PHYSICAL REVIEW VOLUME 172, NUMBER 2 10 AUGUST 1968

Magnetocrystalline Anisotropy of Europium Selenide*

R. F. Brown, A. W. Lawson, and Glen E. Everett
Department of Physics, University of California, Riverside, California

(Received 26 February 1968)

The first- and second-order magnetocrystalline anisotropy constants of EuSe have been measured by a ferromagnetic-resonance technique at microwave frequencies and 1.3°K on single-crystal spheres of about 100 μ diam. The angular dependence of the resonant field for rotation in a $\{110\}$ crystallographic plane yields both K_1/M and K_2/M. The ferromagnetic-resonance linewidth was 60 Oe. The quantities K_1/M and K_2/M were measured to be -50 ± 6 and -83 ± 16 Oe, respectively. The cubic crystal-field splitting parameters b_4 and b_6 have been determined on the basis of Wolf's single-ion mechanism to be 4.5×10^{-4} and -1.3×10^{-4} cm^{-1}/ion, respectively. The results are compared with those of EuO and EuS and with cubic host lattices that have been doped with Eu^{++} ions.

INTRODUCTION

CONSIDERABLE research[1–7] has been done recently on the europium chalcogenides. These ionically bound compounds have the NaCl crystal structure. Each Eu^{++} ion exhibits a net magnetic moment of nearly 7 μ_B. Early work showed EuO, EuS, and EuSe to be ferromagnetic at low temperatures (with paramagnetic Curie temperatures of 77, 16, and 6°K, respectively) and EuTe to be antiferromagnetic (with a Néel temperature of 7.8°K). Enz *et al.*[3] suggested two competing exchange interactions between the magnetic europium ions in these compounds. Later work has indicated that the magnetic structure of europium selenide is complicated by an antiferromagnetic phase[8–10] that is dependent on both temperature and applied magnetic field. The europium chalcogenides are therefore a system of four fcc arrays of coupled net magnetic moments differing only in lattice spacing. Systematic measurement of the magnetic properties of each compound should contribute to an understanding of the dependence of the exchange interactions on lattice spacing.

Several theories have been presented to explain the existence of anisotropy in magnetic materials. The two theories most often quoted are due to Van Vleck[11] and to Wolf.[12] The applicability of these different approaches can be determined by comparing the measured values of the anisotropy with predicted values. According to Van Vleck,[11] magnetic anisotropy can arise from interionic couplings which are dipolar and quadrupolar in form. He derived an expression for the first-order anisotropy constant in terms of these pseudodipolar and pseudoquadrupolar coupling constants. Cooper and Keffer[13] then calculated the paramagnetic linewidth in terms of Van Vleck's coupling constants. According to Von Molnar and Lawson,[14] the paramagnetic linewidth expression of Cooper and Keffer is consistent with the 1.2-kOe linewidth of EuS [14] and the 1.4-kOe linewidth of EuO [15] solely on the basis of the classical magnetic dipolar interactions. To be in agreement with the room-temperature linewidths, which are explained by the classical dipolar interactions, they conclude that the Van Vleck interionic contribution to the first-order anisotropy must be less than 0.3 Oe in magnitude for both EuO and EuS. Dillon and Olsen[15] and more recently Miyata and Argyle[16] measured the first-order anisotropy in EuO to be −190 and −230 Oe, respectively. Franzblau, Everett, and Lawson[17] determined the first- and second-order anisotropy constants of EuS to be −19.6 and −4.6 Oe, respectively. In both EuO and EuS the anisotropy constants are much too large to be accounted for by Van Vleck's theory.

Wolf's single-ion crystal-field mechanism[12] has been invoked to explain the anisotropy in the europium compounds. Miyata and Argyle[16] compare both the first-order anisotropy and the magnetization of EuO as functions of temperature with the predictions of Wolf's theory. According to Wolf, the cubic crystal field can give rise to magnetic anisotropy in ferromagnetic insulators. The anisotropy constants must

---

* Work supported in part by the U.S. Atomic Energy Commission. AEC Report No. UCR 34 P77-14.

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

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

[3] U. Enz, J. F. Fast, S. Van Houten, and J. Smit, Philips Res. Rept. **17**, 451 (1962).

[4] S. Van Houten, Phys. Letters **2**, 215 (1962).

[5] R. L. Wild and R. D. Archer, Bull. Am. Phys. Soc. **7**, 440 (1962).

[6] T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, J. Appl. Phys. **34**, 1345 (1963).

[7] T. R. McGuire and M. W. Shafer, J. Appl. Phys. **35**, 984 (1964).

[8] S. J. Pickart and H. A. Alperin, Bull. Am. Phys. Soc. **10**, 32 (1965).

[9] J. C. Suits and B. E. Argyle, Phys. Rev. Letters **14**, 687 (1965).

[10] G. Busch, J. Appl. Phys. **38**, 1386 (1967).

[11] J. H. Van Vleck, Phys. Rev. **52**, 1178 (1937).

[12] W. P. Wolf, Phys. Rev. **108**, 1152 (1957).

[13] B. R. Cooper and F. Keffer, Phys. Rev. **125**, 896 (1962).

[14] S. Von Molnar and A. W. Lawson, Phys. Rev. **139**, A1598 (1965).

[15] J. F. Dillon, Jr., and C. E. Olsen, Phys. Rev. **135**, A434 (1964).

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

[17] M. C. Franzblau, Glen E. Everett, and A. W. Lawson, Phys. Rev. **164**, 716 (1967).

then relate to the crystal-field splitting parameters. The large decrease in magnitude of the anisotropy between EuO and EuS has been compared[14,17] to the large change in crystal-field splitting parameters determined as a function of lattice spacing for coupled pairs of Eu^{++} ions in cubic host lattices of CaO, SrO, and BaO.[18–20] The splitting parameters of EuO [16] and EuS [17] calculated according to Wolf's model are of the same order of magnitude as the measured splitting parameters of Eu^{++} ions in cubic host lattices.

Ferromagnetic resonance at microwave frequencies (21.48 GHz) and 1.3°K was done as a function of sample rotation on oriented single-crystal spheres. The magnetic anisotropy constants were determined from the angular dependence of the resonant field. Sample asphericity was taken into account in the analysis technique. The crystal-field splitting parameters were calculated from the anisotropy constants on the basis of Wolf's model. The calculated splitting parameters are compared with those of EuO and EuS and with the measured crystal-field splitting parameters of Eu^{++} ions in several host lattices.

Although antiferromagnetism has been reported in EuSe,[8–10] under the conditions of this experiment europium selenide is ferromagnetic. The resonant field varied between 7.5 and 7.8 kOe. Suits and Argyle[9] reported that at 4.2°K a magnetic field of more than 20 kOe was required to produce a saturated ferromagnet. At 1.9°K, however, 8.0 kOe is sufficient for pure ferromagnetism. McGuire and Shafer[7] reported that at 1.6°K EuSe appears to be a saturated ferromagnet above 7.0 kOe. Specific-heat measurements on EuSe by White, McCollum, and Callaway[21] indicate a $T^{3/2}$ dependence below 1.3°K in zero magnetic field. Ferromagnetic coupling contributes a $T^{3/2}$ dependence to the specific heat,[22] whereas antiferromagnetic coupling contributes a T^3 term[23] (which is inseparable from the phonon contribution). These measurements indicate that europium selenide can be treated as a saturated ferromagnet at temperatures below 1.6°K and magnetic fields above 7.0 kOe.

Following a review article on ferromagnetic resonance by Kittel,[24] magnetic anisotropy can be described in terms of an energy associated with the alignment of magnetic spins in various crystallographic directions. This directionally dependent orientation energy is written in terms of parameters which characterize the material and the cosines of the angles between the principal crystal axes and the net magnetization. This free energy must have the same symmetry as the crystal, which is cubic for the europium chalcogenides. For cubic systems the energy expression takes the form

$$E_A=K_1(l^2m^2+m^2n^2+n^2l^2)+K_2l^2m^2n^2, \qquad (1)$$

where l, m, and n are the direction cosines with respect to $\langle 100\rangle$ directions and K_1 and K_2 are the first- and second-order anisotropy constants (although that terminology does not necessarily imply relative magnitude). The experiment was designed to measure K_1 and K_2.

The resonant condition for a saturated single-crystal ferromagnet in a magnetic field has been given by Kittel.[24] It is assumed that the sample is ellipsoidal with geometric demagnetizing factors N_x, N_y, and N_z along the principal axes of the ellipsoid. It is also assumed that the dc magnetic field H_0 is applied in the z direction along a principal axis of the ellipsoid. The resonant condition is then

$$\omega_0=\gamma\{[H_0+(N_x-N_z)M+H_x{}^a]\times[H_0+(N_y-N_z)M+H_y{}^a]\}^{1/2}, \qquad (2)$$

where $H_x{}^a$ and $H_y{}^a$ are functions which depend on K_1/M, K_2/M, and the crystallographic orientation of the sample with respect to the dc magnetic field, M being the saturation magnetization. The functions $H_x{}^a$ and $H_y{}^a$ have been determined explicitly for the special cases that either a $\{100\}$ [24] or a $\{110\}$ [25] crystallographic plane contains both the dc applied field and the microwave magnetic field. The functions can be expressed as sums of $\cos 2\theta$, $\cos 4\theta$, and $\cos 6\theta$ terms, the coefficients containing the parameters K_1/M and K_2/M, and θ is the angle between the dc field and a $\langle 100\rangle$ direction. The effect of geometrical demagnetization appears in the form of differences of the ellipsoidal demagnetizing factors. For spherical samples $N_x=N_y=N_z=\frac{1}{3}$ and no shape dependence appears in the resonant condition.

For the special cases mentioned above and for spherical samples, the resonant condition can be written as

$$H_0=A+B\cos 2\theta+C\cos 4\theta+D\cos 6\theta, \qquad (3)$$

where H_0 is the applied magnetic field for resonance, A contains all constant terms and B, C, and D relate to the anisotropy constants as follows: For a sample rotated such that a $\{100\}$ crystallographic plane contains both the dc and microwave magnetic fields,

$$B=0,$$
$$C=-(5K_1/4M-K_2/8M),$$
$$D=0.$$

Similarly, for a sample rotated such that a $\{110\}$ plane contains both the dc and microwave magnetic fields,

$$B=-(5K_1/4M+5K_2/128M),$$
$$C=-(15K_1/16M+15K_2/64M),$$
$$D=21K_2/128M.$$

---

[18] A. J. Shuskus, Phys. Rev. **127**, 2022 (1962).

[19] J. Overmeyer and R. J. Gambino, Phys. Letters **9**, 108 (1964).

[20] B. A. Calhoun and J. Overmeyer, J. Appl. Phys. **35**, 989 (1964).

[21] H. W. White, D. C. McCollum, and J. Callaway, Phys. Letters **25A**, 388 (1967).

[22] F. J. Dyson, Phys. Rev. **102**, 1230 (1956).

[23] R. Kubo, Phys. Rev. **87**, 568 (1952).

[24] C. Kittel, Phys. Rev. **73**, 155 (1948).

[25] L. R. Bickford, Jr., Phys. Rev. **78**, 449 (1950).

Both anisotropy constants K_1/M and K_2/M can be determined from the rotational dependence of the resonant field in a $\{110\}$ plane via the coefficients of the $\cos 4\theta$ and $\cos 6\theta$ terms. The $\{100\}$ plane rotation has only a $\cos 4\theta$ term due to anisotropy. The coefficient of this term is a linear combination of the two anisotropy constants. A $\{100\}$ plane rotation can thus be used as a consistency check but does not provide an independent determination of K_1 and K_2.

EXPERIMENTAL METHOD

The europium selenide was synthesized by the direct reaction of europium and selenium metals at 1200°C in a sealed evacuated quartz ampule. By introducing sufficient selenium to both react the europium and produce a selenium vapor overpressure of approximately 30 atm at temperature, EuSe crystallites as large as 0.3–0.5 mm in largest dimension were formed. Emission-spectrograph and neutron-activation analyses were used to identify impurities.[26] The analysis showed this material to contain 1000 ppm silicon and 2200 ppm oxygen. A fractional distillation method similar to that used by Von Molnar and Lawson[14] to grow EuS was used to purify and grow crystals of EuSe. Using a carbon crucible and maintaining a vacuum of 1×10^{-6} Torr and a temperature difference of 150°C (with a maximum of 1700°C) over the length of the crucible, EuSe transported to the cooler end of the crucible forming a matrix of crystals up to 0.3 mm on a side. This distilled material had 10 ppm silicon and 400 ppm oxygen. No other detectable impurity was found either before or after distillation. As previously mentioned, spherical samples eliminate demagnetization considerations and are preferable. The technique for grinding spheres involved air tumbling crystals against a cushioned, abrasive surface and has been described in detail elsewhere.[27] Samples on the order of 100–150 μ in diam were ground to within approximately 1% of spherical. The samples were annealed at 1050°C *in vacuo* for about 10 h. The ferromagnetic linewidth decreased by about a factor of 2 upon annealing. An annealing temperature of 1100°C gave no additional linewidth reduction but did affect the surface appearance of the polished spheres. Crystal orientation to within 1° was achieved by a Buerger precession x-ray technique.[28] The apparatus was a standard microwave spectrometer and employed a balanced bridge. Magnetic-field modulation and phase-sensitive detection of the rectified microwave signal yielded data in the form of the first derivative of the power absorption versus dc magnetic field. The microwave cavity was similar to that used by Tannenwald.[29] The sample could be rotated during the experiment with the axis of rotation perpendicular to both the applied dc field and the microwave magnetic field.

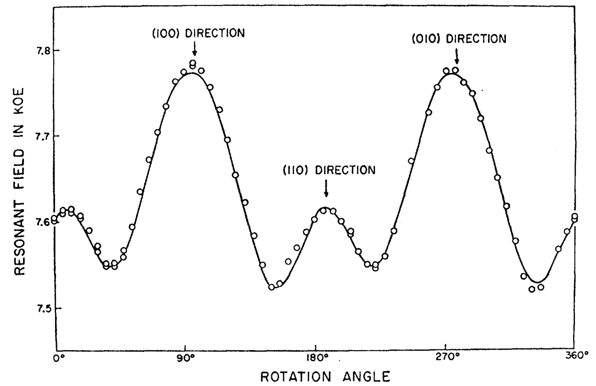

FIG. 1. Resonant field as a function of rotation angle in an EuSe single-crystal sphere oriented such that a $\{110\}$ crystallographic plane contains both the applied dc and the microwave magnetic fields. The circles are data points. The solid line is the least-squares fit of the resonant condition including ellipticity to the data.

Examination of the samples under a microscope at various stages of the sphere-grinding process showed that the crystals became ellipsoids first, then ground themselves more spherical. It was assumed, therefore, that the primary departure from sphericity would be ellipticity. An ellipsoidal sample, however, will contribute a $\cos(2\theta+\alpha)$ term to the angular dependence of the resonant condition.[14] The phase α allows that the ellipsoidal principle axis may not lie in a $\langle 100\rangle$ direction. The coefficient of this $\cos(2\theta+\alpha)$ term contains differences of the demagnetizing factors and is zero for spherical samples. The demagnetizing coefficient for EuSe samples with major to minor axis ratio of 1.01 is approximately 30 Oe. The $\cos(2\theta+\alpha)$ term is the first term in an harmonic expansion of the demagnetization for an arbitrarily shaped sample. Asphericity which is different from ellipticity would therefore contribute $\cos(4\theta+\beta)$, $\cos(6\theta+\delta)$, and higher-order terms, in principle affecting the determination of K_1/M and K_2/M. Any such contribution due to nonelliptical asphericity, however, was less than the experimental uncertainty.

The resonant field as a function of rotation in a particular crystallographic plane was measured at 6° intervals over at least 180°. The data were then computer fit to the multiparameter resonant condition, Eq. (3), with the additional $\cos(2\theta+\alpha)$ term corresponding to that crystallographic plane. The anisotropy constants were calculated from the coefficients of the relevant cosine terms. Figure 1 shows the results of an experimental run in which the sample was rotated in a

---

[26] The analyses were kindly provided by H. W. White and were also quoted in Ref. 21.

[27] R. F. Brown, M. C. Franzblau, and J. W. Battles, Rev. Sci. Instr. **38**, 1591 (1967).

[28] M. J. Buerger, *The Precession Method in X-Ray Crystallography* (John Wiley & Sons, Inc., New York, 1964).

[29] P. E. Tannenwald, Massachusetts Institute of Technology, Lincoln Laboratory, Technical Report No. 71, 1954 (unpublished).

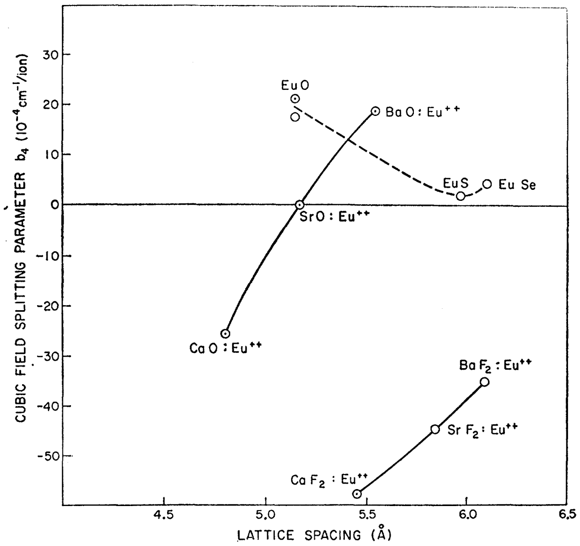

FIG. 2. The crystal-field splitting parameter b_4 versus lattice spacing determined for EuO, EuS, EuSe, and Eu^{++} ions in various host lattices.

{110} crystallographic plane. The circles are the data points and the solid line is the plot of the resonant condition (including ellipticity) using the computed parameters.

THEORY

As discussed in the Introduction, the two theories most often quoted to explain magnetic anisotropy are due to Van Vleck[11] and to Wolf.[12] The first-order anisotropy constants of EuO [15,16] and EuS [17] are too large to be accounted for by Van Vleck's mechanism. Wolf's theory deals with the splitting of the degenerate magnetic spin state (in this case the $4f$ level) by the crystal field. It shows that cubic crystal-field splitting and an applied magnetic field would yield a free energy of the same form as Eq. (1). Anisotropy is therefore predicted by the crystal-field splitting. Paramagnetic resonance experiments on Eu^{++} ions in cubic host lattices[15–19,30,31] have determined the host crystal-field splitting parameters. Wolf's theory has been extended to the spin-$\frac{7}{2}$ system by Baker *et al.*[31] The spin Hamiltonian for a single ion in an $^8S_{7/2}$ ground state may be written as

$$\mathcal{H}=g\mu_B\mathbf{H}\cdot\mathbf{S}+B_4[\hat{O}_4{}^0+5O_4{}^4]+B_6[\hat{O}_6{}^0-21O_6{}^4], \quad (4)$$

where the $O_j{}^i$ are spin operators and B_4 and B_6 are constants related to the splitting parameters by

$$b_4=60B_4, \qquad b_6=1260B_6. \quad (5)$$

Von Molnar[32] related these cubic crystal-field splitting parameters to the magnetic anisotropy constants, the results being

$$K_1=b_4f(y)+b_6g(y), \qquad K_2=b_6h(y), \quad (6)$$

where

$$f(y)=(5/Z_0)(-7+13y+3y^2-9y^3-9y^4+3y^5+13y^6-7y^7),$$

$$g(y)=(7/2Z_0)(-3+15y-27y^2+15y^3+15y^4-27y^5+15y^6-3y^7),$$

$$h(y)=(1/2Z_0)(462-1155y+2079y^2-1155y^3-1155y^4+2079y^5-1155y^6+462y^7), \quad (7)$$

and

$$Z_0=(1+y+y^2+\cdots+y^7),$$

where

$$y=\exp(-g\mu_BH_{\mathrm{eff}}/kT). \quad (8)$$

The effective magnetic field H_{eff} in the exponential is the sum of the applied magnetic field and the molecular field.[33] The crystal-field splitting parameters b_4 and b_6 can thus be determined from the measured anisotropy constants K_1 and K_2.

RESULTS

The paramagnetic resonance was observed on a distilled single crystal of arbitrary shape at room temperature. Using DPPH [34] as a calibration, the g

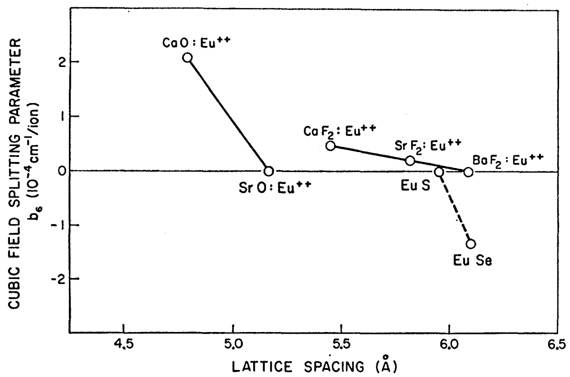

FIG. 3. The crystal-field splitting parameter b_6 versus lattice spacing determined for EuO, EuS, EuSe, and Eu^{++} ions in various host lattices.

---

[30] R. S. Title, Phys. Letters **6**, 13 (1963).

[31] J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) **A247**, 141 (1958).

[32] S. Von Molnar, Ph.D. thesis, University of California, Riverside, 1965 (unpublished).

[33] Errors have been found in the expressions for $f(x)$ and $g(x)$ in the paper of Franzblau, Everett, and Lawson (Ref. 17), corresponding to our expressions $f(y)$ and $g(y)$in Eq. (7). The coefficient of the $\cosh\frac{7}{2}x$ term in $f(x)$ should be -70, and the coefficients of the $\cosh\frac{3}{2}$, $\cosh\frac{5}{2}x$, and $\cosh\frac{7}{2}x$ terms in $g(x)$ should be -189, $+105$, and -21, respectively.

In addition, numerical errors were made in the calculations of both b_4 and b_6 from the measured anisotropy constants for EuS. The splitting parameter b_4 should be 1.80×10^{-4} cm^{-1}/ion instead of 0.27×10^{-4} cm^{-1}/ion and b_6 should be -0.07×10^{-4} cm^{-1}/ion instead of -0.02×10^{-4} cm^{-1}/ion.

[34] L. Van Guervan, A. Van Itterbeed, and L. De Lart, in *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962*, edited by W. Low (Academic Press Inc., New York, 1963).

TABLE I. Crystal-field splitting parameters b_4 and b_6 for Eu^{++} ions in various host lattices. The measured anisotropy constants K_1/M and K_2/M are included for the europium chalcogenides.

Compound	Lattice parameter (Å)	K_1/M (Oe)	K_2/M (Oe)	b_4 (10^{-4} cm^{-1}/ion)	b_6 (10^{-4} cm^{-1}/ion)	Ref.
$CaO:Eu^{++}$	4.80			−25.7	2.1	18
EuO	5.14	−190	···	17.5	···	15
		−230	···	21.2	···	16
$SrO:Eu^{++}$	5.16			0	0	19
$CaF_2:Eu^{++}$	5.45			−57.9	0.5	31
$BaO:Eu^{++}$	5.54			19	···	19
$SrF_2:Eu^{++}$	5.86			−44.9	0.24	30
EuS	5.96	−19.6	−4.6	1.8	−0.07	17
$BaF_2:Eu^{++}$	6.18			−36	0	30
EuSe	6.19	−50	−83	4.5	−1.3	a

[a] This work.

value was determined to be 2.04. The linewidth was 1.4 kOe. The angular dependence of the magnetic field for resonance in the ferromagnetic state was measured on samples oriented such that the dc field always lay in a {110} crystallographic plane. Measurements were made on seven different samples. Three of the samples were from material that had not been distilled and four were from material that had. The linewidths of samples from undistilled material were approximately 100 Oe and from distilled material were 50–75 Oe. The g value at ~1.3°K was found to be 1.98±0.01 and was apparently unchanged due to distilling the starting material. The first- and second-order anisotropy constants were measured to be $K_1/M = -50\pm6$ Oe and $K_2/M = -83\pm16$ Oe. The saturation magnetization is 13 700 G for EuSe.[3,4] The anisotropy constants are

$$K_1 = -(5.4\pm0.6)\times10^4\ \mathrm{erg/cm^3}$$
$$= -(1.6\pm0.2)\times10^{-2}\ \mathrm{cm^{-1}/ion},$$
$$K_2 = -(9.1\pm1.8)\times10^4\ \mathrm{erg/cm^3}$$
$$= -(2.7\pm0.6)\times10^{-2}\ \mathrm{cm^{-1}/ion}.$$

The cubic crystal-field splitting parameters can be calculated on the basis of Wolf's theory by using Eqs. (6)–(8). The value of the molecular field for EuSe was determined from the magnetization as a function of temperature measurements of Enz *et al.*[3] In the presence of a large magnetic field (32.1 kOe), they found the magnetization to be described by a Brillouin function consistent with molecular field theory. The best fit of the Brillouin function to the data resulted with an internal molecular field value at $T=0$°K of 2.98×10^4 Oe. At 1.3°K, the Brillouin functions for zero magnetic field and 32.1 kOe differ from this value by no more than 2%. Therefore, using this value of the molecular field in Eq. (8) gives the cubic field splitting parameters of EuSe to be

$$b_4 = (4.5\pm0.5)\times10^{-4}\ \mathrm{cm^{-1}/ion},$$
$$b_6 = -(1.3\pm0.3)\times10^{-4}\ \mathrm{cm^{-1}/ion}.$$

DISCUSSION

Consistent with the conclusions of Von Molnar and Lawson[14] in EuS, the paramagnetic linewidth in EuSe can also be explained in terms of classical dipolar broadening. The anisotropy constant K_1/M is therefore too large to be explained by the Van Vleck mechanism based on the estimate of Von Molnar and Lawson.[14] This is also consistent with the conclusions of Miyata and Argyle[16] for EuO. The cubic crystal-field splitting parameters b_4 and b_6 calculated from the anisotropy constants on the basis of Wolf's single-ion mechanism are of the same magnitude as those determined for Eu^{++} ions in other host systems. Table I summarizes the crystal-field splitting parameters determined from anisotropy measurements in the europium chalcogenides and directly for Eu^{++} ions in various host lattices. Figures 2 and 3 compare the parameters b_4 and b_6, respectively, determined for Eu^{++} ions in the various host lattices as functions of lattice spacing. The splitting parameters of both the oxide and fluoride systems doped with Eu^{++} ions are monotonic functions of lattice spacing. Specifically, b_4 increases and b_6 decreases with increasing lattice parameter. Measurements of the first-order magnetic anisotropy in the three ferromagnetic europium chalcogenides, however, indicate b_4, as calculated on the basis of Wolf's model, goes through a minimum and is positive. The second-order anisotropy constant has not been measured in EuO. From Eq. (6), b_4 depends on both K_1 and K_2. However, the measurement of K_2 should make only a small correction to the determination of b_4 (unless K_2 is several times as large as K_1). The splitting parameter b_6 is determined by the value of K_2 and has not been measured for EuO. The parameter b_6 is negative for both EuS and EuSe with the latter having the larger magnitude. At present this dependence of b_4 and b_6 on lattice spacing is not understood.

Experiments to determine K_1/M and K_2/M in EuO as well as the temperature dependence of the anisotropy constants in the three ferromagnetic europium chalcogenides are in progress. The results of these experiments, and in particular the temperature dependence, should more critically test the single-ion mechanism as being the source of magnetic anisotropy in this series of compounds.

SUMMARY

The first- and second-order magnetocrystalline anisotropy constants of EuSe are $K_1/M=-50\pm6$ Oe and $K_2/M=-83\pm16$ Oe. On the basis of Wolf's single-ion mechanism, the cubic crystal-field splitting parameters have been calculated to be $b_4=(4.5\pm0.5)\times10^{-4}$ cm^{-1}/ion and $b_6=-(1.3\pm0.3)\times10^{-4}$ cm^{-1}/ion. The comparison of these values with b_4 and b_6 determined from anisotropy measurements in EuO and EuS indicate a minimum in b_4 as a function of lattice spacing. This is in contrast to the monotonically increasing values of b_4 for Eu^{++} ions as a function of lattice spacing in oxide (CaO, SrO, and BaO) and fluoride (CaF, SrF, and BaF) host systems. The value of b_6 is negative and decreases with increasing lattice parameter for EuS and EuSe, which is consistent with the other cubic host systems.

ACKNOWLEDGMENTS

We thank H. W. White for furnishing the impurity analyses of the europium selenide used in the experiment. We also thank Dr. M. C. Franzblau for developing the computer program used to fit the resonant condition to the data.

PHYSICAL REVIEW VOLUME 172, NUMBER 2 10 AUGUST 1968

Dielectric, Thermal, and Pyroelectric Properties of Ferroelectric $\mathrm{LiTaO_3}$

A. M. GLASS
Bell Telephone Laboratories, Murray Hill, New Jersey

(Received 4 March 1968)

Measurements of the dielectric constant κ, specific heat c_p, and pyroelectric coefficient dP_s/dT of $\mathrm{LiTaO_3}$ have been made over the temperature range from 25 to 700°C. The experimental technique enabled all these measurements to be made simultaneously or consecutively on the same sample. In each of these measurements pronounced anomalies were observed at the ferroelectric Curie temperature $T_C=618$°C, clearly indicating a transition of the second order. From the pyroelectric and specific-heat measurements, the temperature dependence of the spontaneous polarization has been obtained to within 5% accuracy. At temperatures T where $T/T_C\gtrsim0.9$ it was found that $P_s^2\propto(T-T_C)$ and $1/\kappa\propto(T-T_C)$, in accordance with thermodynamic theory, and the specific-heat data are entirely consistent with these measurements.

I. INTRODUCTION

It has been known for several years that $\mathrm{LiTaO_3}$ is ferroelectric up to about 600°C.[1] Ferroelectric hysteresis loops were observed in this material under certain conditions, and the spontaneous polarization was found to be an increasing function of temperature up to 470°C.

Recently, a great deal of interest in this material has been revived owing to its large electro-optic coefficients and its use for devices.[2] However, with Czochralski-grown crystals[3] no ferroelectric hysteresis loops have been observed owing to the high coercive field at low temperatures, and the high conductivity at elevated temperatures. In this work attempts to switch $\mathrm{LiTaO_3}$ below 500°C, using platinum electrodes, were unsuccessful. Even at 550°C the switching time was several minutes with 10 000 V/cm.

Two measurements of the spontaneous polarization P_s of $\mathrm{LiTaO_3}$ have recently been reported. The first measurements, by a static pyroelectric technique,[4] yielded a room-temperature value of $P_s=50\pm2\ \mu\mathrm{C/cm^2}$. Measurements of P_s up to 450°C were reported in this work. The second measurements[5] were obtained by switching $\mathrm{LiTaO_3}$ at room temperature using liquid electrodes and very high pulsed fields ($\sim5\times10^5$ V/cm). These experiments were limited to the temperature range 0 to 100°C since an aqueous electrolyte was used.

---

[1] B. T. Matthias and J. P. Remeika, Phys. Rev. **76**, 1886 (1949).

[2] R. T. Denton, F. S. Chen, and A. A. Ballman, J. Appl. Phys. **38**, 1611 (1967).

[3] A. A. Ballman, J. Am. Ceram. Soc. **48**, 112 (1965).

[4] H. Iwasaki, N. Ushida, and T. Yamada, Japan. J. Appl. Phys. **6**, 1336 (1967).

[5] S. H. Wemple, M. DiDomenico, and I. Camlibel, Appl. Phys. Letters **12**, 209 (1968).