Magnetocrystalline Anisotropy of Europium Sulfide*

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The first- and second-order magnetocrystalline anisotropy constants, K_1 and K_2, of EuS were measured by a ferromagnetic resonance technique. The measurements were performed at 21.48 GHz and 1.35°K, and the sample was a small, highly polished strain-free single-crystal sphere, oriented so that the (110) plane contained both the rf and static magnetic fields. The linewidth was of order 10 Oe, the narrowest observed in a chalcogenide of europium and indicates the degree of perfection and purity of the sample. K_1/M and K_2/M (where M is the saturation magnetization) were determined to be -19.6 ± 1.0 and -4.6 ± 0.3 Oe, respectively. The cubic crystal-field splitting parameters b_4 and b_6 were calculated on the basis of Wolf's single-ion mechanism, and were determined to be $(0.268\pm0.014)\times10^{-4}$ and $(-0.019\pm0.09)\times10^{-4}$ cm^{-1}, respectively. The results are compared with the behavior of the Eu^{++} ion in cubic host lattices.

I. INTRODUCTION

RECENTLY, europium sulfide has become the subject of much research, as its magnetic behavior can be described both by semiclassical models such as the molecular-field approximation[1] and the localized spin model,[2] and by spin-wave theory.[3] The present authors have demonstrated[4] that the temperature dependence of the ferromagnetic resonance linewidth behaves as predicted by the Landau and Liftshitz equations of motion.[5]

The magnetocrystalline anisotrophy of EuS has been investigated in this laboratory by Von Molnar and Lawson[6] prior to the work described in Ref. 4, and it was concluded that Wolf's single-ion mechanism[7] could account for the magnitude of the first-order anisotropy constant K_1. The value of K_1 was not determined, but rather an upper limit of 30 Oe was assigned. Their sample exhibited a resonance linewidth of 75 Oe in the ferromagnetic region. Because of improvements in sample preparation during the investigation described in Ref. 4, which resulted in better sphericity and a decrease of the linewidth to ~5 Oe, it seemed worthwhile to reexamine the magnetic anisotropy of EuS in an attempt to determine the anisotropy constants.

The anisotropy energy E_a for a cubic crystal is given by[8]

$$E_a=K_1(\alpha_1^2\alpha_2^2+\alpha_2^2\alpha_3^2+\alpha_3^2\alpha_1^2)+K_2\alpha_1^2\alpha_2^2\alpha_3^2, \quad (1)$$

where the α_i are direction cosines of the magnetization with respect to the cube edges. Because the effective anisotropy field contributes to the *precessional* frequency of the magnetization and since this field depends on the relative crystallographic direction, it is possible to determine K_1 and K_2 in a resonance experiment by observing the variation of the applied static magnetic field required for resonance as a function of the angle between a crystal axis and the static field. The resonance condition may be expressed as

$$\omega/\gamma=H_{\rm appl}+H_a(\theta)=H_{\rm eff}, \quad (2)$$

in which $H_{\rm appl}$ is the applied field, $H_a(\theta)$ is the anisotropy field, and $H_{\rm eff}$ is the effective field, equal to the frequency ω divided by magnetomechanical ratio γ.

The anisotropy constants are incorporated by adding to the equation of motion a torque due to anisotropy, which gives rise to terms in Eq. (2) which involve K_1 and K_2. The angular variation of $H_a(\theta)$ depends on the crystallographic plane in which the applied d.c. magnetic field lies. Since for cubic crystals, the (110) plane contains the principal crystallographic directions ⟨100⟩, ⟨110⟩, ⟨111⟩, measurements are usually made with samples oriented in this plane, for then a single measurement of the angular dependence of $H_a(\theta)$ gives information about the anisotropy along the principal axes of the unit cell. In general, the resonant condition is[9]

$$H_{\rm eff}=[[H_{\rm appl}+(K_1/M)f_x(\theta)+(K_2/M)g_x(\theta)+\Delta_1N\cdot M]\times[H_{\rm appl}+(K_1/M)f_y(\theta)+(K_2/M)\times g_y(\theta)+\Delta_2N\cdot M]]^{1/2}, \quad (3)$$

where Δ_1N and Δ_2N are appropriate demagnetizing factors (which differ from zero only if the sample is aspherical), M is the saturation magnetization, and f_x, f_y, g_x, g_y are known trigonometric functions. Von Molnar and Lawson[6] performed their measurements with a sample oriented such that the static field was contained in a {100} plane. They observed an excursion in $H_{\rm appl}(\theta)$ of 800 Oe upon which was superimposed a variation

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of order 75Oe (1% of H_{eff}), which was used to compute an upper limit for K_1. The large variation in resonant field could be explained by a deviation from sphericity of 7% in their sample. This result indicated the need for specimens which were much more spherical, so that a small contribution to the angular variation of the applied field from the anisotropy would not be obscured by the effect of asphericity. Such samples were prepared in the course of the investigation described in Ref. 4 and were employed in the present experiment.

II. EXPERIMENTAL METHOD

The preparation of starting material and subsequent growth of single crystals of EuS were as described by Von Molnar and Lawson.[6] The fabrication of strain-free, highly polished (0.5 μ) spheres of diameter <0.1 mm is discussed in detail elsewhere,[4,10] and employs an air-driven tumbling device based on the method of Bond and others.[11] The degree of asphericity of the samples was, in the best cases, too small to be detected under magnification of 80 powers, and, as will be discussed, resulted in excursions in resonant field of 50 Oe, a factor of 16 smaller than observed by Von Molnar and Lawson.[6] These samples exhibited the most narrow ferromagnetic resonance lines observed in a chalcogenide of europium.

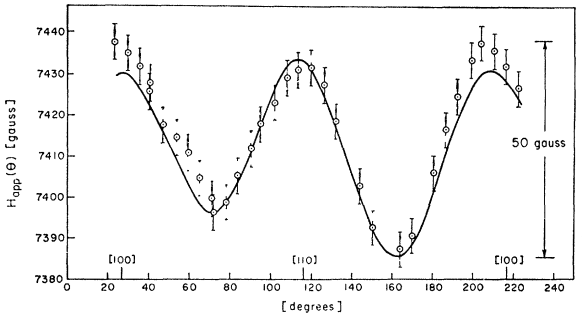

FIG. 1. The variation of resonant field $H_{\text{appl}}(z)$ as a function of angle between the static magnetic field and an arbitrary reference direction, with the specimen mounted such that the static and rf magnetic fields lie in a {110} plane.

The microwave apparatus was identical to that employed by Von Molnar and Lawson[6] and employed phase-sensitive detection. The magnetic field was determined with a rotating coil gaussmeter in conjunction with a differential voltmeter to a precision of $\pm 0.5\%$.

The sample was mounted on a rotatable post in a cavity based on the design of Tannenwald,[12] which resonated at a frequency of 21.48 GHz at ~ 1.3°K. The specimens were oriented on the post by means of x-ray precession photographs, to within ± 0.5° of the desired orientation. The measurement of the anisotropy consisted of recording the variation of $H_{\text{appl}}(\theta)$, the applied static magnetic field, as a function of θ, the angle between the [100] direction and $H_{\text{appl}}(\theta)$. With the sample mounted in the cavity, the uncertainty in the angle between the magnetic field and the crystallographic axes is estimated to be ± 3°.

TABLE I. Crystal-field parameters b_4 and b_6 in two types of host lattice, listed in order of increasing lattice parameter. The present results are included for each crystal type.

Host	a_0(Å)	T(°K)	$b_4(10^{-4}\ \text{cm}^{-1})$	$b_6(10^{-4}\ \text{cm}^{-1})$
CaO	4.88	4.2	-50.6 ± 0.5	1.5 ± 0.5[a]
SrO	5.14	4.2	0.0 ± 5	0.0 ± 5[b]
BaO	5.54	4.2	19.0[c]	...
EuS	5.96	1.35	0.268 ± 0.014	-0.019 ± 0.09
CaF_2	5.46	90	-58 ± 0.8	0.5 ± 0.2[d]
SrF_2	5.79	300	-44.9 ± 0.5	0.24 ± 0.5[e]
EuS	5.96	1.35	0.268 ± 0.014	-0.019 ± 0.09
BaF_2	6.20	300	-61.0 ± 0.7	0.0 ± 0.7[e]

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[d] J. M. Baker, B. Bleaney, and W. Hayes, Proc. Roy. Soc. (London) A**347**, 141 (1958).
[e] R. S. Title, Phys. Letters **6**, 13 (1963).

III. RESULTS AND DISCUSSION

Figure 1 illustrates the variation of $H_{\text{appl}}(\theta)$ as a function of angle between a ⟨100⟩ direction and the static magnetic field, with the sample in a {110} orientation (both the rf and static magnetic fields were contained in this plane).

In order to extract K_1 and K_2 from the data, Eq. (3) was expanded to first order following the treatment of Brown.[13] It is assumed that the sample shape may be approximated by an ellipsoid of revolution. Then rotation of the sample around any axis not a principal axis of the ellipsoid causes a variation in $H_{\text{appl}}(\theta)$ of period π and amplitude e, separated in phase from the anisotropy contribution by phase angle ϕ. Within this approximation, which greatly simplifies interpretation of the data, Eq. (3) may be written

$$H_{\text{eff}} = AH_0 + B\cos 2\theta + C\cos 4\theta + D\cos 6\theta + E\sin 2\theta, \quad (4)$$

TABLE II. Magnetocrystalline anisotropy constants of europium chalcogenides, listed in order of increasing lattice parameter.

Chalocogenide	a_0(Å)	K_1/M (Oe)	K_2/M (Oe)
EuO	5.14	-190[a]	...
EuS	5.96	-19.6 ± 1.0	-4.6 ± 0.3
EuSe	6.20	-45	-80[b]

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[12] P. E. Tannenwald, M.I.T. Lincoln Laboratory, Technical Report No. 71, 1954 (unpublished).
[13] R. F. Brown (private communication).

in which

$$\begin{aligned} H_0 &= \text{an estimate of the mean value of } H_{\text{appl}}, \\ A &= \text{a numerical coefficient representing the mean value of } H_0, \\ B &= -(5/4)K_1/M+(5/128)K_2/M+e\cos\phi, \\ C &= -(15/16)K_1/M-(15/64)K_2/M, \\ D &= (21/128)K_2/M, \\ E &= -e\sin\phi. \end{aligned} \tag{5}$$

Equation (4) represents the angular variation of $H_{\text{appl}}(\theta)$ in a form convenient for a computer analysis which employs all of the experimental data, and is much less laborious than the usual handfitting methods. Because of the estimated 3° uncertainty in the position of the [100] axis relative to the angle θ, this calculation is repeated at small angular intervals over the possible range of variation of the starting angle. The criterion for choosing the proper set of constants $A,\cdots,E$ is a minimum in the standard deviation.

The following values were obtained for the data presented in Fig. 1: $K_1/M=-19.6\pm1.0$ Oe, $K_2/M=-4.6\pm0.3$ Oe, $e=18.0\pm1.0$ Oe. The standard deviation of the data from the least-squares fitted curve (the solid line in Fig. 1) was 4.4 G, about 8% of the total excursion. The estimated error in the anisotropy constants is much smaller, however, because the coefficients $A,\cdots,E$ varied more slowly than the deviation.

The value of 18 G for the amplitude of the ellipticity indicates that in this particular orientation the departure from sphericity of the specimen was less than 1%. It should be noted that the fitted curve has extrema which coincide (within the estimated error) with the [110] and [100] axes, as anticipated.[14]

For rotation of the magnetic field in a {100} plane, the anisotropy should vary as $[5/4K_1/M-1/8K_2/M]\cos4\theta$, and from the results of the (110) plane measurement would be expected to have an excursion of ~22 G. Attempts to determine the value of this coefficient and thereby provide a consistency check with the (110) plane results were unsuccessful because of a very large asphericity contribution, characteristically of order 300 G. This large background variation of resonant field as a function of angle has precluded obtaining reliable values of the coefficient of the anisotropy for the (100) plane.

Von Molnar and Lawson[6] demonstrated that Van Vleck's[15] interionic model, which considers dipole-dipole interactions between magnetic ions and ignores the effect of crystalline fields, could not account for the magnitude of K_1/M in either EuO or EuS, since this model predicted a value of <-0.3 Oe. Wolf,[7] on the other hand, neglects the effect of dipolar interactions on the grounds that for materials with $g=2.00$ such as EuS, this type of coupling will be negligible. As will be demonstrated, the cubic crystal-field splitting parameters for the Eu^{++} ion in the EuS lattice can be derived from the anisotropy constants, on the basis of Wolf's single-ion mechanism. The "spin Hamiltonian" for a single ion in a ${}^8S_{7/2}$ ground state may be written[16]

$$H=g\beta\mathbf{H}\cdot\mathbf{S}+B_4[O^0_4+5O^4_4]+B_6[O^0_6-21O^4_6], \tag{6}$$

where the O operators describe the cubic crystalline field, and B_4 and B_6 are constants to be determined which are related to the crystal-field splitting parameters b_4 and b_6 by

$$b_4=60B_4, \qquad b_6=1260B_6. \tag{7}$$

Using the results of LaCroix[17] and Baker *et al.*,[18] and following the treatment of Wolf as extended to the case $S=\frac{7}{2}$ by Von Molnar,[19] the anisotropy constants and the crystal-field splitting parameters are found to be linearly related as given by

$$K_1=f(x)b_4+g(x)b_6, \qquad K_2=h(x)b_6, \tag{8}$$

where

$$\begin{aligned} f(x) &= \{\sum_{m=-S}^{S}\exp(mx)\}^{-1}(-90\cosh\tfrac{1}{2}x+30\cosh\tfrac{3}{2}x+130\cosh\tfrac{5}{2}x-140\cosh\tfrac{7}{2}x), \\ g(x) &= \{\sum_{m=-S}^{S}\exp(mx)\}^{-1}(105\cosh\tfrac{1}{2}x-159\cosh\tfrac{3}{2}x+30\cosh\tfrac{5}{2}x-42\cosh\tfrac{7}{2}x), \\ h(x) &= \{\sum_{m=-S}^{S}\exp(mx)\}^{-1}(-1155\cosh\tfrac{1}{2}x+2079\cosh\tfrac{3}{2}x-1155\cosh\tfrac{5}{2}x+462\cosh\tfrac{7}{2}x), \\ x &= g\beta H'/kT. \end{aligned} \tag{9}$$

Here $H'=H_{\text{ext}}+\lambda M$, where λM is the Weiss field and is the total internal magnetic field. The solution of

[14] The position of the minimum in $H_{\text{appl}}(z)$ is shifted from the [111] axis by about 5°, in agreement with the predictions of this model. See Ref. 9 for a discussion of this effect.
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Eq. (8) yields the following values for the crystal-field parameters:

$$b_4 = (0.268 \pm 0.014) \times 10^{-4}\text{cm}^{-1},$$

$$b_6 = (-0.019 \pm 0.009) \times 10^{-4}\text{cm}^{-1}.$$

Table I compares values of b_4 and b_6 for the Eu^{++} ion in hosts of two different cubic structures. The oxides have the NaCl structure, as does EuS, and the fluorides have the fluorite structure. The host lattices are listed in order in increasing lattice parameter. The strong dependence of the crystal-field parameters on interatomic separation, illustrated in Table I, is consistent with the small values inferred for EuS on the basis of our results. In particular, the change in sign of b_4 in the oxides, occurring at SrO, suggests a possible explanation for the small values of b_4 and b_6 exhibited by EuS. Table II lists the available data concerning K_1/M and K_2/M in the europium chalcogenides, which indicate that b_4 may be going through a minimum as a function of lattice parameter, rather than changing sign. The variation in b_4 in the fluoride series reinforces this opinion. One cannot easily extend this comparison to EuTe, the last number of the chalcogenide series, because it is an antiferromagnetic with a complicated spin arrangement.

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Theory of Toeplitz Determinants and the Spin Correlations of the Two-Dimensional Ising Model. III

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We study the asymptotic behavior, for large separations, of the spin-spin correlation function $\langle \sigma_{0,0}\sigma_{M,N}\rangle$ in the two-dimensional Ising model, where the two spins are not necessarily on the same row. Besides the limiting value for infinite separation, which is the square of the spontaneous magnetization, we evaluate the two leading terms in the asymptotic expression in each of the two cases $T<T_c$ and $T>T_c$. It is found that the nearest singularity of the generating function for the correlation is quite simple in the case $T>T_c$, but much more complicated for $T<T_c$. In an Appendix, we also give exactly in a very simple form the correlation $\langle \sigma_{0,0}\sigma_{N,N}\rangle$ for symmetrical Ising lattice at the critical temperature T_c.

1. INTRODUCTION

IN a previous paper on the two-dimensional Ising model,[1] the asymptotic form for large separation of the spin-spin correlation function $\langle \sigma_{0,0}\sigma_{0,N}\rangle$ was given for two spins in the same row. In this paper, we shall give the asymptotic form of the correlation function $\langle \sigma_{0,0}\sigma_{M,N}\rangle$ for arbitrary M and N, when M^2+N^2 is large. Since the case $M=0$ or $N=0$ is already treated in I, we shall, without loss of generality, assume both M and N to be positive. As in I, we have to treat the three cases $T<T_c$, $T>T_c$, $T=T_c$, separately. We shall, however, give the asymptotic form of the correlation function only for the cases $T<T_c$ and $T>T_c$, where the results in I can be regarded as a special case of our results here. These results are summarized in Sec. 5. For the case $T=T_c$, we shall give in Appendix A the correlation function $\langle \sigma_{0,0}\sigma_{N,N}\rangle$ for a symmetrical Ising model. The asymptotic form of $\langle \sigma_{0,0}\sigma_{M,N}\rangle$ for arbitrary M and N at $T=T_c$ has not been obtained. In other words, we carry out the program outlined in Sec. 8(Aa) of I.

2. CORRELATION $\langle \sigma_{0,0}\sigma_{M,N}\rangle$

Let us consider a two-dimensional Ising lattice with $2\mathfrak{M}\times 2\mathfrak{N}$ lattice sites. The lattice sites at the boundary are assumed to join in such a way that $(0, -\mathfrak{N}+1)$ and $(M, \mathfrak{N})$ are nearest neighbors. More precisely, we assume $\mathfrak{M}$ to be multiple of M, and the Hamiltonian is taken to be

$$-E_1 \sum_{m=-\mathfrak{M}+1}^{\mathfrak{M}} \Big[\sigma_{m,-\mathfrak{N}+1}\sigma_{m+M,\mathfrak{N}} + \sum_{n=-\mathfrak{N}+1}^{\mathfrak{N}-1} \sigma_{m,n}\sigma_{m,n+1}\Big]$$

$$-E_2 \sum_{m=-\mathfrak{M}+1}^{\mathfrak{M}} \sum_{n=-\mathfrak{N}+1}^{\mathfrak{N}} \sigma_{m,n}\sigma_{m+1,n}, \qquad (2.1)$$

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† National Science Foundation Senior Postdoctoral Fellow. Permanent address: Harvard University, Cambridge, Massachusetts.
[1] T. T. Wu, Phys. Rev. **149**, 380 (1966). The paper is hereafter referred to as I. For a related article, see B. M. McCoy and T. T. Wu, *ibid.* **155**, 438 (1967), which is II in the series.