quency is directly proportional to the change in activation energy. Let us represent the NH_4^+ torsional oscillator as a harmonic oscillator for which the entropy is[12]

$$S=R\{x/(e^x-1)-\ln(1-e^{-x})\}, \qquad (1)$$

where $x=h\nu/kT$ and ν is the frequency separation between levels. For NH_4^+ ion reorientations $x\approx1$ at T_c and hence $\Delta S\approx0.2$ cal °K^{-1} mole^{-1}, in close agreement with the observed anomalous entropy of ADP.

The relatively large splittings in the deuteron resonance of the antiferroelectric phase of ADP probably is associated with the greater crystal distortions in ADP as compared to KDP. As pointed out by Nagamiya,[2] the transition in ADP may be explained by a reversal in the ordering in energy of the Slater configurations of protons on a PO_4 tetrahedron. This effect appears to be due almost exclusively to the ammonium ions since substitution of Tl^+ for NH_4^+ in ADP alters the transition temperature and above 33% of Tl results in normal dielectric behavior.[13] As indicated clearly by the electron-resonance results, the proton dynamics do not change greatly from KDP and the entire difference between the dielectric behavior of KDP and ADP may be ascribed to the reversal of Slater energies of proton configurations about the phosphate tetrahedra.

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[12] S. Glasstone, *Theoretical Chemistry* (D. Van Nostrand Co., Inc., New York), p. 381.

[13] W. Merz, Helv. Phys. Acta **10**, 273 (1947).

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Metamagnetism in Eu_3O_4

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The magnetic properties of the metamagnet Eu_3O_4 are analyzed using molecular-field theory. For the antiferromagnetic ground state, it is assumed that linear, ferromagnetic chains of spins (Eu^{2+}) are polarized along the c axis of the orthorhombic unit cell, with neighboring chains antiparallel. The weakly magnetic ions Eu^{3+} provide an apparently inert magnetic background. Exchange constants are deduced from the paramagnetic Curie temperature $\theta_p=5$°K and the critical field $H_c=2.4$ kOe. The constants for first- and second-neighbor Eu^{2+} interactions are $J_1/k\sim0.3$°K and $J_2/k\sim-0.02$°K, respectively. An anisotropy field of 7 kOe is derived from the transverse magnetic susceptibility at low temperatures. This value is also obtained from a magnetic dipolar sum. Theoretical estimates of the ordering temperature give $T_c\sim5$°K, as observed.

I. INTRODUCTION

METAMAGNETIC behavior has been observed in Eu_3O_4 at liquid-helium temperatures.[1] The magnetic ordering has been interpreted,[1] tentatively, with a simple, "linear-chains" model for the magnetic structure. In this paper, the model will be treated in more detail. It will be shown to provide a satisfactory description of the experimental parameters, T_N, θ_p, H_c, and H_A (Néel point, paramagnetic Curie point, critical field, and anisotropy field, respectively). The influence of trivalent europium on the magnetic properties of this oxide will be carefully considered.

This study of metamagnetism in Eu_3O_4 provides new information on interactions in magnetic compounds of the form AB_2O_4. It will be shown that the exchange interactions are predominantly ferromagnetic in Eu_3O_4, despite the antiferromagnetic ground state. Useful comparisons are made with the properties of the isomorphous oxides,[2] $SrGd_2O_4$ and $SrEu_2O_4$, and chalcogenides,[3] EuL_2X_4, with $L=$ Lu, Y, Sc and $X=$ S, Se.

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‡ Supported by the U.S. Air Force Office of Scientific Research.

[1] L. Holmes and M. Schieber, J. Appl. Phys. **37**, 968 (1966).

[2] M. Schieber, R. G. Gordon, and S. L. Hou, in *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and the Physical Society, London, 1965), p. 499.

[3] F. Hullinger and O. Vogt, Phys. Letters **21**, 138 (1966).

TABLE I. Studies of magnetic ordering in Eu_3O_4.

Measurement	Form of sample	Applied magnetic field (kOe)	Ordering temp (°K)	Proposed magnetic structure	Ref.
Magnetization	Powder	15.2–19.3	7.8	None stated[a]	b
Magnetization	Powder	10.3	77	Ferrimagnetic	c
Magnetization	Crystal chips	0–8	5	Metamagnetic ($H_c \leq 2.4$ kOe)	d
Mössbauer (Eu^{2+})	Powder	0	6.2±0.3	···	e

[a] Procedures appropriate to a ferro- or ferrimagnet were used to process the data.
[b] See Ref 5.
[c] See Ref 6.
[d] See Ref. 1.
[e] See Ref. 7.

II. CRYSTAL STRUCTURE AND MAGNETIC PROPERTIES

Orthorhombic Eu_3O_4 (Fig. 1) is isomorphous with calcium ferrite ($CaFe_2O_4$), space group *Pnam*, with the ions Eu^{2+} and Eu^{3+} occupying the sites of calcium and iron, respectively, in that structure.[4] The divalent ions are at the positions

$$x, y, \tfrac{1}{4};\quad \bar{x}, \bar{y}, \tfrac{3}{4};\quad \tfrac{1}{2}-x, \tfrac{1}{2}-y, \tfrac{3}{4};\quad \tfrac{1}{2}+x, \tfrac{1}{2}+y, \tfrac{1}{4},$$

with $x=0.2481$ and $y=0.3525$.[4] The divalent ions form "chains" parallel to the c axis, with a spacing of 3.5 Å between ions on a chain, and with neighboring chains separated by 5.6 Å.

The magnetic behavior of Eu_3O_4 has been studied in several laboratories.[1,5–7] Some of the results (Table I) are apparently contradictory. A critical discussion of the experiments is therefore given in Appendix A. For the purposes of this paper, the magnetic properties of Eu_3O_4 may be summarized as follows:

(*i*). *Ordered regime.* The compound Eu_3O_4 is antiferromagnetic below $T_N \sim 5$ or 6°K with a low field metamagnetic transition (Fig. 2). The limiting value of the critical field along the c axis at low temperatures, corrected to zero demagnetizing field, is given by $H_c = 2.4$ kOe.[1]

(*ii*). *Paramagnetic regime.* The inverse paramagnetic susceptibility, plotted against temperature (Fig. 3), shows a positive Curie-Weiss intercept. By subtracting off the contributions of the ions Eu^{3+}, as measured[2] in the isomorphous compound $SrEu_2O_4$, the susceptibility above 20°K can be reproduced with a Currie-Weiss law of the form $C/(T-\theta_p)$, where $\theta_p = 5$°K, and where the constant C is given by the value for the free-ion Eu^{2+} to within 1%.

III. THE MODEL

The observation of a positive Curie-Weiss intercept (Fig. 3) for Eu_3O_4 shows that the interactions in this compound are predominantly ferromagnetic. It is shown in the following sections that the magnetic properties at low temperatures are determined almost exclusively by the strongly magnetic ions Eu^{2+} (ground state ${}^8S$ as compound to ${}^7F_0$ for Eu^{3+}). It is reasonable to assume that the strongest interactions (ferromagnetic) couple nearest neighbors of Eu^{2+}, and that weaker interactions (antiferromagnetic) couple more distant neighbors to give, over all, an antiferromagnetic ground state. A model consistent with this picture is used in this paper. In this model, neighboring ferromagnetic chains interact weakly to give an antiferromagnetic ground state, as indicated in Fig. 1(b). The high-field metamagnetic state is produced by reversing half of the chains to

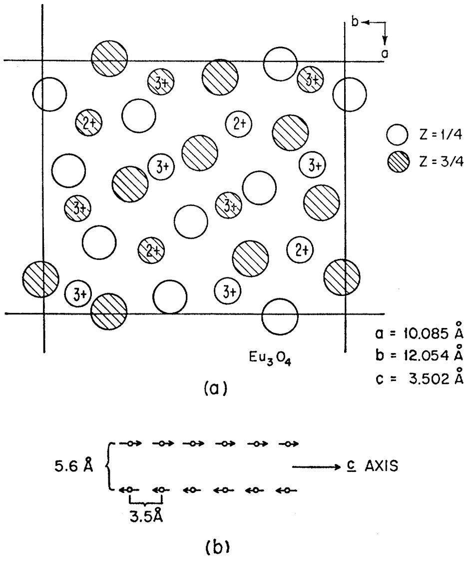

FIG. 1. (a) Unit cell of Eu_3O_4 [after Rau (Ref. 4)]. Large circles, oxygen; small circles, divalent and trivalent europium. (b) Neighboring chains of Eu^{2+}. Arrows show proposed magnetic structure (see text).

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[4] R. C. Rau, Acta Cryst. **20**, 716 (1966).
[5] A. A. Samokhralov, V. G. Bamburov, N. V. Volkenshteyn, T. D. Zotov, A. A. Ivakin, Yu. N. Morozov, and M. I. Simonova, Fiz. Metal. i Metalloved. (USSR) 20, 308 (1965). [English transl.: Phys. Metals Metallog. **20**, 138 (1965)].
[6] F. F. Y. Wang, Phys. Status Solidi **14**, 189 (1966).
[7] H. Wickman (private communication).

bring all of the spins into alignment with the field. The critical field is low, because only the relatively weak, interchain interactions are affected by the metamagnetic transition.

The four ions of divalent europium in the unit cell (Fig. 1) lie on two pairs of chains which intersect the unit cell at $z=\frac{1}{4}$ and $z=\frac{3}{4}$, respectively. The model to be used in this paper has the "same" arrangement of spins on both pairs of chains, i.e., spin "up" at x, y, $\frac{1}{4}$ and $\frac{1}{2}-x$, $\frac{1}{2}-y$, $\frac{3}{4}$ and spin "down" at $\bar{x}$, $\bar{y}$, $\frac{3}{4}$ and $\frac{1}{2}+x$, $\frac{1}{2}+y$, $\frac{1}{4}$ or vice versa. This arrangement (space group *Pn′am*) has a slightly lower magnetic dipolar energy than the alternative arrangement (space group *Pnam*) in which, say, both of the spins at $z=\frac{1}{4}$ are reversed. Choosing the latter arrangement would have no qualitative influence on the analysis in Sec. IV, and, quantitatively, would only slightly change the value obtained for one of the constants (viz., J_2/k).

IV. THEORY AND INTERPRETATION

In this section expressions for θ_p, H_c, and H_A are derived from molecular field theory and applied to Eu_3O_4. Values are obtained for the exchange coupling nearest and next-nearest neighbors of divalent europium. Simple calculations of the ordering temperature are given to show that the exchange constants are consistent with the observed Néel point. Some of the details of the theory are relegated to the Appendices.

A. Paramagnetic Curie Temperature

For a system of identical spins S at temperatures $T \gg T_N$, the magnetic susceptibility takes the form $\chi = C/(T-\theta_p)$, with

$$\theta_p = \tfrac{2}{3}S(S+1)\sum_m Z_m(J_m/k). \qquad (1)$$

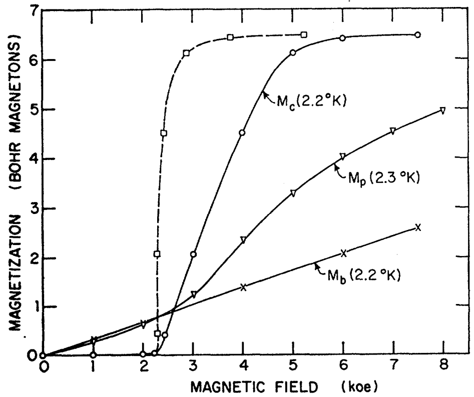

FIG. 2. Magnetization curves for Eu_3O_4. Curve M_p is for a powder sample, M_b and M_c are for the b and c axes of a single crystal fragment. Dashed curve shows M_c corrected for assumed demagnetizing field ($1.27\ \pi M_c$).

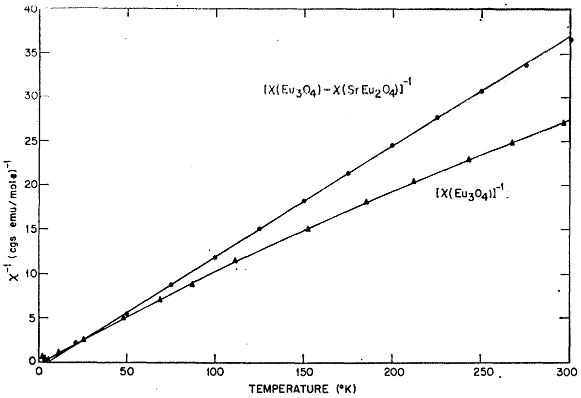

FIG. 3. Powder susceptibilities. Observed values have been plotted after correction for Lorentz and demagnetizing fields (net effect less than 1% above 50°K).

Here Z_m is the number of mth nearest neighbors, and J_m is the exchange coupling with mth neighbors.[8] Equation (1) is not directly applicable to the compound Eu_3O_4, because two distinct magnetic ions are present. However, it can be shown (Appendix B) that at high temperatures

$$\chi(Eu_3O_4) - \chi(SrEu_2O_4) = C(Eu^{2+})/[T-\theta(T)], \qquad (2)$$

with

$$\theta(T) = \theta_2[1+Tf(T)/\theta_2]. \qquad (3)$$

The temperature $\theta_2 = \lambda_2 C(Eu^{2+})$ is proportional to the interactions among the divalent ions Eu^{2+}, as given by the Weiss constant λ_2. The function $f(T)$ is given in Eq. (B-12) and is proportional to the Weiss constant λ_{23} coupling the spins of the ions Eu^{2+} with the spins of the ions Eu^{3+}. With coupling $\lambda_{23} \sim \lambda_2$, the result (3) would predict a variation in the intercept θ of $+40\%$ or -180% for λ_{23}/λ_2 positive or negative, respectively, in going from 100 to 300°K. No clear temperature dependence in θ can be seen in Fig. 3, although there is some scatter in the data. As a first approximation, therefore, it may be assumed that the net interactions coupling ions Eu^{2+} to ions Eu^{3+} are relatively weaker than the interactions among the divalent ions, and that the intercept $\theta_p = 5$°K represents, through Eq. (1), a reasonable measure of the exchange interactions among the divalent ions. It may be noted that the magnetic dipolar interactions would not influence θ_p to first order in the susceptibility, since they average to zero for an isotropic sample of powder.[9]

B. Critical Field

An expression for the critical field H_c is obtained by equating the exchange and magnetic dipolar energies

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[8] J. S. Smart, *Effective Field Theories of Magnetism* (W. B. Saunders Co., Philadelphia, Pa., 1966).

[9] J. H. Van Vleck, J. Chem. Phys. **5**, 320 (1937), especially pp. 326–7.

lost with the Zeeman energy gained in the metamagnetic transition. The result (Appendix C), for a sample with negligible demagnetizing fields, is

$$H_c=\tfrac{1}{2}[\Delta h_0^{\text{dip}}-\tfrac{4}{3}\pi N\mu_s+\Delta h^{\text{exch}}], \qquad (4)$$

where $\Delta h_0^{\text{dip}}-\frac{4}{3}\pi N\mu_s$ and Δh^{exch} are the decrease in magnetic dipolar field and effective exchange field, respectively, on a given spin in going from the antiferromagnetic configuration to the final state. These fields can be calculated on the assumption that each ion Eu^{2+} ($g=2$, $S=\frac{7}{2}$) carries a moment $\mu_s=7\mu_B$. A lattice summation to calculate Δh_0^{dip} has been extended with a computer to a radius $R_0=100$ Å, at which point the change in Δh_0^{dip} produced by a 10% change in R_0 was found to be less than 0.5%. The calculated values, $\Delta h_0^{\text{dip}}=2.58$ kOe and $\frac{4}{3}\pi N\mu_s=2.55$ kOe, combine to give

$$\Delta h_0^{\text{dip}}-\tfrac{4}{3}\pi N\mu_s=0.03 \text{ kOe}. \qquad (5)$$

C. Exchange Constants

As a first approximation, two exchange constants have been included in the theory. The constant J_1 couples nearest neighbors Eu^{2+} (separated by 3.5 Å on a given chain), and the constant J_2 couples next-nearest neighbors Eu^{2+} (separated by 5.6 Å and on adjacent chains). For the configuration of spins in Fig. 1(b), the change in effective exchange field, Δh^{exch}, in Eq. (4) is related to the constant J_2 by the equation

$$\Delta h^{\text{exch}}=-14J_2/\mu_B. \qquad (6)$$

Substituting the experimental results, $\theta_p=5°\text{K}$ and $H_c=2.4$ kOe, in Eqs. (1) and (4), and solving for J_1 and J_2 gives

$$J_2/k=-0.023°\text{K}, \qquad (7)$$

$$J_1/k=0.26°\text{K}\sim 0.3°\text{K}. \qquad (8)$$

The inaccuracies inherent in extrapolating the differences between two independent measurements (Fig. 3) to obtain the intercept θ_p do not justify greater than one-place accuracy in the result (8). In view of the difficulties in interpreting the magnetic data, it is reassuring that the ferromagnetic constant J_1/k found here [Eq. (8)] is of the order of magnitude of the constant $J_1/k=0.75°\text{K}$ in the compound EuO (separation 3.6 Å between ions Eu^{2+}).[10]

D. Anisotropy

The anisotropy field may be estimated from the transverse susceptibility at low temperatures. The magnetizations, M_a and M_b, are $\sim 2\times 10^3$ cgs emu/mole at low temperatures and in an applied field of 1 kOe.[1] With demagnetizing factors $\sim 2\pi$, these magnetizations correspond to a susceptibility

$$\chi_\perp \sim 2.5 \text{ cgs emu/mole}. \qquad (9)$$

An expression for the transverse susceptibility $\chi_\perp$ may be obtained from molecular field theory for a Néel antiferromagnet with two sublattices. If λ_{AB} is the Weiss constant coupling the sublattices, H_A the anisotropy field, and M_s the saturation magnetization per sublattice, then

$$\chi_\perp=M_S/(\lambda_{AB}M_S+H_A). \qquad (10)$$

Taking a saturation magnetization corresponding to $7\mu_B$ per atom, and taking $\lambda_{AB}M_S=H_c\simeq 2.4$ kOe, the value

$$H_A\simeq 7 \text{ kOe} \qquad (11)$$

is obtained from Eqs. (9) and (10).

In principle, the anisotropy can arise from four sources: (a) crystalline fields on the ions Eu^{2+}, (b) magnetic dipolar interactions, (c) anisotropic exchange, (d) exchange interactions between the ions Eu^{2+} and Eu^{3+}, with spin-orbit coupling from trivalent europium to the lattice. The crystalline fields are expected to have only a small effect on divalent europium, since it is an S-state ion.

The contributions to the anisotropy field from magnetic dipolar interactions may be evaluated from sums over the lattice. As a first approximation, the dipolar interactions between chains of ions Eu^{2+} may be neglected [cf. Eq. (5)]. For a single, long chain of spins the dipolar interactions give rise to an anisotropy field.

$$H_A^{\text{dip}}=\tfrac{3}{4}h_{\parallel}^{\text{dip}}, \qquad (12)$$

where $h_{\parallel}^{\text{dip}}$ is the dipolar field on a given spin when all of the other spins lie parallel to the axis of the chain (Appendix D). For the ions Eu^{2+}, with magnetic moment $7\mu_B$ at saturation in the compound Eu_3O_4, $H_A^{\text{dip}}\sim 7$ kOe. Thus, the magnetic dipolar interactions are sufficiently large to explain the observed anisotropy, without having to invoke anisotropic exchange or coupling to trivalent europium.

E. Ordering Temperature

The ordering temperature of an antiferromagnet may be calculated, using the theory of molecular fields,[8] from an appropriate equation of self-consistency. Consider an antiferromagnet consisting of n identical sublattices of spins S. The magnetization of the ith sublattice may be written

$$M_i=\chi_i(T)\,(H+\sum_j \lambda_{ij}M_j), \qquad (13)$$

where $\chi_i(T)$ is an approximation to the magnetic susceptibility of the sublattice, obtained by ignoring the interactions included in the Weiss field $\sum_j\lambda_{ij}M_j$.

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[10] E. L. Boyd, Phys. Rev. **145**, 174 (1966).

TABLE II. Approximations to the ordering temperature in Eu_3O_4. Observed $T_N \sim 5°K$.

Approximation	$\chi_i(T)$	Equation of self-consistency	T_c (°K)
A. Standard molecular field	$(N\mu_B^2/3k)\{g^2S(S+1)/T\}$	$1=(\lambda^{\text{near}}+\lambda^{\text{far}})\chi_i(T_c)$	7.4
B. Weakly interacting Ising chains (derived for spin $\frac{1}{2}$)[a]	$(N\mu_B^2/3k)\{[g^2S(S+1)/T]\exp[4JS(S+1)/3kT]\}$	$1=\lambda^{\text{far}}\chi_i(T_c)$	5.6
C. Weakly interacting Heisenberg chains (classical limit)[b]	$(N\mu_B^2/3k)\{[g^2S(S+1)/T]\times[1+U(k)/1-U(k)]\}$	$1=\lambda^{\text{far}}\chi_i(T_c)$	3.5
	with $U(K)=\coth K-K^{-1}$ and $K=2JS(S+1)/kT$		

[a] After Stout and Chisholm (Ref. 12). [b] After Fisher (Ref. 14).

In the antiferromagnetic state, the magnetizations of sublattices i and j are either parallel or antiparallel:

$$M_i=\epsilon_{ij}M_j, \tag{14}$$

where ϵ_{ij} is plus or minus one for parallel or antiparallel magnetizations, respectively. Combining these relations and setting $H=0$ gives the equation of self-consistency for the ordering temperature T_c;

$$1=\chi_i(T_c)\sum_j \lambda_{ij}\epsilon_{ij}. \tag{15}$$

In the standard molecular-field approximation, the susceptibility $\chi_i(T)$ is set equal to its limit C/T at high temperatures, where $C=N\mu_B^2g^2S(S+1)/3k$. With isotropic interactions, this is known to give too high a value for the ordering temperature for a given set of exchange constants.[8] One would expect to obtain a more reliable result from Eq. (15) if the dominant interactions could be included explicitly in the susceptibility $\chi_i(T)$, and only the weaker interactions included as molecular fields. Two approximations of this sort have been carried out for weakly interacting, linear chains. The first, by Sato[11] and, independently, by Stout and Chisholm,[12] is based on the Ising model for spin $\frac{1}{2}$, which includes only the z component of the exchange coupling neighboring spins on a chain. A discrepancy of a factor of 2 between Sato's result and that of Stout and Chisholm is easily resolved by taking care to include only once the interactions between chains in the approach of Sato.[13] The second approximation is based on the magnetic susceptibility of a linear chain with isotropic exchange between neighboring spins. The susceptibility $\chi_i(T)$ was calculated for this case by Fisher[14] in the classical limit ("infinite" spin).

The ordering temperature for the compound Eu_3O_4 has been calculated (Table II) for each of the approximations described above. The magnetic structure of Fig. 1(b) has been used as a model, and the influence of trivalent europium ignored. One would expect the trivalent europium to have a relatively slight effect on the ordering temperature because of the second-order nature of the polarization of the spins in the ground state $^7F_0$ (see Sec. V).

In carrying out the calculations in Table II, the interactions have been divided into "near" interactions (between nearest neighbors) and "far" interactions (between all other neighbors) in the antiferromagnetic state. In approximations (B) and (C), the "near" interactions have been included explicitly in the susceptibilities $\chi_i(T)$. As a rough approximation, the magnetic dipolar effects have been included in the Weiss constants;

$$\lambda=\lambda_{\text{exch}}+\lambda_{\text{dip}}. \tag{16}$$

The contributions from dipolar and exchange interactions have been evaluated from the constants J_1 and J_2 above, and from the sums of dipolar fields over the lattice;

$$\lambda_{\text{exch}}^{\text{near}}=1.0k/Ng^2\mu_B^2, \qquad \lambda_{\text{dip}}^{\text{near}}=0.23k/Ng^2\mu_B^2, \tag{17}$$

$$\lambda_{\text{exch}}^{\text{far}}=0.094k/Ng^2\mu_B^2, \qquad \lambda_{\text{dip}}^{\text{far}}=0.047k/Ng^2\mu_B^2. \tag{18}$$

The interactions between nearest neighbors have been incorporated into the constant J in approximations (B) and (C), Table II, by setting $4J/Ng^2\mu_B^2$ equal to λ^{near}.

The susceptibilities $\chi_i(T)$ for the Ising and Heisenberg chains, Table II, are valid only for $S=\frac{1}{2}$ and for the classical limit, respectively. When written as in Table II, the expressions do give the correct limit $C/(T-\theta_p)$ for spins S at high temperatures, with $\theta_p=4JS(S+1)/3k$, as may be readily verified.

The ordering temperatures in Table II range from 3.5 to 7.4°K and are of the order of magnitude of the observed Néel temperature, $T_N \sim 5°K$.

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[11] H. Sato, J. Phys. Chem. Solids **19**, 54 (1961).

[12] J. W. Stout and R. C. Chisholm, J. Chem. Phys. **36**, 979 (1962).

[13] For details see L. Holmes, thesis, Harvard University, 1966 (unpublished).

[14] M. E. Fisher, Am. J. Phys. **32**, 343 (1964).

V. DISCUSSION

In interpreting the data for Eu_3O_4, the ions Eu^{3+} have been ignored, except at high temperatures, where $\chi(Eu^{3+}) \sim \chi(Eu^{2+})$. The approximation of neglecting the influence of trivalent europium is based on the second-order nature of the polarization of the spin in this ion at low temperatures. For equivalent coupling J between the pairs of ions Eu^{2+}–Eu^{3+} and Eu^{2+}–Eu^{2+}, the energies of interaction are related by

$$\Delta e(Eu^{2+}\text{–}Eu^{3+}) \sim (J/E_{10})\,\Delta e(Eu^{2+}\text{–}Eu^{2+}), \quad (19)$$

where E_{10} is the separation ($\sim$330 cm^{-1}) between the levels $^7F_0$ and $^7F_1$ of the ion Eu^{3+}, and Δe is the depression of the ground state, per ion, as a result of exchange. For $J \sim 0.1$ cm^{-1} [Eq. (8)], the interaction $\Delta e(Eu^{2+}\text{–}Eu^{3+}) \sim 10^{-2}\ \Delta e(Eu^{2+}\text{–}Eu^{2+})$, and $\Delta e(Eu^{2+}\text{–}Eu^{3+})$ may be neglected as a first approximation.

The validity of this approximation for Eu_3O_4 is confirmed by the very similar magnetic behavior[3] of divalent europium in isomorphous chalcogenides EuL_2X_4, with $L=$ Lu, Y, Sc (diamagnetic ions) and $X=$ S, Se. In liquid helium, these compounds are ferromagnetic, for $L=$ Y, or metamagnetic, for $L=$ Lu and Sc. The Curie-Weiss intercepts are all positive, and range from 4°K, for $EuLu_2Se_4$ and EuY_2Se_4, to 8°K, for $EuSc_2S_4$, as compared to 5°K for Eu_3O_4.

The positive Curie-Weiss intercepts for the chalcogenides EuL_2X_4 show that in these compounds, as in Eu_3O_4, the ions Eu^{2+} are coupled by ferromagnetic exchange. Similar ferromagnetic coupling was observed previously in the series of compounds EuO, EuS, EuSe, and EuTe.[15,16] Detailed studies of this new series of compounds may lead to an improved understanding of the exchange mechanism for divalent europium. The mechanism is not thoroughly understood, and has been a subject of considerable interest in recent years.[17]

The magnetic behavior of the compound Eu_3O_4 may also be compared to that of the isomorphous oxide $SrGd_2O_4$. Here the weakly magnetic ions Eu^{3+} have been replaced by the strongly magnetic ions Gd^{3+} (isoelectronic with ions Eu^{2+}) and the strongly magnetic ions Eu^{2+} by nonmagnetic ions Sr^{2+}. The magnetic susceptibility of this compound has a broad peak at 2.8°K which has been ascribed to antiferromagnetic ordering.[2] A sample of powder showed no evidence, however, of metamagnetism in fields of up to 8 kOe.[1] The dimensions of the unit cell are about the same as those for Eu_3O_4,[2] while the ionic radius of trivalent gadolinium is somewhat smaller than that of divalent europium. The paramagnetic Curie temperature is -6°K,[2] which shows that the interactions are predominantly antiferromagnetic. There may be strong contributions from coupling of the closely space ions Gd^{3+} within a unit cell, as has been found for the ions Fe^{3+} in the isomorphous compound $CaFe_2O_4$.[18] In any case, it is clear than relatively strong antiferromagnetic interactions would have to be overcome in any metamagnetic transition.

The apparent inertness of the trivalent europium in the compound Eu_3O_4 contrasts to the situation in europium iron garnet ($Eu_3Fe_5O_{12}$). In the latter compound, the ordering temperature is virtually unchanged when nonmagnetic yttrium is substituted for europium,[19] showing that here, too, the ions Eu^{3+} have only a slight influence on the ordering temperature. However, the anisotropy field in yttrium iron garnet (YIG) is increased from <0.1 kOe to 5 kOe with the substitution of europium for yttrium,[20] whereas the calculations of Sec. IV D showed that the anisotropy in Eu_3O_4 could be obtained from magnetic dipolar interactions among the divalent ions alone. The explanation is that the coupling of neighbors Eu^{3+}–Fe^{3+} in europium iron garnet (EuIG) is small compared to the coupling within the iron sublattices, but large compared to the analogous coupling of neighbors Eu^{3+}–Eu^{2+} in Eu_3O_4.

VI. SUMMARY

The metamagnetism of Eu_3O_4 has been interpreted with the model of linear chains for the antiferromagnetic ground state. The trivalent ions provide an apparently inert magnetic background for the divalent europium spins. Exchange constants

$$J_1/k \sim 0.3°\text{K} \quad \text{and} \quad J_2/k \sim -0.02°\text{K}$$

coupling nearest and next-nearest neighbors, respectively, of divalent europium are deduced from θ_p and H_c. The Néel point is consistent with these values for the exchange constants. An anisotropy field $H_A \simeq 7$ kOe is derived from magnetic dipolar interactions, in agreement with the magnetic data.

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APPENDIX A. EXPERIMENTS ON Eu_3O_4

The results of four separate experiments on different samples of Eu_3O_4 are summarized in Table I. The reported values for the ordering temperature range 5–77°K. The results are subject to three sources of error: (1) sample impurity (possible presence of EuO), (2) low critical-field metamagnetism (high magnetic fields may obscure antiferromagnetism), and (3) errors of temperature measurement in the difficult region 4–10°K.

It may be noted that reported differences of 10–20% or more in the ordering temperature are not uncommon for compounds of divalent europium. In the chalcogenide series, EuO has been assigned transition points from 69 to 77°K,[16,21] EuS from 16 to 18°K,[15,16] and EuTe from ~6° to 11°K.[5,16,22,23] However, the value (77°K) which Wang reported[6] for Eu_3O_4 is clearly out of line with the results of other experiments (Table I). It may also be noted that McGuire[24] has measured the magnetization of polycrystalline Eu_3O_4 at 77 and 300°K without observing a transition. It seems likely that Wang's sample was corrupted with EuO, which orders ferromagnetically at ~77°K.[21] Wang states that EuO could have been present in amounts of up to 5% by weight.

The metamagnetic transition in Eu_3O_4 shows up clearly in single-crystal data at low fields and gives a pronounced S shape to the magnetization curve for a polycrystalline sample (Fig. 2). Apparently, Samokhralov *et al.*[5] missed this transition by taking data only at high fields (15–19 kOe).

The metamagnetic transition is appreciably broadened in a powder due to the random orientation of the particles relative to the applied field. This effect makes it very difficult to analyze the data at the field strengths used by Samokhralov *et al.*, and it casts some doubt on the value (7.8°K) which they obtained for the ordering temperature. A comparison may be made with the compound EuSe, which was initially[15,16,20] thought to be a ferromagnet, based on the magnetization in high fields, and only later[25] found to be an antiferromagnet with a low-field metamagnetic transition. Early estimates of the Curie temperature, from the data at high fields, range from 5.5 to 8°K,[15,16,22] whereas the specific heat in zero field showed a sharp peak at 4.58 ± 0.03°K (a *lower* temperature).[23] Under similar conditions, Samokhralov *et al.* may have overestimated the ordering temperature for Eu_3O_4 by relying exclusively on the data at high fields.

APPENDIX B. CALCULATION OF THE INFLUENCE OF TRIVALENT EUROPIUM ON THE PARAMAGNETIC SUSCEPTIBILITY IN Eu_3O_4

The magnetization per mole of the compound Eu_3O_4 may be written

$$\mathbf{M}=\mathbf{M}(\mathrm{Eu}^{2+})+2\mathbf{M}(\mathrm{Eu}^{3+}), \qquad (\mathrm{B1})$$

where $\mathbf{M}(\mathrm{Eu}^{3+})$ and $\mathbf{M}(\mathrm{Eu}^{2+})$ are magnetizations per mole of the ions Eu^{3+} and Eu^{2+}, respectively. From the molecular-field approximation at high temperatures (for negligible saturation),

$$\mathbf{M}(\mathrm{Eu}^{2+})=\chi_i(\mathrm{Eu}^{2+}) \times[\mathbf{H}_0+\lambda_2\mathbf{M}(\mathrm{Eu}^{2+})+2\lambda_{23}\mathbf{M}_S(\mathrm{Eu}^{3+})], \qquad (\mathrm{B2})$$

$$\mathbf{M}(\mathrm{Eu}^{3+})=\mathbf{F}(\mathbf{H}_0,\mathbf{H}_{\mathrm{ex}})$$

$$\mathbf{H}_{\mathrm{ex}}=\lambda_{23}\mathbf{M}(\mathrm{Eu}^{2+})+\lambda_3\mathbf{M}_S(\mathrm{Eu}^{3+}). \qquad (\mathrm{B3})$$

In Eqs. (B2) and (B3), the Weiss constants are

$$\lambda_2=\sum_j J_{ij}(\mathrm{Eu}^{2+}\text{–}\mathrm{Eu}^{2+})/2N\mu_B{}^2, \qquad (\mathrm{B4})$$

$$\lambda_3=\sum_j J_{ij}(\mathrm{Eu}^{3+}\text{–}\mathrm{Eu}^{3+})/2N\mu_B{}^2, \qquad (\mathrm{B5})$$

$$\lambda_{23}=\sum_j J_{ij}(\mathrm{Eu}^{2+}\text{–}\mathrm{Eu}^{3+})/2N\mu_B{}^2, \qquad (\mathrm{B6})$$

where N is Avogadro's number. The quantity $\mathbf{M}_S(\mathrm{Eu}^{3+})$ is the portion of the magnetization $\mathbf{M}(\mathrm{Eu}^{3+})$ arising from the polarization of the electronic spins [the magnetization $\mathbf{M}(\mathrm{Eu}^{2+})\equiv\mathbf{M}_S(\mathrm{Eu}^{2+})$ since divalent europium has the ground state ^8S], while χ_i represents the magnetic susceptibility with negligible interactions among the ions. The form of the function $\mathbf{F}(\mathbf{H}_0,\mathbf{H}_{\mathrm{ex}})$ was given by Wolf and Van Vleck[26]:

$$\mathbf{F}(\mathbf{H}_0,\mathbf{H}_{\mathrm{ex}})=\frac{8N\mu_B{}^2}{E_1[1+3\exp(-E_1/kT)]} \times\left\{(\mathbf{H}_0+2\mathbf{H}_{\mathrm{ex}})\left[1+\left(\frac{15}{8}\frac{E_2}{E_2-E_1}-1\right)\exp(-E_1/kT)\right]+\frac{3E_1}{16kT}(3\mathbf{H}_0+2\mathbf{H}_{\mathrm{ex}})\exp(-E_1/kT)\right\}, \qquad (\mathrm{B7})$$

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[21] B. T. Matthias, R. M. Bozorth, and J. M. Van Vleck, Phys. Rev. Letters **7**, 160 (1961).

[22] G. Busch, P. Junod, M. Risi, and O. Vogt, in *Proceedings of the International Conference on Semiconductors, Exeter, 1962* (Institute of Physics and Physical Society, London, 1962), p. 727.

[23] G. Busch, P. Junod, R. G. Morris, J. Muheim, and W. Statius, Phys. Letters **11**, 9 (1964).

[24] T. R. McGuire (private communication).

[25] G. Will, S. J. Pickhart, H. A. Alperin, and R. Nathans, J. Phys. Chem. Solids **24**, 1679 (1963).

[26] W. P. Wolf and J. H. Van Vleck, Phys. Rev. **118**, 1490 (1960).

where E_1 and E_2 are the spacings of the levels $^7F_1$ and $^7F_2$ above the ground state $^7F_0$ ($E_1 \sim 330$ cm^{-1}, $E_2 \sim 990$ cm^{-1}). The formula (B7) provides a reasonably good approximation to the magnetization $\mathbf{M}(\mathrm{Eu}^{3+})$ at temperatures below 300°K where few ions are excited to the state $^7F_2$ and where the effects[27] on the magnetization of splittings of the level $^7F_1$ in a crystalline potential are slight.

Strictly speaking, the term $2\lambda_{23}\mathbf{M}_S(\mathrm{Eu}^{3+})$ in Eq. (B2) should be replaced by a series of terms $\sum_i \lambda_{23}{}^i n^i \mathbf{M}_S{}^i(\mathrm{Eu}^{3+})$, where n^i is the molar fraction of ions Eu^{3+} on inequivalent site i. However, this refinement is unnecessary in the present calculation, since only an estimate of the sum of the interactions is desired, and this may be represented by the constant $2\lambda_{23}$.

Exchange fields $\lambda\mathbf{M}_S(\mathrm{Eu}^{3+})$ were treated by Bozorth and Van Vleck[28] at low temperatures where virtually all of the moment comes from matrix elements connecting the levels $^7F_0$ and $^7F_1$, giving $\lambda\mathbf{M}_S(\mathrm{Eu}^{3+}) = 2\lambda\mathbf{M}(\mathrm{Eu}^{3+})$. The factor 2 arises from the definition

$$\lambda = \sum_j 2J_{ij}/Ng^2\mu_B{}^2.$$

with $g=2$, consistent with the usual definition for ions in S states, used here to permit placing the same coefficient λ_{23} in Eqs. (B2) and (B3) and to give a direct comparison of exchange interactions in the ratio

$$\lambda_{23}/\lambda_2 = \sum_j J_{ij}(\mathrm{Eu}^{2+}\text{–}\mathrm{Eu}^{3+}) \Big/ \sum_j J_{ij}(\mathrm{Eu}^{2+}\text{–}\mathrm{Eu}^{2+}).$$

At higher temperatures, the ratio of spin to total magnetic moment for Eu^{3+} depends on the relative populations of the various states, and an expression analogous to Eq. (B7) is necessary for the quantity $\mathbf{M}_S(\mathrm{Eu}^{3+})$. The formula

$$\mathbf{M}_S(\mathrm{Eu}^{3+}) = 2\mathbf{F}(\mathbf{H}_0, \mathbf{H}_{\mathrm{ex}}) - \frac{2N\mu_B{}^2}{kT}\frac{\exp(-E_1/kT)}{1+3\exp(-E_1/kT)}(3\mathbf{H}_0+2\mathbf{H}_{\mathrm{ex}}) \tag{B8}$$

may be derived by noting that

$$\begin{aligned}\mathbf{M}_S(\mathrm{Eu}^{3+}) &\equiv \langle 2\mu_B\mathbf{S}\rangle_{\mathrm{Eu}^{3+}} \\ &\equiv 2(\mu_B\langle\mathbf{L}+2\mathbf{S}\rangle_{\mathrm{Eu}^{3+}} - \mu_B\langle\mathbf{J}\rangle_{\mathrm{Eu}^{3+}}).\end{aligned} \tag{B9}$$

The first term in the parentheses in Eq. (B9) is $\mathbf{F}(\mathbf{H}_0, \mathbf{H}_{\mathrm{ex}})$, while the second term may be obtained from Eq. (B7) by noting that $\langle {}^7F_0 | \mathbf{J} | {}^7F_1\rangle = 0$ and $\langle {}^7F_1 | \mathbf{J} | {}^7F_1\rangle = \frac{3}{2}\langle {}^7F_1 | \mathbf{L}+2\mathbf{S} | {}^7F_1\rangle$, whence

$$\mu_B\langle\mathbf{J}\rangle_{\mathrm{Eu}^{3+}} = \frac{N\mu_B{}^2}{kT}\frac{\exp(-E_1/kT)}{1+3\exp(-E_1/kT)}(3\mathbf{H}_0+2\mathbf{H}_{\mathrm{ex}}). \tag{B10}$$

In the present notation, the quantity $\chi(\mathrm{Eu_3O_4}) - \chi(\mathrm{SrEu_2O_4})$, plotted in Fig. 3, becomes

$$\{M - 2F[H_0, \lambda_3 M_S(\mathrm{Eu}^{3+})]\}/H_0.$$

This may be transformed, using Eqs. (B1) to (B8), and neglecting terms of higher than second order in the susceptibilities, to the form of Eq. (2), with

$$\theta(T) = \lambda_2 C(\mathrm{Eu}^{2+})\left\{1 + \frac{6\lambda_{23}T}{\lambda_2 C(\mathrm{Eu}^{2+})}\left[\chi_i(\mathrm{Eu}^{3+}) - \frac{3N\mu_B{}^2}{kT}\frac{\exp(-E_1/kT)}{1+3\exp(-E_1/kT)}\right]\right\}. \tag{B11}$$

This reduces to Eq. (3) with the definition

$$f(T) = 6\lambda_{23}\left[\chi_i(\mathrm{Eu}^{3+}) - \frac{3N\mu_B{}^2}{kT}\frac{\exp(-E_1/kT)}{1+3\exp(-E_1/kT)}\right]. \tag{B12}$$

APPENDIX C. THEORETICAL EXPRESSION FOR THE CRITICAL FIELD

An expression for the critical field H_c for a metamagnetic transition of the spins in Fig. 1(b) may be obtained by equating the energy of the initial and final states (subscripts i and f, respectively).

$$E_f{}^{\mathrm{Zee}} + E_f{}^{\mathrm{dip}} + E_f{}^{\mathrm{exch}} = E_i{}^{\mathrm{dip}} + E_i{}^{\mathrm{exch}} + E_i{}^{\mathrm{Zee}}, \tag{C1}$$

where the superscripts "Zee," "dip," and "exch" refer to Zeeman, dipolar, and exchange interactions, respectively. Let N be the density of ions Eu^{2+}, with moment $\mu_S = 7\mu_B$ at saturation, and suppose that the magnetic field lies along the axis of polarization of the spins. Then the energies in Eq. (C1) may be written

$$\Delta E^{\mathrm{Zee}} = E_f{}^{\mathrm{Zee}} - E_i{}^{\mathrm{Zee}} = -N\mu_S H_c, \tag{C2}$$

$$\Delta E^{\mathrm{dip}} = E_f{}^{\mathrm{dip}} - E_i{}^{\mathrm{dip}} = -\tfrac{1}{2}N\mu_S \sum_{k\neq j}[h_{jk}{}^{\mathrm{dip}}(f) - h_{jk}{}^{\mathrm{dip}}(i)], \tag{C3}$$

$$\Delta E^{\mathrm{exch}} = E_f{}^{\mathrm{exch}} - E_i{}^{\mathrm{exch}}, \tag{C4}$$

where $h_{jk}{}^{\mathrm{dip}}$ is the magnetic dipolar field at ion j due to ion k. The Zeeman energy in the antiferromagnetic state has been neglected since it is small at low temperatures. The dipolar energy in the final state includes a contribution from the demagnetizing energy. The in-

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[27] A. Frank, Phys. Rev. **48**, 765 (1935); M. Schieber and L. Holmes, J. Appl. Phys. **36**, 1159 (1965).

[28] R. M. Bozorth and J. H. Van Vleck, Phys. Rev. **118**, 1493 (1960).

crease in dipolar energy may be written

$$\Delta E^{\mathrm{dip}}=-\tfrac{1}{2}N\mu_S\sum_{k\neq j}^{\mathrm{sphere}}\left[h_{jk}{}^{\mathrm{dip}}(f)-h_{jk}{}^{\mathrm{dip}}(i)\right]-\tfrac{1}{2}N\mu_S(\tfrac{4}{3}\pi-D)N\mu_S,\quad\text{(C5)}$$

where the quantity $(\frac{4}{3}\pi-D)N\mu_S$ is the sum of the Lorentz and demagnetizing fields. It is convenient to reference the various changes in energy to the change in effective field h on a given spin;

$$\Delta h_0{}^{\mathrm{dip}}\equiv\sum_{k\neq j}^{\mathrm{sphere}}\left[h_{jk}{}^{\mathrm{dip}}(i)-h_{jk}{}^{\mathrm{dip}}(f)\right],\qquad\text{(C6)}$$

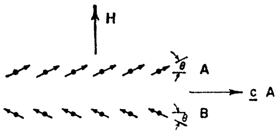
$$\Delta h^{\mathrm{exch}}\equiv\Delta e^{\mathrm{exch}}/\mu_S,\qquad\text{(C7)}$$

where $\Delta e^{\mathrm{exch}}=e_i{}^{\mathrm{exch}}-e_f{}^{\mathrm{exch}}$ is the decrease in exchange coupling of a given ion to its neighbors. The signs in definitions (C6) and (C7) have been chosen to make $\Delta h_0{}^{\mathrm{dip}}$ and Δh^{exch} into positive quantities for the compound $\mathrm{Eu_3O_4}$. With these definitions the equations above may be combined to give

$$H_c=\tfrac{1}{2}\left[\Delta h_0{}^{\mathrm{dip}}+\Delta h^{\mathrm{exch}}-(\tfrac{4}{3}\pi-D)N\mu_S\right].\qquad\text{(C8)}$$

In deriving Eq. (C8), the energy of the system after the transition has been set equal to the energy at which the antiferromagnetic configuration becomes unstable. This implies that both states of the system can exist at the critical value H_c of the magnetic field. For a finite sample, however, the demagnetizing fields spread the transition over a range $DN\mu_S$ of magnetic field. Equation (C8) is only valid, therefore, for the limiting case of a very long, needle-shaped sample, which has the axis of polarization of the spins along the axis of the needle. For such a sample, $D=0$, and the metamagnetic transition is broadened negligibly by demagnetizing fields. This restriction to needle-shaped samples does not constitute a serious limitation on the theory, for it is a simple matter to correct the experimental data to zero demagnetizing field for comparison with the predictions of Eq. (C8).

FIG. 4. Spins of an uniaxial antiferromagnet in a transverse magnetic field.



APPENDIX D. MAGNETIC DIPOLAR ANISOTROPY FOR LONG, FERROMAGNETIC CHAINS

Consider two long, ferromagnetic chains forming an antiferromagnet with two sublattices, A and B. The spins are rotated through an angle θ in an applied field H perpendicular to the axis of the chains (Fig. 4). The angularly dependent portion $U(\theta)$ of the internal energy may be written

$$U(\theta)=-2M_SH\sin\theta+2H_AM_S\sin^2\theta-\lambda_{AB}M_S{}^2\cos2\theta\qquad\text{(D1)}$$

in the notation of Sec. IV D. The magnetic dipolar energy associated with a pair of spins on a given chain varies with the angle θ as the function $\frac{1}{2}(1-3\cos^2\theta)$. Therefore, the magnetic dipolar energy associated with one chain may be written

$$\tfrac{1}{2}\sum_i\boldsymbol{\mu}_i\cdot\sum_{j\neq i}\mathbf{H}_{ij}{}^{\mathrm{dip}}=\tfrac{1}{4}M_Sh_{||}{}^{\mathrm{dip}}(1-3\cos^2\theta),\qquad\text{(D2)}$$

where $h_{||}{}^{\mathrm{dip}}$ is the dipolar field on a given spin from all of the other spins, with $\theta=0$. If the magnetic dipolar interactions between the chains are neglected, then the dipolar energy of the system is twice as large as the result (D2), since there are two sublattices. Comparing the angularly dependent terms in Eqs. (D1) and (D2) gives

$$2H_A{}^{\mathrm{dip}}M_S\sin^2\theta=\tfrac{3}{2}M_Sh_{||}{}^{\mathrm{dip}}\sin^2\theta\qquad\text{(D3)}$$

or

$$H_A{}^{\mathrm{dip}}=\tfrac{3}{4}h_{||}{}^{\mathrm{dip}}.\qquad\text{(D4)}$$