

Ferromagnetic and Paramagnetic Resonance in EuS*

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Ferromagnetic and paramagnetic resonance has been observed in single crystals of EuS. A standard microwave spectrometer, operating near 22 Gc/sec, was used to measure the power absorption at 1.4 and 300°K. The resonance line width, 75 Oe at 1.4°K, was found to be approximately 1200 Oe at room temperature. An upper limit of 30 Oe has been established for the magnitude of the magnetocrystalline anisotropy field, in contrast to the value of -190 Oe found for EuO. The paramagnetic line width is explained solely on the basis of spin-spin interactions. The anisotropy results are understood in terms of crystal-field perturbations of the magnetic Eu²⁺ ion.

I. INTRODUCTION

THE properties of the europium chalcogenides (EuO, EuS, EuSe, EuTe) have been of considerable interest ever since Matthias *et al.*¹ discovered that EuO is ferromagnetic. These primarily ionic compounds have the NaCl structure and their resistivities² and optical absorption spectra³ suggest that they may be classified as semiconductors. With the exception of EuTe, which is antiferromagnetic, all of them are ferromagnets at low temperatures.² In addition, the Eu²⁺ ion has, according to Hund's rules, a $S_{7/2}$ ground state and should be relatively insensitive to crystalline fields. The Heisenberg⁴ model of localized spins and the molecular-field approximation⁵ should consequently be valid.

This conclusion has stimulated much research,⁶⁻⁹ which has demonstrated that the localized spin model is essentially correct. Indeed, Charap,¹⁰ using spin-wave theory, was able to make a simultaneous fit of Boyd's NMR data and the low-temperature specific-heat data of McCollum¹¹ in EuS. This treatment led to the conclusion that the nearest-neighbor exchange energy $J_1/k=0.20^\circ\text{K}$ and that the next-nearest-neighbor exchange energy $J_2/k=0.08^\circ\text{K}$. These values for J_1

and J_2 are in agreement with molecular-field estimates.¹² Further confirmation for these exchange energies came from EPR studies¹³ of coupled pairs of Eu²⁺ ions in CaO and SrO, where it was found that $J_1>0$ and $|J_2|\ll J_1$. Nonetheless, the foregoing experimental and theoretical arguments have not given any direct evidence of the microscopic source of the exchange.

The purpose of this paper is to report the results of paramagnetic and ferromagnetic resonance experiments in single-crystal EuS. Cooper and Keffer¹⁴ have suggested that measurements of the paramagnetic line width ΔH and first-order magnetocrystalline anisotropy constant K_1 can lead to an absolute determination of Van Vleck's¹⁵ pseudodipolar coupling constant D and pseudoquadrupolar coupling constant Q .

Kanamori¹⁶ has reviewed the microscopic origin of these "pseudo" terms. He has pointed out that such interactions, if they exist, are almost entirely of an electrostatic nature. The electrostatic interactions consist of Coulomb interactions, direct-exchange interactions, and indirect-exchange interactions. Their strength, according to Wolf,¹⁷ is roughly proportional to $(g-2)^4$, where g is the spectroscopic splitting factor. Experimental determinations of g , D , and Q should consequently help in understanding the origin of inter-ionic coupling processes.

Section II of this report discusses the experimental details of sample preparation and microwave measurements. Sections III and IV present the experimental results and a discussion of these results in the light of present theoretical knowledge.

Since the inception of this investigation, Dillon¹⁸ has reported similar experiments in EuO. As will be shown, the EuS results are consistent with Dillon's work. The conclusion is, that the pseudodipolar and pseudoquadrupolar mechanisms are not important in EuS.

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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, *Proceedings of the International Conference on Semiconductors, Exeter* (The Institute of Physics and the Physical Society, London, 1962), p. 727.

³ G. Busch, P. Junod, and P. Wachter, *Phys. Letters* **12**, 11 (1964).

⁴ W. Heisenberg, *Z. Physik* **38**, 411 (1926).

⁵ P. Weiss, *J. Phys.* **6**, 661 (1907).

⁶ T. R. McGuire, B. E. Argyle, M. W. Shafer, and J. S. Smart, *Appl. Phys. Letters* **1**, 17 (1962); *J. Appl. Phys.* **34**, 1345 (1963).

⁷ S. Van Houten, *Phys. Letters* **2**, 215 (1962); U. Enz, J. F. Fast, S. Van Houten, and J. Smit, *Phillips Res. Rept.* **17**, 1451 (1962).

⁸ R. L. Wild and R. D. Archer, *Bull. Am. Phys. Soc.* **7**, 440 (1962).

⁹ D. T. Teaney and V. L. Moruzzi, *Bull. Am. Phys. Soc.* **8**, 55 (1963).

¹⁰ S. H. Charap and E. L. Boyd, *Phys. Rev.* **133**, A811 (1964).

¹¹ D. C. McCollum and J. Callaway, *Phys. Rev. Letters* **9**, 377 (1962); *Phys. Rev.* **130**, 1741 (1963).

¹² T. R. McGuire and M. W. Shafer, *J. Appl. Phys.* **35**, 984 (1964).

¹³ B. A. Calhoun and J. Overmeyer, *J. Appl. Phys.* **35**, 989 (1964).

¹⁴ B. R. Cooper and F. Keffer, *Phys. Rev.* **125**, 896 (1962).

¹⁵ J. H. Van Vleck, *Phys. Rev.* **52**, 1178 (1937).

¹⁶ J. Kanamori, *Magnetism 1* (Academic Press Inc., New York, 1963) pp. 157-167.

¹⁷ W. P. Wolf, *Phys. Rev.* **108**, 1152 (1957).

¹⁸ J. F. Dillon, Jr. and C. E. Olsen, *Phys. Rev.* **135**, A434 (1964).

In addition, a qualitative understanding of the magneto-crystalline anisotropy is possible in terms of Wolf's¹⁷ single-ion mechanism.

II. EXPERIMENTAL METHOD

A review of ferromagnetic resonance has been given by Kittel.¹⁹ He derives the resonance equation for a single-crystal ferromagnet. If the applied magnetic field is contained in a (100) plane of a cubic crystal, the expression becomes

$$\omega_0 = \gamma \left[\{H_z + (N_x - N_z)M + (2K_1/M) \cos 4\theta\} \times \{H_z + (N_y - N_z)M + (K_1/M) (\frac{3}{2} + \frac{1}{2} \cos 4\theta)\} \right]^{1/2}. \quad (1)$$

Here H_z is the applied dc magnetic field. N_x , N_y , and N_z represent the geometric demagnetizing factors along the principal axes of a generalized ellipsoid. M is the saturation magnetization, K_1 is generally referred to as the first-order magnetocrystalline anisotropy constant. The angle between the z axis and a $[100]$ direction is denoted by θ . The constant γ is equal to $g\beta/\hbar$, where g is the spectroscopic splitting factor, β is the Bohr magneton, and \hbar is Planck's constant divided by 2π .

It is seen by inspection of Eq. (1) that a spherical sample is desirable. In that case the resonance frequency ω_0 depends only on the applied field and the anisotropy field K_1/M . Since ω_0 and H_z are measurable quantities, γ (or g) and K_1/M can, in principle, be obtained by measuring the resonance at two points of different θ . In some cases, however, it is advisable to plot out the entire angular variation as a function of resonance field. Any misalignment of the crystal or deviation from sphericity will cause noticeable deviations from the characteristic $\cos 4\theta$ behavior.

The EuS powder was synthesized in a manner similar to that described by Wild and Archer.⁸ Direct measurements of the magnetocrystalline anisotropy require single-crystal samples, so considerable time was given to developing a technique for growing single crystals. Satisfactory crystals were made by heating the powder with an induction heater to approximately 1700°C under vacuum in a shielded graphite crucible. Before beginning the crystal growing procedure, it is advisable to clean the graphite crucible by heating it to 1000°C *in situ* for several hours under vacuum. This removes any surface films and most impurities in the graphite. The system is then flushed with helium and the crucible is carefully removed and loaded with EuS.

As Achard²⁰ points out, europium does not form a carbide. Thus, no unusual precautions are necessary and the powder may be placed in direct contact with the crucible. The system is then slowly evacuated to approximately 20 μ Hg. Operating conditions for making crystals approximately 0.4 mm along a cube edge are as follows: Growing temperature $\geq 1700^\circ\text{C}$; growing time ≥ 6 h; estimated temperature gradient = 200°C.

Upon cooling, one finds a matrix of small crystals deposited on the cap and top edge of the crucible. X-ray powder patterns of material ground from these crystals are in excellent agreement with Nowacki's results.²¹ Spectrographic analysis²² detected the following elements other than europium: 0.024% silicon, 0.0038% magnesium, and 0.014% calcium. No rare earths or paramagnetic impurities were present. Calcium is involved in the rare-earth metallothermic preparation and the silicon content presumably arises from the fact that the Eu_2O_3 is in contact with quartz during its transformation to EuS.

Needles, as well as crystal cubes carefully picked out of the matrix, were used as starting material for the preparation of spheres. Approximately 20 pieces can be machined at one time in a tumbling device similar to the design of I. E. Gugler.²³ Wheels Nos. 37C320-J8E and 37C500-J9E obtained from the Norton Company are used in succession. The resulting roughed-out samples are then examined for sphericity and surface smoothness and separated with a fine hairbrush. The final polish is obtained with the apparatus described by Carter *et al.*²⁴ The abrasive surface is a 4- μ commercial emery cloth glued onto a horizontally rotating wheel. The sample is confined in a suitable hypodermic needle ground flat on the end. Generally, this treatment produced flats on the sample surface, but an air stream (approximately 5 lbs. pressure) directed into the top of the needle produces sufficient turbulence at the sample to prevent preferential grinding of one portion of the surface. Starting with about 50 roughed out pieces, it was possible to make four samples, whose ellipticity did not exceed 10%. The final sample diameter is approximately 0.1 mm.

An accurate determination of nonsphericity was made by photographing the sample to a total enlargement of 160 \times .

The magnetic field H required to sweep out the magnetic domains in a spherical sample must be greater than $\frac{4}{3}\pi M_0$. Here M_0 means the maximum magnetization obtained experimentally at any given temperature in the ferromagnetic region. This means that unless the resonance occurs at $H \geq \frac{4}{3}\pi M_0$, the experiment is being performed on a sample whose magnetization, and consequently, whose rf susceptibility is changing appreciably with the field. Such variations cause asymmetry in the line shape, and for this reason the present experiment was performed at 21.48 and 21.98 Gc/sec. Under these circumstances, since $4\pi M_0 = 13\,600$ G in EuS,⁷ the magnetic field at resonance will be much greater than $\frac{4}{3}\pi M_0 = 4530$ Oe.

The derivative of the power absorption as a function of magnetic field was detected with a standard micro-

²¹ W. Nowacki, Z. Krist. **99**, 339 (1938).

²² Performed by Pacific Spectra Chemical Laboratories, Los Angeles, California.

²³ I. E. Gugler, Pribory i Tekhnika Eksperimenta **5**, 145 (1954).

²⁴ J. L. Carter, E. V. Edwards, and I. Reingold, Rev. Sci. Instr. **30**, 946 (1959).

¹⁹ C. Kittel, J. Phys. Radium **12**, 291 (1951).

²⁰ J. C. Achard, Compt. Rend. **257**, 1087 (1963).

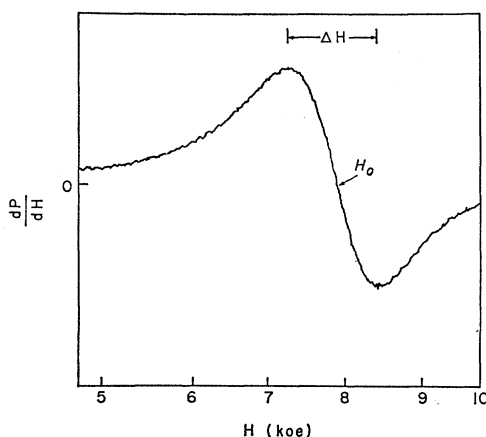


FIG. 1. Derivative with respect to magnetic field of the power absorbed in single-crystal EuS at 300°K. The microwave frequency is 21.98 Gc/sec. The line width ΔH and resonant field H_0 are indicated.

wave spectrometer designed to respond to a field-modulated signal. The static field was measured indirectly by monitoring the current passing through the low-impedance magnet coils. The linearity of the field with current, was checked with a Rawson-Lush type 720 rotating coil gauss meter, and a one-point calibration of the field was then made against the well known g factor of DPPH (diphenylpicrylhydrazil).²⁵

A cavity suitable for single-crystal measurement, similar to the design of Tannenwald,²⁶ was used to investigate the anisotropy field. The crystal, oriented by means of transmission Laue techniques, was mounted on a rotatable post so that the perpendicular to the (100) plane lay along the axis of rotation. The sample was positioned sufficiently far away from the cavity back plate to avoid image effects. The resonance was then observed as a function of crystal orientation with respect to the applied magnetic field.

EuS has a Curie temperature of 16°K.⁷ Provisions were consequently made to immerse the sample into a standard double Dewar system with appropriate pumping facilities to reduce the temperature below the normal boiling of helium. The paramagnetic measure-

TABLE I. Paramagnetic-and-ferromagnetic-resonance data for EuS.

Sample	Temperature (°K)	ΔH (kOe)	g	K_1/M (Oe)
EuS single crystal (arbitrary shape)	300	1.20 ± 0.03	2.002 ± 0.004	...
EuS single crystal sphere ($D=0.1$ mm)	1.4	0.075	1.996 ± 0.010	≤ 30

²⁵ L. Van Gerven, A. Van Itterbeed, and L. DeLaet, *Proceedings of the First International Conference on Paramagnetic Resonance, Jerusalem, 1962* (Academic Press Inc., New York, 1960), p. 905.

²⁶ P. E. Tannenwald, Tech. Rept. 71, MIT Lincoln Laboratory, 1954 (unpublished).

ments were performed at room temperature. Ferromagnetic studies were carried out at 1.4°K.

III. EXPERIMENTAL RESULTS

Table I summarizes the results of the resonance experiment in both the paramagnetic and ferromagnetic regions. Figures 1 and 2 are reproductions of experimental curves and represent some of the better examples of the resonance data. It is to be noted that ΔH is a measure of the distance between points of maximum slope of the power absorption. H_0 defines the field at which the power absorption is a maximum.

At room temperature, in the paramagnetic region, g may be inferred directly from the equation

$$g = (h/\beta)(\nu/H_0). \quad (2)$$

The resonance spectrum was independent of crystal orientation within the experimental error and, consequently, demagnetizing effects were negligible. Furthermore, linewidth corrections were unnecessary because their contribution to H_0 was less than 0.01%. The values for ΔH and g quoted in Table I are averages over all orientations, together with their average error.

In the ferromagnetic region, at 1.4°K, Eq. (1) is applicable. Figure 3 exhibits the angular dependence of H_0 in the ferromagnetic state. Although the theory [see Eq. (1)] predicts a $\cos 4\theta$ dependence due to magnetocrystalline anisotropy, the experiment indicates almost pure $\cos 2\theta$ behavior.

The explanation for this can be obtained from closer examination of Eq. (1). If the sample is not completely spherical, the geometric demagnetization factors no longer cancel and must be included in the resonance condition. Photographic analysis of the sample *in situ* proved that the experiment was being performed on a shape best approximated by an ellipsoid of revolution

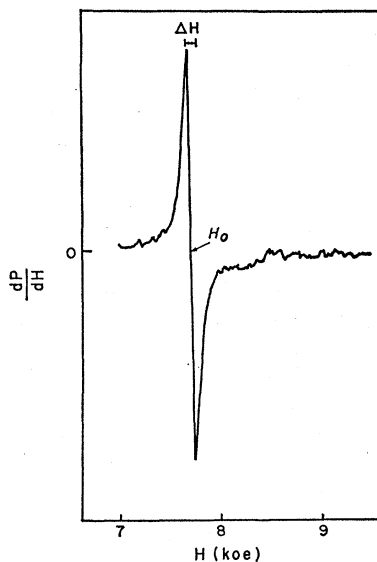


FIG. 2. Derivative with respect to magnetic field of the power absorbed in single-crystal EuS at 1.4°K. The microwave frequency is 21.48 Gc/sec. The line width ΔH and resonant field H_0 are indicated.

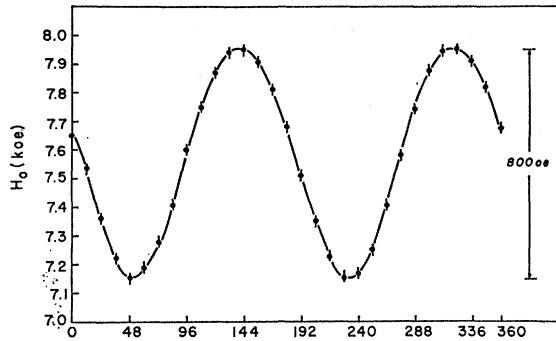


FIG. 3. Resonance field H_0 as a function of sample orientation at 1.4°K . The angle is measured between the incident magnetic field and the $[100]$ direction in the (100) plane.

with axis ratio $R=0.925$. The photograph also recorded the physical position of the ellipsoid with respect to the plane of rotation of the magnetic field. With this information it is possible to derive the angular variation of the resonance condition including geometric demagnetizing effects. Since we were rotating about a minor axis of the ellipsoid, we find

$$\omega_0/\gamma = H_z + \delta H + \delta H^a = H_0 + \delta H + \delta H^a, \quad (3)$$

where, for $H_0 \gg \delta H + \delta H^a$,

$$\delta H = \frac{1}{4}M(1 + 3 \cos 2\theta)\Delta N \quad (4)$$

and

$$\delta H^a = (K_1/4M)(3 + 5 \cos 4\theta). \quad (5)$$

Here ΔN is the difference in magnetization factors between the major and minor axes.

To test the validity of the assumption that the $\cos 2\theta$ behavior is due to geometric effects, we calculate the axial ratio, R , from the experimental data. The peak to peak amplitude, through Eq. (4) is given by

$$\delta H_{\max} = \frac{3}{2}M\Delta N. \quad (6)$$

Substituting the experimental values $\delta H_{\max} = 800$ Oe (see Fig. 3) and $4\pi M = 13\,600$ G (Ref. 7); we obtain $\Delta N = 0.0391$. Thus

$$N_y = N_x = 0.346, \quad N_z = 0.308. \quad (7)$$

Plots of demagnetizing factors as a function of axial

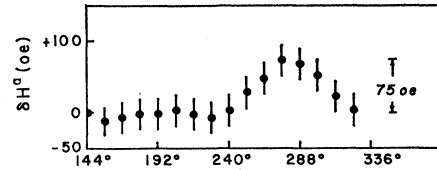


FIG. 4. Deviation of the resonance field H_0 from $\cos 2\theta$ behavior as a function of sample orientation at 1.4°K . The angle is measured between the incident magnetic field and the $[100]$ direction in the (100) plane.

ratio are given by Osborn.²⁷ From these graphs, one obtains $R=0.92$. This is in excellent agreement with the observed value.

Two other pieces of information may be extracted from Fig. 3. First, by adding δH to the data, it is possible to investigate the contribution due to magneto-crystalline anisotropy. With $\delta H^a = (K_1/4M)(3 + 5 \cos 4\theta)$ and the peak to peak amplitude, δH_{\max} , equal to 75 Oe, we find

$$K_1/M \leq 30 \text{ Oe}. \quad (8)$$

Reference is made to Fig. 4 in which the maximum excursion of the curve is associated with the amplitude of a $\cos 4\theta$ variation. In this way we estimate the anisotropy field to be 30 Oe. However, it is clear that the curve of Fig. 4 does not vary as $\cos 4\theta$ and it is highly likely that this residual variation arises from the fact that the specimen is not perfectly ellipsoidal. For this reason we believe that the maximum value of K_1/M is overestimated and that its true value is probably much less.

Secondly, in the region where the deviation from $\cos 2\theta$ behavior is negligible, a g factor may be calculated. The value $g = 1.996 \pm 0.010$ is in good agreement with the predictions of Lacroix²⁸ and a variety of EPR experiments with Eu^{2+} ions.^{13, 29, 30}

IV. CONCLUSIONS

Paramagnetic Region

Cooper and Keffer¹⁴ have calculated the paramagnetic linewidth of a cubic ferromagnet in the high-temperature approximation using their results, we obtain

$$\Delta H = \frac{2 \times 12\pi^{1/2} S(S+1) D^2}{\sqrt{3} g \beta J \left[\frac{3}{8}(2S+3)(2S-1) + \frac{4}{3} S(S+1) \times 21 + 8S(S+1) \right]^{1/2}} = 1020 \text{ Oe}, \quad (9)$$

where the factor $2/\sqrt{3}$ arises from our definition of the line width. The quadrupolar term in Cooper's¹⁴ expression has been neglected. S is the angular momentum quantum number and D and J are the dipolar coupling constant and the exchange energy, respectively. In the evaluation of Eq. (9), the classical expression $D = g^2 \beta^2 / r^3$ has been used. Here r is the distance between neighboring Eu^{2+} ions. J is determined by the molecular

field approximation from the experimental Curie temperature.

Comparison with experiment, where $\Delta H \approx 1200$ Oe, is quite favorable for this type of calculation. One has

²⁷ J. A. Osborn, Phys. Rev. **67**, 351 (1945).

²⁸ R. Lacroix, Helv. Phys. Acta **30**, 374 (1957).

²⁹ A. J. Shuskus, Phys. Rev. **127**, 2022 (1962).

³⁰ J. Overmeyer and R. J. Gambino, Phys. Letters **9**, 108 (1964).

only to look at White's³¹ calculation of linewidths in substances such as MnF₂ and yttrium and gadolinium iron garnets to appreciate this fact. The calculation shows that the linewidth can be explained on the basis of spin-spin interactions only. $D = g^2\beta^2/r^3$ does not include any "pseudo" character, in agreement with the experimentally observed $g = 2.00$. We may, therefore, conclude that the pseudodipolar and pseudo-quadrupolar interactions are negligible in EuS.

Ferromagnetic Region

It is noteworthy that $\Delta H = 75$ Oe. Although this number probably does not represent the intrinsic linewidth of EuS, it does mean that the experiment is being performed on relatively good samples.

The most striking feature of the experimental results at 1.4°K is the magnitude of the anisotropy field, $K_1/M \leq 30$ Oe, compared to the value obtained by Dillon¹⁸ for EuO, $K_1/M = -190$ Oe.

These measurements, incidentally, are consistent with the observation that there is no low-field absorption in EuS, whereas, in the EuO experiment, low-field effects were reported. Dillon¹⁸ attributes these to domain rotation. Since a small anisotropy tends to increase the domain size, less absorption due to domain effects is to be expected in the EuS system.

If it is assumed that interionic processes account for the anisotropy, Van Vleck's result for the pseudodipolar contribution to K_1 should be valid. With $D = (g^2\beta^2)/r^3$, in agreement with the paramagnetic results, the expression yields

$$\left| \frac{K_1}{M} \right| = \left| \frac{9NSD^2}{16zJ} \right| < 0.3 \text{ Oe} \quad (10)$$

for both EuS and EuO. Here N is the number of magnetic ions per unit volume and z is the number of nearest neighbors. Under no circumstances can this mechanism explain the observed magnitudes in EuO and one is forced to consider other possibilities.

A qualitative understanding of the results is possible in terms of Wolf's¹⁷ single-ion mechanism. He derives the contribution to the anisotropy due to crystal-field effects. The resulting expression for K_1 is linear in the crystal-field splitting parameters, b_4 and b_6 . For Eu²⁺ ions $b_4 \gg b_6$. We may, therefore, write to first order

$$K_1 = Cb_4, \quad (11)$$

where C depends only on the ratio of the magnetization to its value at saturation for any $S_{7/2}$ state.

Since the basic physical difference between the several members of the chalcogenide series is their lattice parameter a_0 it is necessary that b_4 show a strong dependence on a_0 . The microscopic source of b_4 in S state systems is not well understood theoretically and predictions of the distance dependence of the splitting are consequently poor. There exists, however, experi-

TABLE II. Cubic-field splitting parameter b_4 for Eu²⁺ in oxide lattices, 4.2°K. The lattice constants of EuO and EuS have been included for comparison.

Lattice	a_0 (Å)	b_4 (10 ⁻⁴ cm ⁻¹)	References
CaO	4.810	-25.7	(29)
EuO	5.141		(7)
SrO	5.160	0	(13)
BaO	5.539	+19	(30)
EuS	5.968		(7)

mental evidence which supports the anisotropy results. Overmeyer and Gambino³⁰ have found that b_4 for Eu²⁺ ions in oxide lattices is very sensitive to changes in lattice parameter. In fact, b_4 goes through zero and changes sign.

Table II summarizes Overmeyer's³⁰ results. It must be pointed out that, as in all experiments where the paramagnetic ion is studied in a host lattice, the Eu²⁺ is an impurity whose surroundings are not exactly like those of Ca²⁺, Sr²⁺, or Ba²⁺. Furthermore, the behavior of the oxides may differ from that of the sulfides. Overmeyer's³⁰ results are, therefore, to be viewed as lending qualitative support to the conclusions that the anisotropy is due to crystal field perturbations.

The temperature dependence of the magnetocrystalline anisotropy is predicted on the basis of Wolf's¹⁷ single-ion mechanism. Furthermore, the selenide and telluride should reflect the dependence of the anisotropy on lattice parameter. We have started to carry out a systematic investigation of these properties in the europium chalcogenide series.

V. SUMMARY

The information derived from the investigation of the paramagnetic and ferromagnetic resonance in EuS may be summarized as follows:

(1) The paramagnetic line width in EuS is found to be 1200 Oe and is explained solely on the basis of magnetic dipole-dipole interactions without invoking more complicated electrostatic mechanisms. The experimental value, $g = 2.002 \pm 0.004$, confirms this conclusion.

(2) An upper limit of 30 Oe has been established for the magnetocrystalline anisotropy field. This is to be contrasted with a field of -190 Oe in EuO. The results are understood in terms of crystal field perturbations of the magnetic Eu²⁺ ion.

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³¹ R. L. White, Phys. Rev. **115**, 1519 (1959).