The main puzzle, of course, is the existence of an equilibrium. One intuitively expects that one of the two structures to have lowest energy, and thus, except for thermal hysteresis effects which are negligible in this case, that one and only one magnetic phase would be observed at a given temperature. Stability estimates, however, must in principle include surface energy and long-range interactions between the phases. From this point of view the two-phase system may represent a disordered superstructure of A and B.

The relationship between the A and B structures can be simply described in terms of the Me–O–Me–O–··· chains of which they are composed. In the B phase the chains are identical; in the A phase they are reversed. If we consider a boundary parallel to the a-c plane between two magnetic domains of the B structure, spins on either side of the boundary are necessarily opposite in sign. The region spanning the boundary, as shown in Fig. 8, has the structure of the A phase. Thus, the A phase is automatically nucleated at domain boundaries of the B phase and, similarly, nuclei of the B phase are generated at domain boundaries of A. If the two-phase configuration results from such a nucleation process, we can offer no explanation at the present time for the growth of these nuclei and the dependence of their ultimate size on temperature and composition.

PHYSICAL REVIEW VOLUME 160, NUMBER 2 10 AUGUST 1967

Magnetoelastic Behavior of Single-Crystal Europium Oxide. I. Thermal Expansion Anomaly

B. E. ARGYLE, N. MIYATA,* AND T. D. SCHULTZ
IBM Watson Research Center, Yorktown Heights, New York
(Received 31 March 1967)

The thermal expansivity of a single crystal of EuO was determined in the temperature range 25 to 250°K by a differential-strain-gauge method. The temperature of the peak in the λ curve of expansivity is 69.2°K, in agreement with the specific-heat measurements. After correcting for the normal lattice expansivity using the Grüneisen theory, we observe that the resulting magnetoelastic component of expansivity α_{me} obeys a *magnetic Grüneisen law*, being proportional to the magnetic specific heat C_m over wide ranges of temperature both above and below the λ transition. Europium oxide can therefore be characterized by a temperature-independent "magnetic" Grüneisen constant, $\partial\ln U_m/\partial\ln V=-5.3$, given by $-3\alpha_{me}C_m^{-1}B_T$, where the isothermal bulk modulus $B_T=1.07\times10^{+12}$ dyn/cm². The *lattice* Grüneisen constant, $\partial\ln U_l/\partial\ln V=1.9$, was similarly derived from the data at temperatures well above the λ anomaly. For U_m, the internal magnetic energy, we also derive the variation with temperature $U_m(T)/U_m(0)$, the variation with pressure $\partial\ln U_m/\partial P=4.9\times10^{-12}$ dyn^{-1} cm², and the value $U_m(0)=-4.9\times10^8$ erg/cm³ at 0°K. Comparison with results of other experiments and with theories based on the Heisenberg Hamiltonian is also presented. The model of D. C. Mattis and T. D. Schultz and of E. Pytte is consistent with the observed proportionality between C_m and α_{me}. A more general model proposed by E. R. Callen and H. B. Callen includes magnetoelastic coupling of unequal strengths to first- and second-nearest neighbors. When the second-neighbor interaction is weaker than the first, this model is also consistent with a single effective magnetic Grüneisen constant not only because the model then differs only slightly from a special case of that of Mattis and Schultz and of Pytte, but also because the spin correlation functions $\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\text{1st neighbor}}$ and $\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\text{2nd neighbor}}$ appear to be nearly proportional to each other over a wide temperature range.

INTRODUCTION

EUROPIUM oxide is an insulating ferromagnet with S-state Eu^{++} ions situated on cubic face-centered sites of the NaCl-type structure. As such EuO represents a nearly ideal Heisenberg lattice of interacting spins making its fundamental magnetic properties especially interesting to study and relate to predictions of theory. In this work (I) the magnetic thermal expansion anomaly is measured and used for describing that part of the magnetic energy which is isotropic with respect to the direction of the magnetization in the crystal. Subsequently, in II, we shall report on the *induced* isotropic and anisotropic (macroscopic) strains which appear upon application of a magnetic field and also investigate the behavior of the transition anomaly in the presence of applied magnetic fields. Previously, we measured the strength of the first-order term in the free energy that depends upon the direction of the magnetization in the crystal (magnetocrystalline anisotropy) and this was compared with predictions of a theory that treats the interaction of the otherwise isolated Eu^{++} ion with its cubic crystal environment.[1]

The meaning and fundamental usefulness of the thermal expansion anomaly for a ferromagnet is evident

* Visiting scientist, presently at Yokohama National University, Minamiku, Yokohama, Japan.

[1] N. Miyata and B. E. Argyle, Phys. Rev. **157**, 448 (1967).

from the fact that for certain assumptions about the nature of the magnetic coupling there exists a rather simple relationship between the magnetoelastic contributions to the thermal expansivity α_{me} and specific heat C_m.[2] The ratio α_{me}/C_m, which may be determined in the region of the λ anomaly by correcting for the nonmagnetic contributions of the lattice, leads to the determination of a "magnetic" Grüneisen parameter $\gamma_m \equiv \partial \ln U_m/\partial \ln V$. This parameter gives information about the dependence of the isotropic magnetic interaction energy U_m on the interatomic separation. We report here measurements of thermal expansivity in a single crystal of EuO. The specific heat of EuO crystals has been extensively investigated by Teaney *et al.*[3] and recently they have quite accurately determined the magnetic part C_m.[4] By a technique based on the Grüneisen theory[5] we also subtract the lattice part $\alpha_l(T)$ from the total expansivity ($\alpha_{me} \equiv \alpha_t - \alpha_l$) and then present a comparison between α_{me} and C_m to give the volume derivative of the exchange energy for our single-phase/single-crystal specimen. Other investigators[6–8] have obtained various values for the pressure derivative of the Curie temperature of polycrystalline EuO by detecting the shift with pressure of the edge of the susceptibility anomaly near the magnetic transition temperature T_c. The special nature of exchange interactions in EuO permits the comparison between these two quantities.

As the ratio $\alpha_{me}(T)/C_m(T)$ is observed to be quite insensitive to temperature over a rather wide temperature range, we may estimate the variation of the effective exchange coupling constant J with temperature arising from the temperature-dependent lattice deformation. In this way we calculate the temperature variation of internal magnetic energy for the *rigid* lattice of spins. Thus, we can also indicate the temperature variation of the short-range isotropic-spin correlation function, and compare the results with quantum-statistical calculations based on the Heisenberg Hamiltonian.

EXPERIMENTAL METHOD

The specimen is a single-crystal (100) disk 5.0 mm in diameter and 0.67 mm thick, cut ultrasonically from a crystal having a (100) natural cleavage face. This crystal was grown by Guerci and Shafter[9] of this laboratory and contained less than $\frac{1}{2}\%$ of a second nonmagnetic phase. Thermal strain was measured by the strain-gauge method. One gauge, attached to the specimen, and three reference gauges, attached to copper plates, comprise a Wheatstone bridge. Paper backed wire gauges (type K19-1S2 manufactured by Kyowa Electronics Industries Company Ltd.) were fastened to the crystal using GA-4 epoxy cement manufactured by the Budd Company. In our experimental arrangement, effects of thermal voltages (e.g., at junctions between the strain gauge leads and the copper leads connecting the bridge to its current supply or detector) are suppressed by thermally stabilizing the critical bridge connections to a common temperature. Temperature uniformity among all bridge components is stabilized by helium exchange gas and an isothermal (copper) enclosure which are in thermal contact with liquid or solid N_2 or Ne. The temperature of these baths was varied by controlling vapor pressure using a fore pump and a Wallace and Tiernan manostat.

Because the bridge unbalance is proportional to the strain difference between EuO and copper, changes in the gauge properties [i.e., resistance r_g and gauge factor $G \equiv (\Delta r_g/r_g)/(\Delta l/l)$] with changing temperature are suppressed in the final curve of α (EuO) versus T (Fig. 1) obtained by adding known data[10] for α(Cu) to our measured difference $\Delta\alpha_{obs} = \alpha_{EuO}(T) - \alpha_{Cu}(T)$. We also note that the ratio $r_g(T)/G(T)$, which essentially sets the calibration for the bridge unbalance, changes only 13% from 300 to 77°K and approximately 1% from 77 to 4.2°K.[11] Treating the calibration as a constant (obtained here as 1.22×10^{-6} strain/μV at 77°K) introduces an error no greater than the fluctuations in the data (Fig. 2). These fluctuations from run to run are believed due to small temperature differences among the four bridge arms.

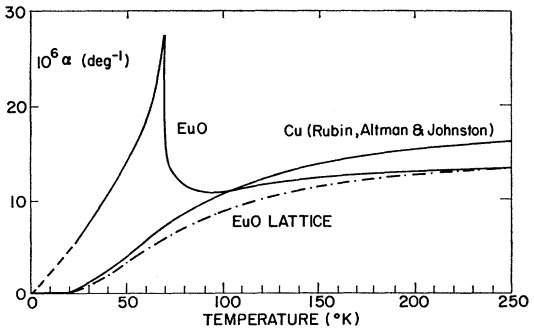

FIG. 1. Solid curves: linear thermal expansivity α versus temperature for EuO and Cu, respectively. Dot-dash curve: lattice contribution α_l estimated for EuO. (See text.)

[2] (a) D. C. Mattis and T. D. Schultz, Phys. Rev. **129**, 175 (1963); (b) E. Pytte, Ann. Phys. (N.Y.) **32**, 377 (1965); (c) E. R. Callen and H. B. Callen, Phys. Rev. **139**, A455 (1965).

[3] V. L. Moruzzi, D. T. Teaney, and C. F. Guerci, Bull. Am. Phys. Soc. **12**, 133 (1967).

[4] D. T. Teaney, V. L. Moruzzi, and C. F. Guerci (private communication).

[5] G. Mie, Ann. Physik **11**, 657 (1903); E. Grüneisen, *ibid.* **26**, 393 (1908); F. Seitz and D. Turnbull, Solid State Phys. **12**, 275 (1961).

[6] R. Stevenson and M. C. Robinson, Can. J. Phys. **43**, 1744 (1965).

[7] G. K. Sokolova, K. M. Demshuk, K. P. Rodionov, and A. A. Samokhvalov, Zh. Eksperim. i Teor. Fiz. **49**, 452 (1965) [English transl.: Soviet Phys.—JETP **22**, 317 (1966)].

[8] D. B. McWhan, P. C. Souers, and G. Jura, Phys. Rev. **143**, 385 (1966).

[9] C. F. Guerci and M. W. Shafer, J. Appl. Phys. **37**, 1406 (1966).

[10] T. Rubin, H. W. Altman, and H. L. Johnston, J. Am. Chem. Soc. **76**, 5289 (1954).

[11] R. Gersdorf, Doctoral thesis, University of Amsterdam, 1962 (unpublished).

The temperature was sensed by a platinum resistance thermometer, type 172A6C2 manufactured by the Rosemount Engineering Company which was imbedded in the copper plate on which the reference strain gauges were attached. Resistance was measured by comparing voltages measured across the platinum thermometer and a Leeds and Northrup 10-Ω standard resistance carrying a 0.1-mA dc current.

Changes in voltage of the bridge unbalance and resistance thermometer were measured by means of an integrating type digital voltmeter (Model 510 manufactured by the Vidar Corporation, Mountain View, California) with a resolution of ± 0.1 μV, which in our arrangement represents a resolution of 1.6×10^{-7} in strain and $\sim$0.001°K in temperature. We read the strain to the nearest 0.1-μV unbalance and temperature to 0.01°K.

EXPERIMENTAL RESULTS

The total expansivity curve for EuO (Fig. 1) was obtained differentially by measuring the Wheatstone bridge unbalance ΔE while the temperature was slowly varied. The slope of ΔE-versus-T data gives the difference in thermal expansivity $[\Delta\alpha\equiv\alpha_{\mathrm{EuO}}(T)-\alpha_{\mathrm{Cu}}(T)$, not shown] between EuO and Cu. Combining this with precise $\alpha_{\mathrm{Cu}}(T)$ data known from optical interferometric measurements[10] gives $\alpha_{\mathrm{EuO}}(T)$ as shown in Fig. 1.

Subtraction of lattice expansivity. We define the incremental expansivity due to magnetoelastic coupling by $\alpha_{\mathrm{me}}=\alpha_{\mathrm{total}}-\alpha_l$. For an experimental determination of α_{me} we must estimate α_l, the lattice contribution. This was estimated from an approximate Grüneisen curve. The Grüneisen theory[5] for thermal expansion gives

$$\alpha_l(T)=\frac{C_v(T)}{3Q_0[1-k(U/Q_0)]^2},$$

where $C_v=f(T/\theta_D)$ is the Debye specific heat characterized by the Debye temperature, Q_0 and k are constants relating to the strength of interatomic forces, and

$$U=\int_0^T C_v(T)\,dT.$$

The quantity in brackets is a small correction which varies slowly with T compared with $C_v(T)$. We may neglect it in comparison to the inaccuracy of our data. Thus, $\alpha_l(T)$ is proportional to the specific heat $C_l(T)$, and the α_l-versus-T curve is shaped by the constants Q_0 and θ_D. To estimate α_l we note that EuO and copper have nearly the same Θ_D (325°K for Cu [10] and 335°K for EuO [4]). Also, the expansivity data for copper fit the Grüneisen theory very well, the deviations that occur below 110°K [10] being negligible compared with the fluctuation in our data for EuO. The difference between α_l of EuO and of copper observed at high temperatures where magnetoelastic effects in EuO are negligible is evidently due to the constant Q_0. We determine $Q_0(\mathrm{EuO})/Q_0(\mathrm{Cu})=1.21$ from the observed ratio $\alpha(\mathrm{EuO})/\alpha(\mathrm{Cu})=13.3\times10^{-6}/16.1\times10^{-6}$ at 250°K. The curve for $\alpha_l(\mathrm{EuO})$ versus T given in Fig. 1 is then simply obtained by adjusting the curve for copper according to this ratio.

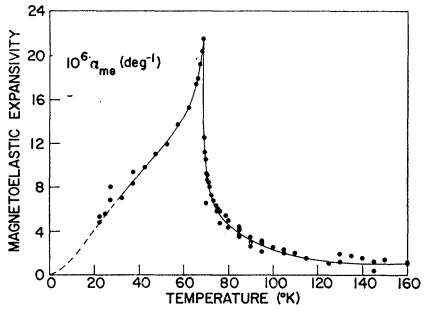

FIG. 2. Magnetoelastic thermal expansivity α_{me} versus temperature for EuO obtained from $\alpha_{\mathrm{total}}-\alpha_l$. (See text.)

Magnetoelastic thermal expansivity and relation to specific heat. Subtraction of the lattice contribution leads to the magneto-elastic expansivity $\alpha_{\mathrm{me}}(T)$ curve of Fig. 2. The data fluctuations are displayed here rather than in Fig. 1. These are not related to the correction for the lattice or to temperature variation of strain gauge properties. They appear to arise from temperature inhomogenities among the bridge components. Figure 2 includes data obtained with temperatures both increasing and decreasing and using each of two different strain gauges oriented along [100] or [110] crystal directions and the results are indistinguishable.[12]

Comparison between magnetoelastic expansivity and magnetic specific heat is presented in Fig. 3, where $\alpha_{\mathrm{me}}(T)$ from our measurements is plotted versus $C_m(T)$ for the temperature range 25 to 160°K. The error bars are an estimate of a maximum error based on just the fluctuations appearing in the C_m data of Teaney *et al.*[4] and the α_{me} of Fig. 2. For temperatures close to T_c, mean values and limits of error are difficult to determine due to the discontinuity in the slope of α_{me} and C_m versus T. We therefore omit in Fig. 3 the data for $|T-T_c|\leq5$°K. It is noteworthy, however, that α_{me} attains its peak (Fig. 2) at the same temperature (69.2°K) as the peak in C_m.[3] Also, the ratio of magnetic to lattice contributions at T_c is about 5:1 for expansivity (Fig. 1) and is about 1:1 for specific heat.[4]

As will be discussed in detail, the total volume change

[12] Of course, anisotropic strain also occurs within each spontaneously magnetized domain. However, from the quantitative behavior of strain induced by an applied field [given in a subsequent paper (II) by B. E. Argyle and N. Miyata (to be published)] it was shown that in zero field the domains are oriented at random along ⟨111⟩ easy axes. This further demonstrates that macroscopic strain detected in zero field by the strain gauge registers only the isotropic component of spontaneous strain.

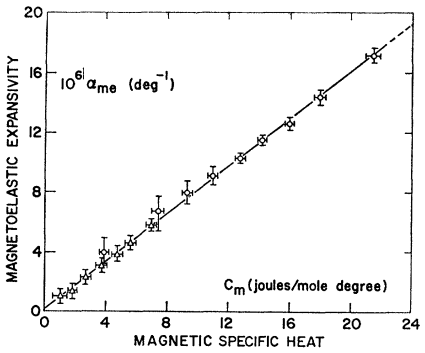

FIG. 3. Magnetoelastic thermal expansivity α_{me} versus magnetic specific heat C_m. Circles and triangles relate to temperatures below (25–64°K) and above (74–140°K) the Curie point (69.2°K), respectively.

between 0 and 300°K is 1.07% as given by

$$\int_0^{300^\circ} 3\alpha_{\text{total}}(T)\,dT$$

and the α(EuO)-versus-T curve of Fig. 1, while the magnetic volume anomaly at 0°K (the volume deformation which the lattice undergoes because it is magnetic) is −0.24% as obtained from

$$\int_{T\gg T_c}^{0} 3\alpha_{\text{me}}(T)\,dT$$

using the curve of Fig. 2. In each case, extrapolation from 20 to 0°K was approximated by a $T^{3/2}$ law to account for spin waves.

THEORY

To interpret the measured values of the total expansivity α_t and total specific heat at constant volume C_t in the light of the estimated contributions from purely lattice effects α_l and C_l, we recall the model discussed in some detail, for example, by Mattis and Schultz,[2a] and by Pytte.[2b]

In this model the Hamiltonian has the form

$$H=H_l+H_m, \tag{1}$$

where H_l is the "pure lattice" Hamiltonian (the Hamiltonian if the ions had no magnetic moments) and for H_m it is assumed first that it involves only spin-spin interactions (i.e., vanishing external field), second that all spin-spin interactions depend on the average density of the lattice but on no other lattice variables, and third that the only dependence on the average density is through a multiplicative function $\lambda(v)$ common to all terms of H_m. Thus for a general Heisenberg model

$$\begin{aligned} H_m&=\sum_{(ij)} -2J_{ij}(v)\,\mathbf{S}_i\cdot\mathbf{S}_j \\ &=\lambda(v;\,v_0)\sum_{(ij)} -2J_{ij}(v_0)\,\mathbf{S}_i\cdot\mathbf{S}_j \\ &=\lambda(v;\,v_0)\hat{H}_m, \end{aligned} \tag{2}$$

where $\lambda=J(v)/J(v_0)$. The reference Hamiltonian $\hat{H}_m$ is independent of the average atomic volume $v\equiv V/N$, depending only on a standard reference volume v_0 which will drop out of all calculations.

For this model the *total* free energy for volume V in vanishing external field is

$$F_t(\beta,V)=F_l(\beta,V)+F_m(\beta,V), \qquad \beta=1/kT, \tag{3}$$

where, in view of Eq. (2), F_m has the form

$$\begin{aligned} F_m(\beta,V)&=-\beta^{-1}\ln \text{Tr}\exp(-\beta H_m) \\ &=-\beta^{-1}\ln \text{Tr}\exp[-\beta\lambda(v)\hat{H}_m] \\ &\equiv\beta^{-1}\hat{F}_m(\beta\lambda(v)). \end{aligned} \tag{4}$$

Thermodynamic quantities characterizing the pure lattice, which we have estimated, are derivable from F_l. Thus for the pressure, isothermal compressibility, specific heat, and expansivity of the pure lattice one has

$$p_l=-(\partial F_l/\partial V)_T, \tag{5a}$$

$$K_l=V^{-1}[(\partial^2 F_l/\partial V^2)_T]^{-1}, \tag{5b}$$

$$C_l=\partial/\partial T(\partial/\partial\beta(\beta F_l)), \tag{5c}$$

$$\alpha_l=\tfrac{1}{3}(-K_l)(\partial^2 F_l/\partial V\partial T). \tag{5d}$$

The corresponding quantities for the total system, p_t, K_t, C_t, and α_t, which are measurable, are expressible in terms of F_t by equations analogous to (5a)–(5d).

If one defines p_m, K_m, and C_m by analogous equations in terms of F_m, one sees immediately that

$$p_t=p_l+p_m, \tag{6a}$$

$$1/K_t=1/K_l+1/K_m, \tag{6b}$$

$$C_t=C_l+C_m. \tag{6c}$$

However, an analogous definition for α_m does not lead to a similar additive relation. Rather one finds

$$\begin{aligned} \alpha_t&=\tfrac{1}{3}K_t(\partial p_t/\partial T)_V \\ &=\tfrac{1}{3}K_t[(\partial p_l/\partial T)_V+(\partial p_m/\partial T)_V] \\ &=(K_t/K_l)\alpha_l+(K_t/K_m)\alpha_m. \end{aligned} \tag{6d}$$

Thus what we shall call magnetic expansivity is

$$\alpha_m\equiv-\tfrac{1}{3}K_m\frac{\partial^2 F_m}{\partial V\partial T}=\frac{K_m}{K_t}\alpha_t-\frac{K_m}{K_l}\alpha_l, \tag{7}$$

while the incremental expansivity due to magnetoelastic interactions is

$$\alpha_{\text{me}}\equiv\alpha_t-\alpha_l=(K_t/K_l-1)\alpha_l+(K_t/K_m)\alpha_m. \tag{8}$$

The difference between α_m and α_{me} is due to the fact that the total pressure p_t, and not the partial pressures p_l and p_m, is held fixed in defining the total expansivity.

If we specialize F_l to the form assumed in the Mie–Grüneisen theory,

$$F_l(V,\beta)=U_l(V)+T\eta(T/\theta), \tag{9}$$

with θ a function only of V and with η some appropriate function, we have the well-known relation

$$\alpha_l=\frac{K_lC_l}{3V}\frac{d\ln\theta}{d\ln V}=\frac{K_lC_l}{3V}\gamma_l, \tag{10}$$

where $\gamma_l\equiv d\ln\theta/d\ln V$ is the Mie-Grüneisen constant for the pure lattice.

Similarly, for the special form for F_m in Eq. (4), one obtains the relation

$$\alpha_m=-\frac{K_mC_m}{3V}\frac{d\ln\lambda}{d\ln V}=-\frac{K_mC_m\gamma_m}{3V}, \tag{11}$$

where $\gamma_m\equiv d\ln\lambda/d\ln V$ is a magnetic Grüneisen "constant" which is also expressible in terms of the exchange parameter simply as $\gamma_m=d\ln J/d\ln V$. Using (10) and (11) in (8) one obtains

$$\alpha_{\rm me}=(1/3V)[(K_l-K_l)C_l\gamma_l-K_lC_m\gamma_m]. \tag{12}$$

From Eq. (6b) this can be expressed in terms of K_l and K_m:

$$\alpha_{\rm me}=-(1/3V)\frac{K_l}{1+K_l/K_m}\left|\frac{K_l}{K_m}C_l\gamma_l+C_m\gamma_m\right|. \tag{13}$$

It is useful to compare K_l with K_m. For the particular form of F_m that we are considering we have

$$K_m^{-1}=-\frac{T}{V}C_m\gamma_m^2+\frac{U_mV}{\lambda}\frac{d^2\lambda}{dV^2}, \tag{14}$$

where $U_m(T)$ is given by

$$\int_\infty^T C_m dT.$$

Neglecting the second term compared with the first, which is especially valid near the critical point where $C_mT\gg|U_m|$, we see from (10) and (14) that

$$\left|\frac{K_l}{K_m}\right|\simeq\frac{3\alpha_lV}{C_l\gamma_l}\frac{T}{V}C_m\gamma_m^2=(3\gamma_m\alpha_lT)\left(\frac{C_m}{C_l}\right)\left(\frac{\gamma_m}{\gamma_l}\right). \tag{15}$$

Near the critical point, it will be seen from the observations on EuO that this reduces to

$$|K_l/K_m|\simeq\tfrac{1}{65}(C_m/C_l). \tag{16}$$

Since the largest C_m's measured have only been $\simeq C_l$,[13] we can assume that for all experimentally attainable temperatures $|K_l/K_m|\ll1$, so that

$$\alpha_{\rm me}=-(K_l/3V)[(K_l/K_m)C_l\gamma_l+C_m\gamma_m]$$
$$=-(K_l\gamma_mC_m/3V)[1-3T\gamma_m\alpha_l]. \tag{17}$$

We may anticipate that near the critical point, the term $3T\gamma_m\alpha_l$ is small ($\simeq0.006$) and slowly varying, so that $\alpha_{\rm me}$ and C_m are very closely proportional as functions of T. Since $\alpha_{\rm me}$ can be measured with much greater accuracy than C_m, magnetoelastic measurements appear to be a superior tool for the study of the critical region. However, since the expected deviation of C_m at constant pressure from C_m at constant volume (the quantity of fundamental theoretical interest) is very small, while the proportionality of $\alpha_{\rm me}$ to C_m rests on further assumptions, the higher precision of magnetoelastic experiments is not an unmixed blesssing.

From what we have said it might seem that the proportionality of $\alpha_{\rm me}$ to C_m is evidence for the model of Eq. (1) *et seq.* We wish to point out that other models can apparently lead to a similar behavior. For example, consider the Heisenberg model where the interaction strength with nth-nearest neighbors is characterized by an exchange coupling strength J_n and where we assume that J_1, J_2, etc. all depend only on the volume but not necessarily in the same way. Thus

$$H_m=-J_1(V)\sum_{\rm 1st\ neighbor}\mathbf{S}_i\cdot\mathbf{S}_j$$
$$-J_2(V)\sum_{\rm 2nd\ neighbor}\mathbf{S}_i\cdot\mathbf{S}_j-\cdots. \tag{18}$$

As before, $\alpha_m=-\frac{1}{3}K_m(\partial^2F_m/\partial T\partial V)$, but in the present model one finds that

$$\partial F_m/\partial V=-(dJ_1/dV)\sum_{\rm 1st}\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle$$
$$-(dJ_2/dV)\sum_{\rm 2nd}\langle\mathbf{S}_i\cdot\mathbf{S}_j\rangle+\cdots, \tag{19}$$

so that, using translational invariance,

$$\alpha_m=+\frac{K_mN}{3V}[z_1J_1\gamma_1(\partial\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\rm 1st}/\partial T)_v$$
$$+z_2J_2\gamma_2(\partial\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\rm 2nd}/\partial T)_V+\cdots], \tag{20}$$

where $\gamma_1=d\ln J_1/d\ln V$, $\gamma_2=d\ln J_2/d\ln V$, etc., and z_n is the number of nth-nearest neighbors. Using (6b), which also is valid for this model, we obtain

$$\alpha_{\rm me}\simeq+\frac{K_tN}{3V}\left[z_1J_1\gamma_1\left(\frac{\partial\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\rm 1st}}{\partial T}\right)_V\right.$$
$$\left.+z_2J_2\gamma_2\left(\frac{\partial\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\rm 2nd}}{\partial T}\right)_V+\cdots\right], \tag{21}$$

again using the inequality $|K_m|\gg K_t$. This is to be compared with the magnetic contribution to the specific heat:

$$C_m=N[J_1z_1(\partial\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\rm 1st}/\partial T)_V$$
$$+J_2z_1(\partial\langle\mathbf{S}\cdot\mathbf{S}'\rangle_{\rm 2nd}/\partial T)_V+\cdots]. \tag{22}$$

[13] In principle, as we get closer and closer to T_c, C_m increases without bound, so that sufficiently close to T_c, $C_m\gg C_l$ and $K_l>K_m$. When such a situation obtains, (17) is to be replaced by

$$\alpha_{\rm me}=-(K_l/3V)[(K_m/K_l)\gamma_mC_m+\gamma_lC_l]$$
$$=-(\alpha_l/3T\gamma_m\alpha_l)[1-3T\gamma_m\alpha_l],$$

showing that although C_m may be singular, $\alpha_{\rm me}$ is not. However, the situation $C_m\gg C_l$ is far from reached in EuO, because C_m is only slowly increasing function of T for $T\lesssim T_c$, and long before such large values of C_m are reached [an extrapolation of the logarithmic behavior gives $C_m=65C_l$ when $(T_c-T)/T_c=10^{-700}$ °K], the logarithmic singularity is rounded off by finite-size effects.

Callen and Callen[2c] have considered such a model with $J_3=J_4=\cdots=0$. Noting that $|J_2|z_2 \ll J_1 z_1$ for EuO [14] and assuming that $z_2(d|J_2|/dV) \ll z_1(dJ_1/dV)$, they remark that C_m and α_{me} should then be proportional. It is apparent from the above equations for α_{me} and C_m that this proportionality can also occur if only $\partial\langle \mathbf{S}\cdot\mathbf{S}'\rangle_{1st}/\partial T$ and $\partial\langle \mathbf{S}\cdot\mathbf{S}'\rangle_{2nd}/\partial T$ are proportional or if the second quantity is much smaller than the first. In fact, these two temperature derivatives appear, from the results of the Callen and Callen cluster calculations [Fig. 4 of Ref. 2(c)], to be about equal above $\sim T_c/5$. Thus the proportionality of C_m and α_{me} is not in itself an indication of a preference for one model over another.

INTERPRETATION OF EXPERIMENTAL DATA

1. Evaluation of Magnetoelastic Coupling Strength

The slope of $\alpha_{me}(T)$ versus $C_m(T)$ in Fig. 3 is $(0.80\pm0.04)\times10^{-6}$ moles/J. This number includes as the largest systematic error the uncertainty in correcting the lattice contribution to the observed specific heat. The magnetic Grüneisen parameter $\gamma_m \equiv \partial \ln\lambda/\partial \ln V$ is given by Eq. (17), which simplifies to

$$\alpha_{me} = -K_l \gamma_m C_m / 3V \qquad (23)$$

as we have remarked, provided

$$C_m \ll 65 C_l \quad \text{and} \quad 3T\gamma_m\alpha_l \ll 1,$$

both of which hold. Under these assumptions the constancy of the slope in Fig. 3 implies that $\gamma_m K_l$ is independent of T in which case γ_m is also constant, the increase of K_l with increasing temperature being only about 1% for this high-melting-point material (2300°K). For the model in which $\gamma_1 \neq \gamma_2$, Eq. (23) measures an effective γ_m which can also be temperature-independent in the temperature region where the spin correlation functions $\langle \mathbf{S}\cdot\mathbf{S}'\rangle_{1st}$ and $\langle \mathbf{S}\cdot\mathbf{S}'\rangle_{2nd}$ have slopes proportional to one another. We obtain then $\gamma_m=-5.3\pm0.3$ by using the known bulk modulus for EuO ($B_T=1.07\times10^6$ bar),[8] determined at room temperature, to estimate its lattice compressibility ($K_l=B_T^{-1}=0.94\times10^{-6}$ bar^{-1}). Similarly, we find for the *lattice* Grüneisen constant $\gamma_l=1.9$, as determined from Eq. (10) using total-expansivity and specific-heat data at temperatures $T \gtrsim 3T_c$, where magnetic contributions are negligible.

We can now test the consistency of assuming that $3T_c\,|\,\gamma_m\,|\,\alpha_l \ll 1$ and that near $T_{c'}$ $|\,K_l/K_m\,| \simeq \frac{1}{64}(C_m/C_l)$. At T_c, numerical evaluation gives $3T_c\,|\,\gamma_m\,|\,\alpha_l = 3(69)(5)(6\times10^{-6}) \simeq 0.006$. Also near T_c, $|\,K_l/K_m\,| \simeq (0.006)(5.3)(1.9)^{-1} C_m/C_l \simeq \frac{1}{64}(C_m/C_l)$. Our result $\gamma_m=-5.3$ may then be considered an accurate representation of the isotropic magnetoelastic interaction (exchange striction) in EuO. This value contrasts sharply with the value $\gamma_m \simeq -10/3$ which Bloch[15] has pointed out occurs repeatedly in numerous insulating 3d transition-metal compounds that exhibit a superexchange coupling mechanism.

2. Comparison with Pressure Dependence of T_c

Since for this model there is only one independent magnetic energy, which is proportional to $\lambda \equiv J(v)/J(v_0)$, the Curie temperature must also be proportional to λ. In the definition of $\gamma_m \equiv \partial \ln\lambda/\partial \ln V$, we may then replace $\partial \ln\lambda$ by $\partial \ln T_c$. Then using $T_c=69$°K and $K_l=0.94\times10^{-6}$ bar^{-1} we obtain $\partial T_c/\partial p = 0.34\pm0.02$ deg/kbar. This result appears to be consistent with the values 0.46 ± 0.10,[6,16] 0.40 ± 0.10,[7] and 0.37 ± 0.10[8] deg/kbar observed directly by various investigators for *polycrystalline* EuO from measurements of the pressure induced shift in the susceptibility anomaly at T_c.

3. Evaluation of Magnetic Internal Energy

The internal magnetic energy at 0°K, which is usually determined from the area under the specific-heat anomaly

$$U_m = \int_{T\gg T_c}^{T=0} C_m dT,$$

can alternatively be estimated from the area under the expansion anomaly

$$\delta(0) = \int_{T\gg T_c}^{T=0} 3\alpha_{me}(T)\, dT.$$

The accuracy of this estimation is limited only by the accuracy of the experimental determination of α_{me} and the validity of proportionality between α_{me} and C_m. The validity of the proportionality relations will be at least as uncertain as the determination of C_m, however accurately one determines α_{me}. Nevertheless, a point-by-point determination of α_{me} to find $\delta(0)$ may be simpler than the less detailed measurement of C_m needed to confirm proportionality with reasonable probability.

Thus, according to Eq. (23),

$$U_m(0) = -\delta(0)\, V/K_l\gamma_m.$$

To evaluate $\delta(0)$ we need α_{me} for all temperatures above 0°K. At extremely low temperatures we have extrapolated C_m using a $T^{3/2}$ law derived from spin waves and have assumed the proportionality of α_{me}

[14] T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, J. Appl. Phys. **34**, 1345 (1962).

[15] D. Bloch, J. Phys. Chem. Solids **27**, 881 (1966).

[16] The pressure experiment of Stevenson and Robinson (Ref. 6) provides a value for $\partial \ln T_c/\partial \ln V = -1.7$ which is smaller than is given here by us and by others (Refs. 7, 8). This seems to be connected with their using a compressibility ($K=2.6\times10^{-12}$ dyn/cm^2) that is too small. D. E. Eastman, of this laboratory, essentially verifies the bulk modulus ($B=1.07\times10^{12}$ dyn^{-1} cm^2 $=K^{-1}$ obtained by McWhan *et al.* (Ref. 8). From preliminary measurements of ultrasonic velocity he obtains $c_{11}=17\times10^{11}$, $c_{44}=5.2\times10^{11}$ (cgs) and notes that McWhan's result for B_T gives a reasonable value 7.5×10^{11} for c_{12} by using $B_T \equiv (c_{11}+2c_{12})/3$.

and C_m. We find that $\delta(0)=-0.24\%$, from which the resulting magnetic energy is

$$U_m(0)=-(4.9\pm0.25)\times10^{18}\ \text{erg/cm}^3$$
$$=-1000\pm50\ \text{J/mole}.$$

This is to be compared with the determination of $U_m(0)$ directly from C_m, of

$$U_m(0)=-930\pm50\ \text{J/mole}$$

by Teaney *et al.*,[4] where the given uncertainty is suggested by the internal consistency of their analysis based on the Heisenberg model with localized moments ($S=7/2$) and magnetic entropy $R\ln(2S+1)$. Their procedure of subtracting lattice specific heat uses spin-wave theory at low temperatures and a corresponding-states comparison with data for EuS ($T_c=16.5$°K) at high temperatures.

One may also compare our results with the value

$$U_m(0)=-860\ \text{J/mole}$$

calculated from the exchange coefficients $J_{12}/k_B=0.75$°K and $J_{13}/J_{12}=-0.13$ determined from spin-wave analysis of low-temperature NMR data.[17]

4. Variation of Magnetic Energy with Temperature

From a fundamental standpoint, magnetic energy is obtained from the magnetic specific heat. However, the observed proportionality between $\alpha_{\rm me}$ and C_m in EuO offers the opportunity for an indepenent determination of the variation of $U_m(T)$ with temperature. From the magnetic lattice strain given by the area under the thermal expansivity anomaly, we have simply

$$U_m(T)/U_m(0)=\int_T^\infty \alpha_{\rm me}(T)\,dT \Big/ \int_0^\infty \alpha_{\rm me}(T)\,dT, \quad (24)$$

which is plotted in Fig. 4. This result may be compared with quantum-statistical calculations. Callen and Callen[18] have calculated the scalar correlation function $\langle \mathbf{S}\cdot\mathbf{S}'\rangle/S^2$ from a two-particle cluster theory using various assumed values for $|J_{13}/J_{12}|$. Their results given in Fig. 4 for the case of vanishing second-neighbor interactions are in only qualitative agreement with $U_m(T)/U_m(0)$ obtained from magnetostrain. Ten percent or so of a second-neighbor interaction term in their calculations produces a negligible effect in comparison with the difference shown.

While the Callens' calculation of $\langle \mathbf{S}\cdot\mathbf{S}'\rangle/S^2$ is based on the assumption of a rigid lattice, the observed $U_m(T)/U_m(0)$ may include contributions from the temperature dependence of J which results from thermal strain. We may investigate this question using the total thermal expansivity α_t and using the relation

$$\ln J(T)-\ln J(0)=\int_0^\delta \frac{\partial \ln J}{\partial\delta}\,d\delta \simeq \gamma_m \int_0^T 3\alpha_{\rm me}dT.$$

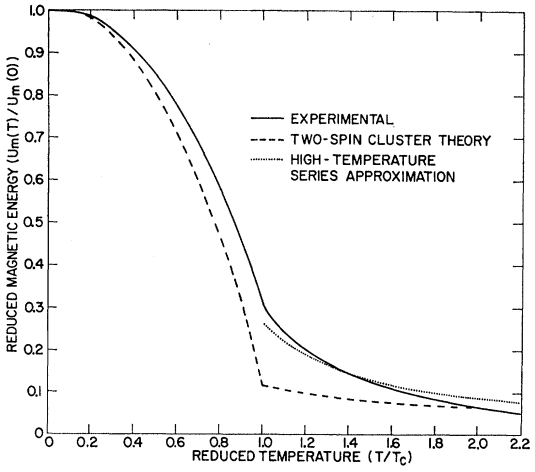

FIG. 4. Solid curve: reduced isotropic magnetic energy versus temperature, estimated from magnetoelastic thermal expansivity. See text. Dashed curve: theoretical calculation of Callen and Callen (Ref. 18) using two-spin cluster approximation and $S=7/2$ with only nearest-neighbor coupling. Dashed curve: theoretical result from high-temperature series approximation of Rushbrooke and Wood calculated (by M. J. Freiser) using $S=7/2$, $J_1/k=0.75$°K, and $J_2=0$.

The observation that $K_t\gamma_m$ is constant, as given by Fig. 3 and Eq. (23), does not mean of course that γ_m is constant. However, the lattice contribution to $\partial K_t/\partial T$ is estimated to be negligible by use of the Wachtman equation[19] giving the temperature variation of B_T for a Mie-Grüneisen force potential.[20] The magneto-elastic contribution to $\partial K/\partial T$ is also small even near T_c as may be estimated using Eqs. (6b) and (16). One finds $(K_t-K_l)/K_t\simeq C_m/65C_t\simeq0.015$. Thus, γ_m can be considered a constant, at least to the accuracy of determining magnetic specific heat and expansivity. The variation of $J(T)$ estimated from the total thermal strain and $\gamma_m=-5.3$ in the above equation is given in Table I. These changes in J caused by thermal expansion are too small and in the wrong sense to explain the discrepancy between the observed $U_m(T)/U_m(0)$ and the two-particle cluster theory.

Using the high-temperature expansion theory of Rushbrook and Wood,[21] Freiser[22] has calculated the nearest-neighbor correlation for a face-centered cubic lattice of spins with $S=7/2$ and nearest-neighbor coupling only. Our experimental results compare more favorably with this theory (see Fig. 4). The differences between theory and experiment near $T/T_c\simeq1.2$ are probably insignificant in relation to our experimental accuracy.

[17] E. L. Boyd, Phys. Rev. **145**, 174 (1966).
[18] H. B. Callen and E. Callen, Phys. Rev. **136**, A1675 (1964).
[19] See, O. L. Anderson, Phys. Rev. **144**, 553 (1966).
[20] A value $\partial K/\partial T\simeq10^{-11}$ bar^{-1} deg^{-1} has been reported by Sokolova *et al.* (Ref. 7), who measured $K(300°\text{K})-K(77°\text{K}\cong 10^{-3}K(300°\text{K})$ for EuO powder by the piston-displacement method.
[21] G. S. Rushbrooke and P. J. Wood, Mol. Phys. **1**, 257 (1958).
[22] M. J. Freiser (private communication).

TABLE I. Variation of exchange coupling constant J with temperature in EuO as estimated from total thermal volume strain

$$\delta \equiv \int_0^T 3\alpha dT$$

and the magnetic Grüneisen parameter $\gamma_m \equiv \partial \ln J/\partial \ln V = -5.3$. See text.

T (°K)	$\int_0^T 3\alpha dT$	$[J(T)-J(0)]/J(0)$ (%)
30	2.7×10^{-4}	−0.14
40	5.5	−0.29
50	9.3	−0.49
60	14.4	−0.76
70	20.8	−1.10
80	24.6	−1.30
90	27.9	−1.47
100	31.2	−1.65
120	37.9	−2.00
140	44.8	−2.37
170	55.4	−2.94
210	71.0	−3.76
240	85.4	−4.53
273	95.8	−5.08
300	106.6	−5.65

SUMMARY

While it is often pointed out that there exists a similarity between the shapes of the magnetic part of the thermal expansivity $\alpha_{me}(T)$ and specific-heat anomaly $C_m(T)$ exhibited by a ferromagnet, this paper presents the first experimental study of these quantities in EuO, for which the magnetic Hamiltonian is especially well defined (predominantly isotropic nearest-neighbor exchange) and amenable to quantum-statistical calculations. It was observed that α_{me} is proportional to C_m over a wide temperature range (at least $25<T<150$°K as limited by the experiment) according to $\alpha_{me}/C_m = (0.80\pm0.04)\ 10^{-6}$ moles/J. This gives the constant value $d\ln U_m/dP = +4.9\times10^{-6}$ bar^{-1} for the pressure derivative of the isotropic magnetic energy. This result, in conjunction with the known compressibility, establishes a value for the magnetic Grüneisen parameter $d\ln U_m/d\ln V = -5.3\pm0.3$, which contrasts sharply with the value $-10/3$ for numerous $3d$-metal compounds. Assuming U_m is proportional to the Curie temperature, the pressure derivative $dT_c/dP = 0.34\pm 0.02$ deg/kbar was obtained which is in reasonable agreement with various results (0.46,[6] 0.40[7], and 0.37[8] all within ±0.1) determined directly by pressure experiments. Assuming U_m is proportional to an effective exchange parameter of magnitude $J\leftrightarrow J_{12} = 0.75k_B$°K derived from spin-wave analysis of NMR data,[17] we find $dJ/da_0 = -2.3k_B$°K/Å which is about three times larger than has been obtained from comparison of paramagnetic Curie temperatures with lattice constants a_0 in the europium-chalcogenide series (EuO, EuS, EuSe, EuTe).[14]

From the magnetic "volume anomaly" at 0°K (area under the $3\alpha_{me}$-versus-T curve), we have obtained the zero-temperature internal magnetic energy $U_m(0) = -1000$ J/mole. This fundamental quantity was compared with the results of two other experiments: $U_m(0) = -930$ J/mole (from specific heat[4]) and $U_m(0) = -860$ J/mole (from spin-wave analysis of NMR data[17]).

The temperature variation of the reduced magnetic energy $U_m(T)/U_m(0)$ was estimated from the reduced spontaneous magnetostrain

$$\int_T^\infty \alpha_{me} dT \Big/ \int_0^\infty \alpha_{me} dT.$$

This variation of magnetic energy may be compared with theoretical predictions for the nearest-neighbor correlation function $\langle \mathbf{S}_l \cdot \mathbf{S}_{l'} \rangle / S^2$. The resulting behavior is qualitatively similar to Callen and Callen's calculations[2c] based on the two-particle cluster approximation,[18] but for $T > T_c$ it is more adequately explained by the high-temperature series approximation of Rushbrook and Wood.[21,22]

ACKNOWLEDGMENTS

We are pleased to acknowledge helpful discussions with M. Freiser, R. Joenk, and S. Methfessel. We are particularly indebted to C. F. Guerci for growing the suitably large and good quality single crystal of EuO.