Magnetocrystalline Anisotropy of Single-Crystal Europium Oxide

N. Miyata* and B. E. Argyle

IBM Watson Research Center, Yorktown Heights, New York

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The first-order cubic anisotropy constant K_1 in EuO single crystal was measured as a function of temperature and applied field by the static torque method. The value at $T=0°K$ is $K_1(0) = -(4.36\pm0.1)\times10^5$ erg/cm³. The variation of K_1 with T and H is uniquely described by the behavior of the measured magnetic moment $\sigma(H, T)$. The observed relationship between $K_1(H, T)/K_1(0, 0)$ and $\sigma(H, T)/\sigma(0, 0)$ is explained by a theory of single-ion interaction with the cubic crystal potential. The cubic crystal-field splitting parameter $b_4 = (21.2\pm0.5)\times10^{-4}$ cm⁻¹/ion obtained from $K_1(0)$ is compared with results for Eu⁺⁺ ions in various other materials.

INTRODUCTION

THE temperature dependence of the magneto-crystalline anisotropy energy of a ferromagnet and, alternatively, its connection with the magnetization $\sigma(T)$ have been the subject of considerable theoretical interest[1] since Akulov[2] first derived in 1936 the 10th-power law for the low-temperature region, $K_1(T)/K_1(0)\sim[\sigma(T)/\sigma(0)]^{10}$. At higher temperatures where the spin deviations are large, the 10th-power law is not valid. The influence of the crystal environment is sensed by each magnetic ion and the temperature behavior is expected to be somewhat different for different mechanisms of anisotropy.[1] It is possible, at least in principle, to identify the ionic species and the mechanism responsible for the magnetocrystalline anisotropy by observing the behavior of K_1 versus temperature and versus concentration of active elements. A single-ion theory has been derived by Wolf[3] considering an individual ion subject to a crystalline field in addition to the Weiss molecular field. The theory has been used successfully for evaluating the origins of anisotropy in ferrites and garnets.[4] The garnet YIG, which has provided the most satisfactory testing ground for this theory[5] has, however, two magnetic sublattices. Consequently, two fitting parameters are adjustable in the comparison between theory and experiment.

With the availability of good quality EuO single crystals,[6] we are now in a position to test the theory in an insulating cubic ferromagnet in which the magnetic Eu²⁺ ions form a single sublattice of spin-only

atomic moments.[7] The dominant mechanism for the magnetocrystalline anisotropy is the splitting of the $^8S_{7/2}$ levels of the $4f$ electrons in the octahedral crystal field. The single-ion theory treated by Wolf[3] uses the molecular-field approximation to derive the effective field which quantizes the atomic magnetic moments along the direction of the magnetization. The theory predicts explicitly the dependence of $K_1(\sigma)$ on the observed magnetization $\sigma(H, T)$ and gives implicitly the variation with temperature and applied magnetic field, $K_1(T, H)$. Other mechanisms that may be considered are two-ion interactions (e.g., magnetic dipole-dipole, electrostatic pseudo-dipolar and pseudo-quadrupolar interactions) and the contribution of magnetoelastic distortion.[4] Von Molnar and Lawson[8] found evidence from the paramagnetic linewidth in EuS that two-ion interactions play a minor role in ferromagnetic Eu-chalcogenides. We estimate for EuO the effects of magnetic dipole-dipole interactions and magnetoelastic distortion on $K_1(0)$ to be small as well.

We describe here measurements of the temperature and field dependence of the first-order cubic anisotropy constant K_1. From magnetization data measured on the same crystal,[9] we derive the dependence of K_1 on σ for a wide range of temperatures and applied fields. The effects of magnetoelastic interaction in EuO (anomalous expansivity and magnetostriction) have been studied previously.[10]

It is interesting to note that in EuO an applied field of 20 kOe is comparable to 1/20th the Weiss field and may generate rather large forced anisotropy. While the forced anisotropy (introduced by a field) in $3d$ metals has occupied the attention of a number of theoretical studies, its magnitude[11-13] $[(\partial K_1/\partial H)/K_1\sim10^{-5}$ to

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

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10^{-6})] is so small that it almost escaped detection in the applied fields commonly available ($\sim$1/200th of the Weiss molecular field).

TECHNIQUE OF MEASURING K_1

The coefficient K_1 in the first-order anisotropic free energy $K_1 \sum_{i<j} \alpha_i^2\alpha_j^2$ (α_i = direction *cosines* of the magnetization) was derived from the torque[14] in an applied field rotating in the (001) plane of a disk-shaped single crystal, 5.0 mm$\times$0.67 mm. The same specimen was also used for measuring anomalous thermal expansivity and magnetostriction.[10] The temperature of the specimen was measured by a Au+2.1 at.% Co versus Cu thermocouple which was calibrated at the temperatures of N_2, Ne, and He liquids. During a run, the specimen and thermocouple were in thermal contact with the liquid bath by means of helium exchange gas. Boiling and freezing temperatures of these reference baths were varied and controlled, using a vacuum forepump and a Wallace and Tiernan manostat. Temperature readings were accurate to within ±0.1°K.

The measured torque curves contained predominantly the term $-K_1(\sin 4\theta)/2$ expected for first-order cubic anisotropy. Here, θ is the angle between the magnetization and the [100] direction. The torque due to second-order magnetocrystalline energy $K_2\alpha_1^2\alpha_2^2\alpha_3^2$ is zero in a {100} crystal plane. Values of K_1 were obtained by averaging the eight extrema of each torque curve for 360° rotation of the field. Small deviations from perfect sin 4θ behavior were always less than 4% of the amplitude at helium temperature. The averaging procedure eliminates those residual torques which contain uniaxial and unidirectional components originating from the shape anisotropy of the specimen and a nonuniform component of applied magnetic field. We have to consider also the possibility that small chips in the peripheral edges of the specimen which were visible under a microscope could contribute to the shape anisotropy. If these chips are cooperatively oriented [(100) is the cleavage plane] they can produce a measurable sin4θ torque. We investigated this question by looking for the fourfold shape effect under conditions where K_1 is very small and σ is rather large. At 77°K and 20 kOe where $K_1 \approx 1\%$ of $K_1(0)$ and $\sigma \approx \frac{1}{2}\sigma(0)$, no such fourfold effect was observed within limits of uncertainty equal to $\pm\frac{1}{4}\%$ of K_1 at 0°K. This chip effect, being magnetostatic in origin, is proportional to the square of the magnetization. Thus, the upper limit on the error in measuring K_1 at absolute zero caused by this fourfold shape effect is $\lesssim \pm1\%$.

FIG 1. Temperature dependence of first-order magnetocrystalline anisotropy constant K_1 and the magnetization σ at fixed internal magnetic fields of 18 and 14 kOe.

The contribution of the magnetoelastic distortion, K_{ME}, to the measured anisotropy can be estimated from the relation[4]

$$K_{ME} = B_1^2/(c_{11}-c_{12}) - (B_2^2/2c_{44}),$$

where B_1 and B_2 are magnetoelastic coupling coefficients and c_{11}, c_{12}, c_{44} are the usual cubic elastic stiffness coefficients. We obtain $K_{ME} \simeq -6\times10^3$ erg/cm^3 by using the constants $B_1(0) = 3.1\times10^6$, $B_2(0) = -86\times 10^6$, which we previously evaluated for EuO,[10] and using elastic constants, $c_{11} = 17\times10^{11}$, $c_{12} = 7.5\times10^{11}$, $c_{44} = 5.2\times10^{11}$ (all in cgs units).[15] Magnetoelastic distortion contributes then only $\sim$1.5% to the observed K_1 at absolute zero.

EXPERIMENTAL RESULTS

The temperature dependence of K_1 is given in Fig. 1 for constant applied internal magnetic fields H_i of 14 and 18 kOe. The value of K_1 at 0°K is $-(4.36\pm 0.1)\times10^5$ erg/cm^3 which may be compared with the value -3.6×10^5 obtained by Dillon[16] using the ferromagnetic resonance. This discrepancy may arise from differences in sample preparation although we have obtained 1% consistency between two different specimens made in this laboratory which have less than 20 ppm of other rare-earth impurity concentrations according to mass spectrographic analysis of similarly prepared crystals. The assigned error in $K_1(0)$ is a maximum error based on $\pm1\%$ calibration error and the $\pm1\%$ maximum fourfold shape anisotropy described previously.

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[14] The recording torque balance which was constructed by B. A. Calhoun of this laboratory, is similar to the design of A. A. Aldenkamp, C. P. Marks, and H. Zijlstra [Rev. Sci. Instr. **31**, 544 (1960)]. The calibration was checked by the method of a current-carrying coil and is accurate to $\pm1\%$.
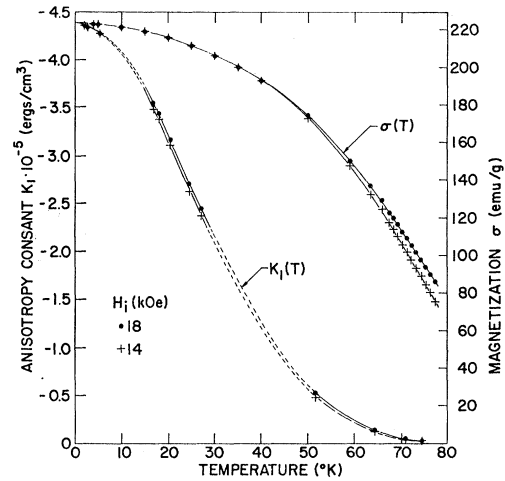
[15] Measured ultrasonically by D. E. Eastman of this laboratory.

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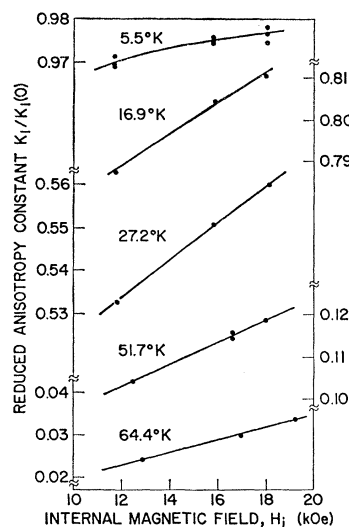
FIG. 2. Reduced anisotropy constant versus applied internal magnetic field H_i at fixed temperatures.

The field dependence of K_1 is given in Fig. 2. It consists of two parts: the intrinsic and the extrinsic field dependence. The major contribution at high temperatures is probably the intrinsic forced anisotropy which is associated with the forced magnetization in a high magnetic field. The extrinsic effect is due to lack of saturation in the material near the edge of the specimen and is largest at the lowest temperatures. The slope of forced anisotropy at 5.5°K and below has the magnitude expected[17] for the extrinsic effect, but we are not sure if it should be so attributed. Nevertheless, this slope is small in relation to the slope at higher
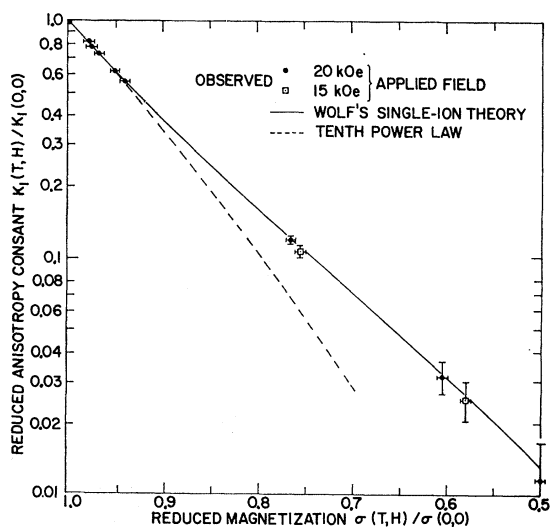

FIG. 3. Reduced anisotropy constant versus reduced magnetization.

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temperatures and at field strengths seven times the saturation field ($\sim$2.7 kOe) for the center of the disk.

Figure 3 shows the reduced anisotropy constant $K_1(T, H)/K_1(0, 0)$ plotted logarithmically against the reduced magnetization $\sigma(T, H)/\sigma(0, 0)$. The theoretical results for the single-ion theory given by Wolf[3], which converges to the 10th-power law as T approaches zero, is also presented. The experimental data follow the single-ion theory quite well.

The temperature dependence of the reduced field derivative of the forced anisotropy $(\partial K_1/\partial H)/K_1(0)$ is displayed in Fig. 4. The data points represent the slopes of the $K_1/K_1(0)$ versus H_i curves given in Fig. 2 evaluated between 16 and 18 kOe. The theoretical curve in Fig. 4 was obtained by combining Wolf's theory[3] in the high-temperature region with the measured high-field susceptibility[9] $(\partial\sigma/\partial H_i)/\sigma(0)$ and, in the low-temperature region, by combining with the
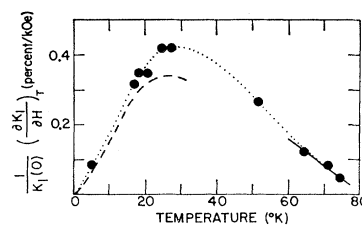

FIG. 4. $\cdots\bullet\cdots$: Observed slope $(\partial K_1/\partial H)/K_1(0)$ of forced anisotropy curves given in Fig. 3 at high magnetic fields. Solid curve: Slope predicted from Wolf's single-ion theory in Ref. 3 and the observed high-field susceptibility of magnetization. Dashed curve: Slope predicted by combining single-ion theory with the susceptibility obtained from unrenormalized spin-wave theory. (See text.)

susceptibility calculated from spin-wave theory[18] but without spin-wave–spin-wave interactions.

DISCUSSION

The previous section and Figs. 3 and 4 show that the temperature and field dependence of the first-order magnetocrystalline anisotropy coefficient K_1 can be represented by a unique function of the magnetization $\sigma(T, H)$ alone. The single-ion theory of Wolf[3] provides such a function which agrees for EuO very well with our experimental results although it is based on the

[18] At low temperatures the magnetization measurements were too insensitive to give accurately the high-field susceptibility. There is evidence that spin-wave theory satisfactorily explains the temperature variation of magnetization up to 10–15°K when evaluated by calculating a lattice sum [(as described by S. Charap and E. Boyd, Phys. Rev. **133**, A811 (1964)] over the Brillouin zone for 30 atomic distances. The field derivative of reduced magnetization $(1/\sigma_0)(\partial\sigma/\partial H)$ at various temperatures was computed by an IBM 7094 using the parameters $J_1/k=0.75°K$, $J_2/J_1=-0.13$, and $4\pi M_0=24\times10^3$ G which were obtained from low-temperature NMR data by E. L. Boyd [Phys. Rev. **145**, 174 (1966)].

not quite realistic molecular-field approximation. Callen and Shtrikman[19] have recently shown that the functional relationship between magnetization and anisotropy constant is essentially model-independent being identical for all renormalized collective excitation theories, e.g., spin-wave theory, the random-phase approximation, other forms of Green's-function theory, as well as the molecular-field theory itself. This explains the good agreement of our anisotropy data with Wolf's single-ion theory even though the molecular-field approximation is too inaccurate to calculate the magnetization behavior, as it neglects the short-range order known to be significant particularly near the Curie point.

The cubic crystal-field parameter b_4 can be estimated from $K_1(0)$ under the assumption that perturbation of single-ion energies by electrostatic crystal field is the dominant mechanism for the anisotropy energy in EuO. We obtain[20] $b_4 = (21.2\pm0.5)\times10^{-4}\mathrm{cm}^{-1}$/ion using our measured $K_1(0) = -(4.36\pm0.1)\times10^5$ erg/cm^3 and the lattice constant $a_0 = 5.145$ Å.

In Fig. 5, values of b_4 for Eu^{++} in several compounds with differences in size of the anion environment are compared. The dashed line is an arbitrary connection between the b_4 value of this paper (EuO) with the b_4 value obtained on EuS by ferromagnetic resonance measurements. Title[21] studied the crystal-field splitting
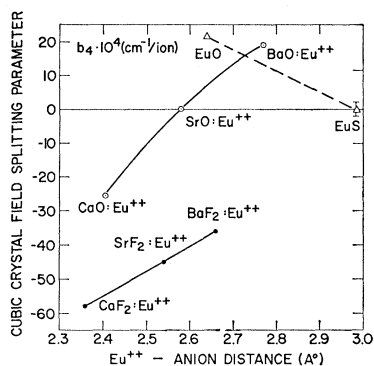

FIG. 5. Cubic crystal-field splitting parameter b_4 versus interionic distance for Eu^{++} ions in various crystals obtained from various experiments. (See text.)

of dilute Eu^{++} in the series CaF$_2$, SrF$_2$, BaF$_2$ having the fluorite structure with eightfold F$^-$ coordination. His observation that $b_4 \propto R^{-4.4}$, where R is the impurity-to-anion distance, suggests that the splitting is linear rather than quadratic in the electrostatic crystalline-field potential $V \propto R^{-5}$.[22] If the same perturbative process is dominant in sixfold coordinated alkaline earth oxides and europium chalcogenides, b_4 is expected to be opposite in sign and to vary in magnitude as R^{-5}. In the case of EuO, b_4 is positive and becomes zero on going to the larger lattice parameter of EuS. This agrees only qualitatively with the point-charge model. At the same time, Overmeyer and Gambino[23] found a completely anomalous situation for the case of dilute Eu^{++} in the series CaO, SrO, BaO, in which case b_4 increases with increasing R and changes sign as also shown in Fig. 5. There is, at present, no explanation of these contradictory results.

The observed agreement with the temperature variation predicted by a single-ion theory does not preclude the possibility of magnetic dipole-dipole, pseudo-dipole, and pseudo-quadrupole interactions. The contribution of the two-ion mechanisms to the temperature curve has not been calculated quantitatively,[1] and qualitatively it can be similar to the single-ion curve. The pseudo-pole-terms are largely electrostatic in origin and difficult to estimate theoretically.[4] Cooper and Keffer[24] showed how the magnitude may be estimated from the high-temperature paramagnetic resonance linewidth ΔH. Von Molnar and Lawson[8] measured $\Delta H = 1.20\pm 0.03$ kOe in EuS and found this to be consistent with an estimate for magnetic dipole-dipole broadening. In other words, there was no need to invoke an electrostatic mechanism. The EPR linewidth in EuO is currently under investigation by D. E. Eastman of this laboratory. We may estimate the contribution of magnetic dipole-dipole energy to $K_1(0)$ by the formula[25]

$$K_1(0) = (-9NS/16Z)(D^2/J)$$

taking J (exchange constant)$\simeq 0.75°k_B$,[26] $S = \frac{7}{2}$, $Z = 12$; D (dipolar coupling constant) is approximately given by $g^2\beta^2/a^3$ with a being the distance between neighboring Eu^{++} ions (3.64 Å). The resulting dipolar anisotropy $\sim 10^3$ erg/cm^3 is negligible compared to the observed $K_1(0) = -4.36\times10^5$ erg/cm^3.

ACKNOWLEDGMENTS

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[20] This splitting parameter b_4 is related to B_4 in the spin Hamiltonian $B_4(O_4^0+5O_4^4)$ [in the notation of Baker, Bleaney, and Hayes, Proc. Roy. Soc. (London) A347, 141 (1958)] by the usual relation 60 $B_4 = b_4$. This spin Hamiltonian is effectively the same as the form $(a/6)(S_x^4+S_y^4+S_z^4)$ used by Wolf, but we must clear up certain discrepancies in the literature as they pertain to a determination of b_4. While the relation $K_1 = ar(y)$ given by Wolf where $y = \exp[-g\beta H_{\mathrm{eff}}/kT]$ gives the splitting parameter in terms of $K_1(0)$ by referring to a calculated value for $r(0)$, the value $r(0) = 8.75$ given in Fig. 4 of Wolf's paper should be -17.5. The calculation for $r(y)$ was based on Eqs. (3c) for energy levels appearing in Ref. 3. Professor Wolf informs us that these equations need to be corrected by a factor of -2 on the right-hand side. This does not, however, affect the interpretation of $K_1/K_1(0)$ versus $\sigma/\sigma(0)$ discussed in this work because the reduced form of the function $r(y)/r(0)$ which connects these quantities is unaltered by the correction. To compare either a or b_4 with $K_1(0)$ we use then $K_1(0) = (-17.5)a = (-17.5)2b_4$, since $a = 2b_4$.

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