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MAGNETIC PROPERTIES OF A Eu_3O_4 *SINGLE CRYSTAL AT LOW TEMPERATURES*

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The temperature dependence of magnetization of a Eu_3O_4 single crystal is measured between 1.7° and 300°K along three different crystallographic directions. The magnetization curves at 4.2°K are typical for a highly anisotropic metamagnetic substance. The antiferromagnetic transition temperature determined from the susceptibility peak in a 1.2-kOe field is 5.3°K. The paramagnetic Curie temperature is derived from the temperature dependence of the inverse susceptibility $\chi^{-1}(T)$. When the Eu^{3+} ion susceptibility is taken into account 7°K is obtained for all three axes. The Eu_3O_4 magnetic structure can be represented by linear chains within which the spins are coupled by ferromagnetic interaction while the interaction between the chains is antiferromagnetic. The exchange integrals are calculated on the basis of the molecular field theory. For ferromagnetic interaction within a linear chain $A_{11} = 0.3k$ and for the antiferromagnetic interaction between linear chains $A_{12} = 0.04k$, where k is the Boltzmann constant. An analysis of the magnetization curves along different axes and estimates of the exchange field based on the Néel temperature show that the anisotropy field is much stronger than the exchange field

EUROPIUM oxide $Eu_3O_4(Eu^{2+}Eu_2^{3+}O_4)$ was first synthesized by Bäringhausen and Brauer in 1962.[1] A detailed description of its crystal structure has been given by Rau.[2] The space group of Eu_3O_4 is $D_{2h}^{16} - P_{nam}$, and its structure is isomorphic to that of $CaFe_2O_4$,[3] with Eu^{2+} ions occupying the calcium sites and Eu^{3+} ions occupying the iron sites. The unit cell of Eu_3O_4 is orthorhombic with the parameters a = 10.10 Å, b = 12.15 Å, and c = 3.51 Å.

The magnetic properties of polycrystalline Eu_3O_4 were investigated for the first time in[4]. Although its behavior resembles superficially that of an ordinary ferromagnet, the T^2 dependence of its spontaneous magnetization is characteristic of antiferromagnets.

Working with a small (0.53 mg) Eu_3O_4 single crystal, Holmes and Schieber[5] observed an antiferromagnetic transition at 5°K and determined that Eu_3O_4 is metamagnetic with a temperature-dependent critical (threshold) field. Almost simultaneously with[5] there appeared a paper by Wang[6] concerning the magnetic properties of polycrystalline Eu_3O_4, which was interpreted to be a ferrimagnet with its Curie temperature at 77°K. For the purpose of testing these conflicting conclusions we have investigated a relatively large single crystal of Eu_3O_4 and present our results in the present communication.

EXPERIMENT

The Eu_3O_4 single crystal was synthesized by the Bridgeman method. It was nearly cubic, having edges about 2.5 mm long and weighing 34 mg. For our measurements, in the range 1.7°–300°K, we used a Domenicali pendulum magnetometer with 5×10^{-5} gauss-cm³ magnetic moment sensitivity. Temperatures were measured with a carbon resistance-type thermometer from 4.2° to 20°K, and with a copper-constantan thermocouple above 20°K. The temperature dependence of magnetization was measured in external fields of 1.2, 13.9, 16, and 17.16 kOe.

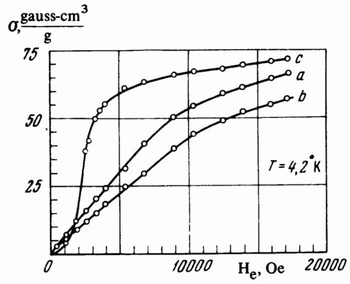

FIG. 1. Magnetization curves of Eu_3O_4 along three perpendicular axes.

The spontaneous magnetization was determined by extrapolating to H = 0 the magnetization measurements pertaining to an identical temperature; the saturation magnetization was determined by extrapolation to H = ∞.

EXPERIMENTAL RESULTS

Figure 1 shows the magnetization curves for three mutually perpendicular axes. The initial segment (up to about H_e = 2 kOe) of the curve for the c axis is typical of antiferromagnets that are magnetized along the axis of antiferromagnetism. When ~2 kOe is reached the magnetization rises sharply almost to saturation. The subsequent small increase can be attributed to the "paraprocess" because of proximity to

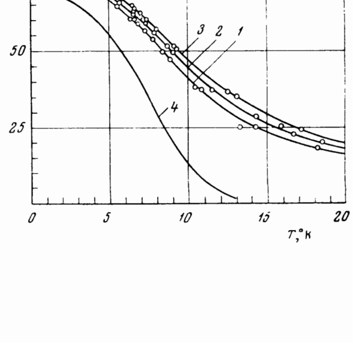

FIG. 2. Temperature dependence of Eu_3O_4 magnetization along the c axis in different magnetizing fields: H_e = (1) 13.94 kOe, (2) 16 kOe, (3) 17.16 kOe, (4) 0, (5) ∞.

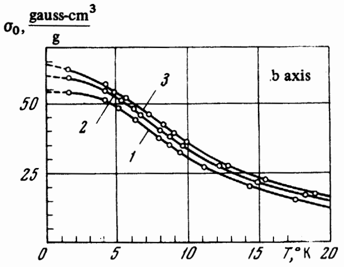

FIG. 3. Temperature dependence of Eu_3O_4 magnetization along the b axis in three different magnetizing fields: (1) 13.94 kOe, (2) 16 kOe, (3) 17.16 kOe.

the transition temperature. For the curves of magnetization along the a and b axes the external field H_e was insufficiently high to produce saturation.

Figures 2 and 3 show the temperature behavior of the magnetization, for different values of H_e, along the c and b axes, where the greatest difference in susceptibility is observed.

By extrapolating the saturation magnetization to 0°K (curve 5 of Fig. 2) the magnetic moment of the Eu^{2+} ion is found to be 7.3 μ_B (μ_B is the Bohr magneton).

Figure 4 shows the temperature behavior of the susceptibility along the c axis for H_e = 1.2 kOe. The maximum at 5.3°K is characteristic of an antiferromagnetic transition.

Figure 5 shows the temperature dependence of the inverse susceptibility $1/\chi$. For the c axis we have the paramagnetic temperature Θ = 5°K; for the a and b axes the extrapolation $\chi^{-1}(T) = (T - \Theta)/C$ yields Θ = 0°K within experimental error limits. It must be taken into account, however, that the Eu^{3+} ions make an appreciable contribution to the susceptibility in the paramagnetic region. Making the appropriate correction by means of Van Vleck's equation,[7] we obtain the identical result Θ = 7°K for all three axes. However, the anisotropy of the susceptibility remains unaffected.

Figure 6 shows the spontaneous magnetization as a function of T^2 and of $T^{3/2}$. It is evident that the T^2 law is observed almost up to the transition temperature.

DISCUSSION OF RESULTS

The character of the magnetization as a function of the magnetic field along the c axis (the sharp rise at $H_e \approx 2000$ Oe in Fig. 1) provided a basis for considering Eu_3O_4 to be metamagnetic or antiferromagnetic with a critical (threshold) field.[5] Figure 7 shows the arrangement of the Eu^{2+} ions in a plane perpendicular to the c axis. Along the c axis the Eu^{2+} ions are arranged in straight lines, with 3.51-Å ionic spacing and no intermediate ions.

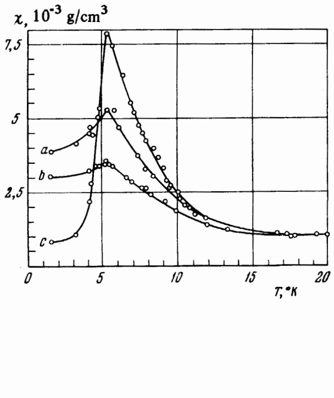

FIG. 4. Temperature dependence of Eu_3O_4 susceptibility along the different axes for H_e = 1.2 kOe.

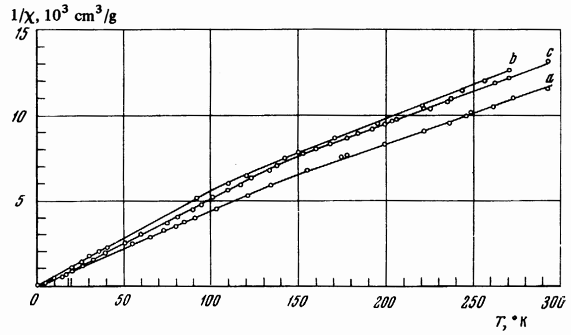

FIG. 5. Temperature dependence of inverse susceptibility along different Eu_3O_4 axes.

In the plane perpendicular to the c axis the Eu^{2+} ions form a broken line along the a axis; the ionic separation is here 5.6 Å. The O^{2-} ions situated between the Eu^{2+} ions are slightly displaced from the straight line connecting the latter. Along the b axis in the same plane the separation of the Eu^{2+} ions is 12.15 Å. Holmes and Schieber[5] proposed the following antiferromagnetic interpretation of this structure.

Spins arranged in a straight line along the c axis are coupled by a positive exchange interaction and form ferromagnetic chains. Spins located in neighboring chains are oriented antiparallel; in[5] the antiparallel orientation of the chains is attributed to dipole-dipole interaction, although the cause could be superexchange. The interaction between chains is much weaker than that between spins of a single chain. Sato[8] explained the magnetic properties of $MnAu_2$ on the basis of this magnetic structure model, which can be used to account for the curve of magnetization along the c axis.

For $H_e < H_{cr}$ (where H_{cr} is the critical or threshold field) the susceptibility is small. When $H_e \approx H_{cr}$ the antiferromagnetic ordering is destroyed and all the ferromagnetic chains are oriented parallel to the applied field as well as mutually parallel; the magnetization then rises sharply.

In connection with the temperature dependence of magnetization along the c axis (Fig. 2) it must be remembered that $H_e \gg H_{cr}$ held true for the measurements, which means that almost all spins were oriented parallel to the applied magnetic field. Therefore the extrapolation of the measured magnetization to $H = 0$ should yield the dependence of spontaneous magnetization in the case of parallel ferromagnetic chains between which a negative interaction remains in effect (curve 4 in Fig. 2). The magnetic structure of Eu_3O_4 can be represented approximately in the form of two equivalent sublattices consisting of linear ferromagnetic chains; here the chains of spins in one sublattice are antiparallel to the chains forming the other sub-

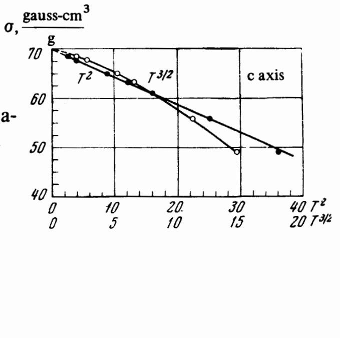

FIG. 6. Spontaneous magnetization of Eu_3O_4 along the c axis as a function of T^2 and of $T^{3/2}$.

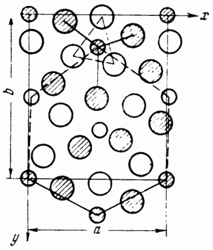

FIG. 7. Arrangement of Eu^{2+} and O^{2-} ions (projected on the x-y plane) in the orthorhombic Eu_3O_4 cell having the parameters a = 10.10 Å, b = 12.15 Å, and c = 3.51 Å. The space group is $D_{2h}^{16} - P_{nam}$. Small shaded circle - Eu^{2+} ion in the plane z = 0; small open circle - same ion in the plane z = ±½c; large shaded circle - O^{2-} ion in the plane z = 0; large open circle - same ion in the plane z = ±½c.

lattice. Therefore the temperature dependence of the spontaneous magnetization for the c axis (Fig. 2) should characterize the temperature dependence of spontaneous magnetization within each sublattice. Figure 6 shows that the spontaneous magnetization depends linearly on T^2, in agreement with the spin-wave theory for antiferromagnets.

Assuming the model of two equivalent sublattices for Eu_3O_4, the molecular field theory can be used to calculate the spin interaction within a sublattice (in a ferromagnetic linear chain) and also between the sublattices. The internal molecular fields in each equivalent sublattice are described by[9]

$$H_1 = n_{11}M_1 - n_{12}M_2, \quad H_2 = n_{11}M_2 - n_{12}M_1,$$

where n_{11} and n_{12} are the coefficients of the molecular field, and $M_1 = M_2$ are the magnetizations of the sublattices.

For metamagnetic substances n_{11} is positive and should be considerably larger than n_{12}. When the paramagnetic temperature Θ and the susceptibility at the transition temperature are known, n_{11} and n_{12} can be determined. For $T_N = 5°K$ and $\Theta = 7°K$ we obtained $n_{11} = 745$ and $n_{12} = 121$, or $n_{11} = 6n_{12}$. The molecular field theory gives the following relation between the exchange integrals and the molecular field coefficients:[10]

$$n_{11} = \frac{2z_{11}A_{11}}{N_1 g^2 \mu_{\text{Б}}^2}, \quad n_{12} = \frac{2z_{12}A_{12}}{N_2 g^2 \mu_{\text{Б}}^2},$$

where A_{11} and A_{12} are exchange integrals; z_{11} is the number of nearest neighbors, for an ion of sublattice 1, which belong to sublattice 1; z_{12} is the number of next-nearest neighbors, for an ion of sublattice 1, which belong to sublattice 2; N_1 and N_2 are the numbers of atoms per unit volume or weight for sublattices 1 and 2, respectively; g is the Landé factor.

For the considered antiferromagnetic structure the ordering within a ferromagnetic chain is determined by the interaction of each ion with its two nearest-neighbor ions that belong to the same chain and are separated from it by the distance 3.51 Å. Therefore $z_{11} = 2$. Each ion of sublattice 1 has 10 neighbors at different distances ranging from 5.6 to 6.6 Å. When we take into account only the nearest of these, at distances of 5.6 Å in the same plane as the considered ion, we will have $z_{12} = 2$. The calculated values of A_{11} and A_{12} are 0.3 and 0.04k, respectively, where k is the Boltzmann constant.

We therefore conclude that Eu_3O_4 is metamagnetic with strong magnetocrystalline anisotropy. The susceptibility anisotropy which also exists in the paramagnetic region appears to result from crystal effects. From the magnetization curves and the exchange field calculated by means of the formula $kT_N \approx \mu H_{ex}$ we conclude that the anisotropy field is considerably greater than the exchange field. The calculated values of A_{11} and A_{12} are, of course, approximate, but were sufficiently close to the evaluated exchange integrals for ferromagnetic EuO ($A_{11} = 0.65k$, $A_{12} = 0.06k$[11]), where the Eu^{2+} ions with a positive interaction are separated by 3.6 Å, while the separation of next-nearest neighbors is 5.14 Å.

The authors are indebted to M. I. Simonova for a discussion of the crystalline structure of Eu_3O_4.

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