Ho, $d \ln T/d \ln V$ is in the range 2.2 to 1.4; whereas in Eu it is zero.[19] These results for europium will be examined within the framework of the theories developed to explain the magnetic properties of the heavy rare-earth metals. The theoretical situation has been summarized by Elliott.[22] The Néel temperature is proportional to

$$T_N \propto (g-1)^2 J(J+1)\frac{ZI^2}{E_F}\sum_\tau G(\tau,q,k_F,\Delta)+K(J),$$

[21] G. K. Sokolova, K. M. Demchuk, K. P. Rodionov, and A. A. Samokhvalov, Zh. Eksperim. i Teor. Fiz. **49**, 452 (1965) [English transl.: Soviet Phys.—JETP (to be published)].

[22] R. J. Elliott, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press Inc., New York, 1965), Vol. IIA, Chap. 7.

where

$(g-1)^2 J(J+1)=$ projection of the $4f$ spin **S** on to the total momentum **J**,

$Z=$ number of conduction electrons,

$I=$ exchange integral between the $6s$, $5d$ electrons and the $4f$ electrons,

$E_F=$ Fermi energy,

$\tau=$ reciprocal lattice vector,

$q=$ vector characterizing the antiferromagnetic screw structure,

$k_F=$ Fermi momentum,

$\Delta=$ superzone energy gap,

$K(J)=$ anisotropy energy.

This expression assumes that the conduction electrons can be described by a free-electron model and that $I$ is independent of $q$ and $k$. The model predicts reasonably well the observed spiral structures and the temperature variation of $q$ in the heavy rare-earth metals and alloys. In principle it should be applicable to europium. However, the simple model (without superzone-boundary effects) predicts a ferromagnetic configuration as $\sum_\tau G(\tau,q,k_F)$ does not have a maximum for $q\neq0$.[23] It may be that a more realistic model for the Fermi surface and the inclusion of the interaction between a divalent and a trivalent model may give a spiral configuration.

The over-all functional dependence of $T_N$ should agree fairly well with the above relation; so that the results can be interpreted in terms of the volume dependence of this relation. In europium the anisotropy term will be negligible as the $4f$ electrons are predominantly in an $S$ state and the crystal structure is bcc. Over a wide range of volume the degree of localization of the $4f$ electrons should not decrease appreciably. Consequently $Z(g-1)^2 J(J+1)$ will be independent of volume (see below). If superzone boundary effects are neglected, $\sum G(\tau,k_F)$ is also independent of volume as the variable is $\tau/2k_F$ and $\tau$ and $k_F$ vary as $1/a$, where $a$ is the lattice parameter.[24] This leads to a volume dependence of $T_N$ equivalent to that derived by Liu for $T_c$ in Gd.[24]

$$\frac{d \ln T_N}{d \ln V}=2\frac{\partial \ln I}{\partial \ln V}-\frac{\partial \ln E_F}{\partial \ln V}. \tag{1}$$

For europium this implies that down to $V/V_0\approx0.8$

$$\frac{\partial \ln E_F}{\partial \ln V}=2\frac{\partial \ln I}{\partial \ln V}.$$

Following the argument of Liu the range of $\partial \ln I/\partial \ln V$

[23] Y. A. Rocher, Advan. Phys. **11**, 233 (1962).

[24] S. H. Liu, Phys. Rev. **127**, 1889 (1962).

is expected to be from $-1$ to $0$ thus giving a range of $\partial \ln E_F/\partial \ln V$ between zero and $-2$. For a free-electron model $-\partial \ln E_F/\partial \ln V$ is equal to the electronic Grüneisen parameter $\gamma_e$. Most values of $\gamma_e$ obtained from thermal-expansion measurements at low temperatures fall in the above range.[25] Therefore, within the framework of the theory outlined above, the observed volume dependence of the Néel temperature is not unreasonable.

In principle, information about the magnetic ordering in europium can be obtained from the pressure dependence of the electrical resistivity. In practice, at high pressures it is difficult to separate the part of the resistance which results from spin disorder scattering from the lattice and residual resistivity terms. Barium and europium are very similar, being divalent, bcc metals with similar conduction electrons, so that $dR/dP$ for Ba is indicative of the pressure dependence of the lattice and residual resistivity of Eu. The relative resistance of Ba decreases, passes through a minimum, and increases rapidly with increasing pressure, suggesting a rather complex behavior.[26] It is unlikely that a reliable value for the pressure dependence of the spin disorder resistivity of Eu can be obtained from the data available.

Finally a word should be said about the popular theory of electronic transitions when the $4f$ shell is nearly empty (Ce), half filled (Eu), and full (Yb). If a continuous transition in Eu from $4f^7$ to $4f^6$ is crudely approximated by a mixture of the end configurations, an estimate of $\partial \ln T_N/\partial \ln Z$ can be made. The change in $\sum_\tau G(\tau,k_F)$ was calculated on the basis of the first four terms. Assuming a free-electron model for $k_F$ and $E_F$ and assuming a $4f^6(^7F_0)$ configuration, the order of magnitude of $\partial \ln T_N/\partial \ln Z$ is $-1$. Inclusion of other multiplet levels in the $4f^6$ configuration will reduce the absolute value of this estimate. Therefore, Eq. (1) should also include a term of the order of $\partial \ln Z/\partial \ln V$. One would expect that this term should become important when the specific volume of "divalent" europium approaches that of trivalent Gd. From an extrapolation of the compression data, the volumes become equal at $\sim 140$ kbar. The drop in $T_N$ observed above $\approx 50$ kbar may reflect an increased interaction

between the $4f^6$ and $4f^7$ configurations. But the possible magnetic ordering observed as high as 460 kbar in the resistivity measurements of Stager and Drickamer must then be explained on the basis of a $4f^6$ configuration.

## B. EuO

The magnetic ordering in the europium chalcogenides has been interpreted in terms of a Heisenberg model and the molecular-field approximation.[4] The Curie temperature is given by

$$T_c = \tfrac{2}{3}S(S+1)(Z_1 J_1 + Z_2 J_2),$$

where $Z_1$ and $Z_2$ are the number of nearest- and next-nearest neighbors; $J_1$ and $J_2$ are the exchange integrals for the nearest- and next-nearest-neighbor interactions, and $S$ is the spin. For EuO, $J_1 \ll J_2$, and $dJ_2/da$, where $a$ is the lattice parameter, is small.[4] To a good approximation $k dT_c/da \approx dJ_1/da$, where $k$ is Boltzmann's constant. From Fig. 4 one obtain $dJ_1/da = -230k$ °K/Å ($d \ln J_1/d \ln a = -17$) at 1 bar. This result is substantially larger in absolute value than would be obtained from a plot of $T_c$ versus Eu-Eu distance for EuO, EuS, and EuSe ($-86k$ °K/Å). This is not surprising as the variation in covalency on going from $O^{2-}$ to $Se^{2-}$ must be reflected in the exchange interaction.

In summary, the compressibility of Eu metal can be expressed by the Birch equation over a volume change of $\approx 40\%$, but the calculated value for $dB_0/dP$ at $P=0$ is surprisingly small (2.8). For Eu ($d \ln T_N/d \ln V) \approx 0$ over a volume change of $\approx 20\%$. On the basis of an indirect-exchange interaction and a free-electron model for the conduction electrons it is shown that this result is not unreasonable. Finally $(d \ln T_c/d \ln V) = -6\pm2$ for europium monoxide which implies a very large dependence of the nearest-neighbor exchange integral $(J_1)$ on interatomic distance.

[25] K. Andres, Phys. Kondensierten Materie 2, 294 (1964).
[26] P. W. Bridgman, Proc. Am. Acad. Arts Sci. 81, 167 (1952).