

Origin of the Magnetic Anisotropy Energy of the Europium Monochalcogenides*

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The origin of the magnetic anisotropy energy of the europium monochalcogenides has been investigated. The contribution from the magnetic dipolar interaction was considered, in addition to the single-ion anisotropy, and the expression for the temperature dependence of the cubic anisotropy constants K_1 and K_2 is derived for various spin values using the molecular-field approximation. It is found that for large spins both K_1 and K_2 increase with temperature, attain a maximum, and then decrease smoothly to zero at the Curie temperature. The origin of the above temperature dependence is discussed. The experimental results for the magnetic-anisotropy measurements are explained in terms of the dipolar interaction and the single-ion anisotropy. The agreement between theory and experiment provides the first clear example of the importance of the dipolar anisotropy energy in cubic ferromagnets.

I. INTRODUCTION

The europium monochalcogenides, EuO, EuS, EuSe, and EuTe are magnetic insulators having the NaCl structure. The ground state of a Eu^{2+} ion is an orbital singlet with spin $S = \frac{7}{2}$. In the crystalline state the magnetic moment of the Eu^{2+} ion is well localized and is about $7\mu_B$. The compounds EuO and EuS are ferromagnetic below 69.2 and 16.5 K, respectively.¹ Although EuSe is antiferromagnetic below 4.6 K, spins in this crystal are ferromagnetically aligned by magnetic fields above 5 kOe.²

The magnetic anisotropy constant and its temperature dependence have been measured by Miyata and Argyle on EuO³ using a torque method and by Everett and co-workers on EuO,⁴ EuS,⁵ and EuSe⁶ using a ferromagnetic-resonance technique. The magnetic anisotropy energy of cubic crystals is represented by

$$E_{\text{anis}} = K_1(\alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_3^2\alpha_1^2) + K_2(\alpha_1^2\alpha_2^2\alpha_3^2), \quad (1)$$

where α_1 , α_2 , and α_3 are the direction cosines of the magnetization with respect to the cube edges. The observed experimental results of K_1 and K_2 are as follows:

(i) K_1 : The signs of K_1 for these crystals are all negative. The magnitude of K_1 of EuO decreases with temperature similar to what is expected from the crystalline field anisotropy energy of one-ion type.⁷ The decrease of K_1 for EuS is less rapid than the prediction of the one-ion model. The magnitude of K_1 for EuSe decreases still more slowly, being almost constant to near the zero-field ordering temperature.

(ii) K_2 : The anisotropy constant K_2 for EuO has positive sign at low temperatures. As the temperature is increased, its value decreases rapidly and passes through zero and then reapproaches zero from the negative side. The temperature dependence of K_2 for EuS is similar to that of EuO, but its tendency is more pronounced. In the case

of EuSe, K_2 starts from negative value at low temperature, its absolute magnitude increases as temperature increases, goes through a maximum, and approaches zero asymptotically. The behavior of this temperature dependence may imply that some anisotropy energy, which has negative sign for both K_1 and K_2 and whose absolute magnitude has a maximum at an intermediate temperature, is superposed onto the usual crystalline field anisotropy energy.

To explain this temperature dependence mentioned above, we considered the following mechanism. Since the ground state of Eu^{2+} is an S state and since its magnetic moment is very large, the anisotropy energy coming from the magnetic dipolar interaction may be considerable and comparable to the crystalline field anisotropy energy of one-ion type. There is, of course, no first-order dipolar contribution to the anisotropy energy because of the cubic symmetry of these crystals. However, the higher-order effects of the dipolar interaction contribute to the cubic anisotropy energy as pointed out by Van Vleck⁸ as early as 1937. This mechanism may be understood in the following way. The dipolar interaction does not commute with the exchange interaction. Thus the dipolar interaction disturbs the perfect parallelism of the spin arrangement in the ferromagnetic state at absolute zero of temperature. The energy associated with the dipolar interaction depends on the direction of the magnetization and therefore contributes to the cubic magnetic anisotropy energy. The mechanism of this interaction is essentially of quantum-mechanical nature. If we assume classical spins, we can show that when the dipolar interaction is weaker than the exchange interaction by a certain amount, a ferromagnetic arrangement of spins is stable and the classical dipolar interaction does not give rise to the anisotropy energy. Actually, the expressions for K_1 and K_2 which are given in Sec. II vanish at absolute zero when a

classical limit is taken. From the standpoint of the spin-wave approximation, it has been shown that the anisotropy energy can be expressed as a zero-point energy of ferromagnetic spin waves.⁹

In obtaining the temperature dependence of the anisotropy energy, Van Vleck used the molecular-field approximation, and Kasuya,¹⁰ Charap and Weiss,¹¹ and Keffer and Oguchi¹² used the spin-wave approximation. Since we have an interest in the semiquantitative nature of the anisotropy energy in the whole temperature range, we discuss the temperature dependence on the basis of the molecular-field approximation.

Van Vleck has obtained the expression for K_1 which comes from the mechanism mentioned above and has given the calculated values for the cases of spin $\frac{1}{2}$ and 1. As seen from his results, the decrease of K_1 with temperature is very slow compared to those of other mechanisms. For large spins, we found the temperature dependence very different from those of the usual mechanism, in which K_1 decreases much more rapidly than the magnetization. It will be seen that K_1 due to the dipolar interaction increases with temperature, attains a maximum, and then decreases smoothly to zero at the Curie temperature. Thus, a broad peak appears around $T/T_C \sim 0.45$ and its height with respect to the value at $T=0$ increases as the value of spin increases. We obtained a similar result for the temperature dependence of K_2 .

By combining the anisotropy energy of this mechanism with the crystalline field anisotropy energy of one-ion type, we could explain semiquantitatively the temperature dependence of the anisotropy energy of the europium chalcogenides.

II. CALCULATION OF DIPOLAR ANISOTROPY ENERGY

The interactions responsible for the magnetic anisotropy energy of the europium monochalcogenides are considered to be the dipolar interaction and the fine-structure coupling of europium ions, i. e., the one-ion mechanism. Since a europium ion has a large magnetic moment, the magnetic dipolar interaction may be considerable. In addition to this magnetic interaction, an anisotropic exchange interaction may exist between ions and this interaction may have the bilinear form with respect to spin components: $\sum_{i,j} \sum_{\alpha,\beta} J_{ij}^{\alpha\beta} S_{i\alpha} S_{j\beta}$. It is seen from symmetry considerations that the interaction between the second-nearest neighbors in the fcc lattice of europium ions should be of the dipolar type. Between the first-nearest neighbors, there may exist, along with a term of the dipolar type, a term of a different type. By neglecting this term, we assume the pseudodipolar-type interaction for the anisotropic exchange interaction. Hereafter, the dipolar interaction includes both the

magnetic and the pseudodipolar interactions. Since there is no contribution to the anisotropy energy from cross terms between the dipolar interaction and the fine-structure coupling, these interactions contribute to the anisotropy energy additively. In this section we calculate the anisotropy energy which comes from the dipolar interaction. The one-ion-type anisotropy energy from the fine-structure coupling will be given in Sec. IV.

We shall consider the Hamiltonian consisting of the exchange, Zeeman, and dipolar interactions. From this Hamiltonian we calculate the free energy which depends on the direction of magnetization and obtain the cubic anisotropy constants K_1 and K_2 . The exchange interaction is expressed as

$$H_{\text{ex}} = - \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j = \sum_{i,j} [J_{ij} \vec{\sigma}_i \cdot \vec{\sigma}_j - 2J_{ij} \vec{S}_i \cdot \vec{\sigma}_j - J_{ij} (\vec{S}_i - \vec{\sigma}_j) \cdot (\vec{S}_i - \vec{\sigma}_j)], \quad (2)$$

where J_{ij} is the exchange integral between the i th and j th ions, \vec{S}_i is the spin of the i th ion, and $\vec{\sigma}_i$ is the thermal average values of \vec{S}_i . We neglect the last term in Eq. (2), which indicates the spin fluctuation. This approximation is equivalent to the molecular-field approximation. If we consider the fact that the values of $\vec{\sigma}_i$'s in the crystal are all equal to each other in the ferromagnetic state, the exchange Hamiltonian is written as

$$H_{\text{ex}} = NJ\sigma^2 - 2J\vec{\sigma} \cdot \sum_i \vec{S}_i, \quad (3)$$

where $J = \sum_i J_{ij}$, and N is the total number of europium ions. The Zeeman energy is

$$H_z = g\mu_B \vec{H} \cdot \sum_i \vec{S}_i. \quad (4)$$

Adding the Hamiltonian (3) and (4), we define the unperturbed Hamiltonian H_0 as

$$H_0 = NJ\sigma^2 + (g\mu_B \vec{H} - 2J\vec{\sigma}) \cdot \sum_i \vec{S}_i. \quad (5)$$

If the dipolar interaction is represented by V , the free energy of this system is written

$$F = -k_B T \ln \text{Tr} e^{-\beta(H_0+V)}, \quad (6)$$

β being $1/k_B T$. Expanding $e^{-\beta(H_0+V)}$ in Eq. (6) in terms of V , we have

$$F = F_0(\sigma) + \Delta F(\sigma, V), \quad (7)$$

where

$$F_0 = NJ\sigma^2 - k_B T \ln \text{Tr} \times \exp \left(-\beta (g\mu_B \vec{H} - 2J\vec{\sigma}) \cdot \sum_i \vec{S}_i \right) \quad (8)$$

and

$$\Delta F(\sigma, V) = -k_B T \ln \left(1 - \frac{\text{Tr} e^{-\beta H_0} \left\{ \int_0^\beta V(\beta_1) d\beta_1 - \int_0^\beta V(\beta_1) d\beta_1 \int_0^{\beta_1} V(\beta_2) d\beta_2 + \dots \right\}}{\text{Tr} e^{-\beta H_0}} \right), \quad (9)$$

in which

$$V(\beta) = e^{\beta H_0} V e^{-\beta H_0}. \quad (10)$$

Taking the derivative of Eq. (7) with respect to σ equal to zero, we obtain

$$\sigma = \frac{\text{Tr} S_z \exp[-\beta(g\mu_B H - 2J\sigma)S_z]}{\text{Tr} \exp[-\beta(g\mu_B H - 2J\sigma)S_z]} - \left(\frac{1}{2NJ} \right) \frac{\partial \Delta F(\sigma, V)}{\partial \sigma}, \quad (11)$$

where S_z is the component of the spin operator along the axis of quantization. The magnitude of σ included in Eq. (7) is determined by solving the above equation. The last term of Eq. (11) gives an anisotropy in the magnitude of σ . We express σ as the sum of an isotropic σ_0 and anisotropic $\Delta\sigma$ part:

$$\sigma = \sigma_0 + \Delta\sigma, \quad (12)$$

with σ_0 being defined by the solution of the equation,

$$\sigma_0 = \frac{\text{Tr} S_z \exp[-\beta(g\mu_B H - 2J\sigma_0)S_z]}{\text{Tr} \exp[-\beta(g\mu_B H - 2J\sigma_0)S_z]}. \quad (13)$$

From Eqs. (11) and (13), $\Delta\sigma$ is expressed by a

function of σ_0 and V and shown to be a quantity of order V^2 . If Eq. (12) is inserted into Eq. (7), the free energy is expressed as a function of σ_0 and V instead of σ and V . The result of the calculation shows

$$F = NJ\sigma_0^2 - kT \ln \text{Tr} \times \exp \left(\beta(2J\sigma_0 - g\mu_B H) \sum_i S_{zi} \right) + \Delta F(\sigma_0) + O((\Delta\sigma)^2). \quad (14)$$

The first and second terms in the right-hand side of Eq. (14) are isotropic terms and do not contribute to the anisotropy energy. The third is the term responsible for the anisotropy energy. We calculate the value of this term to third order with respect to V and obtain the anisotropy constants K_1 and K_2 . The last term is a quantity of order of V^4 and is neglected.

The function $\Delta F(\sigma_0, V)$ given by Eq. (9) is expanded in terms of V . The first-order term in V does not give rise to the anisotropy energy, since this term is quadratic in the direction cosines of the molecular field and the crystals under consideration are of cubic symmetry. The second term is calculated as

$$\Delta F^{(2)} = \frac{1}{z_0} \sum_{\substack{M, M' \\ E_M \neq E_{M'}}} \langle M | V | M' \rangle \langle M' | V | M \rangle \frac{e^{-\beta E_M}}{E_M - E_{M'}} - \frac{1}{2z_0} \sum_{\substack{M, M' \\ E_M = E_{M'}}} \langle M | V | M' \rangle \langle M' | V | M \rangle \beta e^{-\beta E_M}, \quad (15)$$

with

$$z_0 = \sum_M e^{-\beta E_M}, \quad (16)$$

where $|M\rangle$ and E_M denote the eigenstate and eigenvalue of the unperturbed Hamiltonian (5). For the third-order term we have

$$\begin{aligned} \Delta F^{(3)} = & \frac{1}{z_0} \sum_{\substack{M, M', M'' \\ E_M \neq E_{M'} \neq E_{M''}}} \langle M | V | M' \rangle \langle M' | V | M'' \rangle \langle M'' | V | M \rangle \frac{e^{-\beta E_M}}{(E_M - E_{M'})(E_M - E_{M''})} \\ & - \frac{1}{2z_0} \sum_{\substack{M, M', M'' \\ E_M \neq E_{M'} \\ E_M = E_{M''}}} \{ \langle M | V | M' \rangle \langle M' | V | M'' \rangle \langle M'' | V | M \rangle + \langle M | V | M'' \rangle \langle M'' | V | M' \rangle \langle M' | V | M \rangle \} \\ & \times \left\{ \frac{e^{-\beta E_M}}{(E_M - E_{M'})^2} - \frac{\beta e^{-\beta E_M}}{(E_M - E_{M'})} \right\} - \frac{1}{6z_0} \sum_{\substack{M, M', M'' \\ E_M = E_{M'} = E_{M''}}} \langle M | V | M' \rangle \langle M' | V | M'' \rangle \langle M'' | V | M \rangle \beta^2 e^{-\beta E_M}. \end{aligned} \quad (17)$$

The second-order term contributes to K_1 and the third-order term contributes to both K_1 and K_2 .

A. K_1 Contribution from $\Delta F^{(2)}$

The Hamiltonian for the dipolar interaction can be expressed in terms of the spin operators as

$$\begin{aligned} V = & \sum_{i>j} D_{ij}(A + B + C + E); \\ A = & S_{zi} S_{zj} (r_{ij}^2 - 3\xi_{ij}^2), \\ B = & -\frac{1}{4}(S_i^+ S_j^- + S_i^- S_j^+) (r_{ij}^2 - 3\xi_{ij}^2), \end{aligned} \quad (18)$$

$$C = -\frac{3}{2}(S_i^+ S_{\zeta j} + S_{\zeta i} S_j^+) \xi_{ij} (\xi_{ij} - i\eta_{ij})$$

$$- \frac{3}{2}(S_i^- S_{\zeta j} + S_{\zeta i} S_j^-) \xi_{ij} (\xi_{ij} + i\eta_{ij}),$$

$$E = -\frac{3}{4} S_i^+ S_j^+ (\xi_{ij} - i\eta_{ij})^2 - \frac{3}{4} S_i^- S_j^- (\xi_{ij} + i\eta_{ij})^2,$$

where $S_{\zeta i}$ is the ζ component of the spin operator at the lattice site i , and S_i^+ and S_i^- are the spin raising and lowering operators, respectively. The

ζ axis is taken in the direction of the molecular field, and ξ and η axes are perpendicular to the ζ axis and to each other. The coefficient D_{ij} includes the contribution from the magnetic and the pseudo-dipolar interactions. In the case of the pure magnetic dipolar interaction, D_{ij} is equal to $g^2 \mu_B^2 r_{ij}^{-5}$. If the dipolar Hamiltonian, Eq. (18) is inserted into Eq. (15), and the summation over M' is carried out we have

$$\Delta F^{(2)} = \sum_M \frac{e^{-\beta E_M}}{Z_0} \sum_{i>j} \sum_{k>l} D_{ij} D_{kl} \left(-\frac{1}{2} \beta \langle M | S_{\zeta i} S_{\zeta j} S_{\zeta k} S_{\zeta l} | M \rangle (r_{ij}^2 - 3\xi_{ij}^2)(r_{kl}^2 - 3\xi_{kl}^2) \right.$$

$$- \frac{1}{32} \beta \langle M | S_i^+ S_j^- S_k^- S_l^+ + S_i^- S_j^+ S_k^+ S_l^- | M \rangle (r_{ij}^2 - 3\xi_{ij}^2)(r_{kl}^2 - 3\xi_{kl}^2) - \frac{9}{4u} \langle M | S_i^- S_{\zeta j} S_k^+ S_{\zeta l} | M \rangle$$

$$+ S_{\zeta i} S_j^- S_{\zeta k} S_l^+ | M \rangle \xi_{ij} (\xi_{ij} + i\eta_{ij}) \xi_{kl} (\xi_{kl} - i\eta_{kl}) + \frac{9}{4u} \langle M | S_i^+ S_{\zeta j} S_k^- S_{\zeta l} | M \rangle$$

$$+ S_{\zeta i} S_j^+ S_{\zeta k} S_l^- | M \rangle \xi_{ij} (\xi_{ij} - i\eta_{ij}) \xi_{kl} (\xi_{kl} + i\eta_{kl}) - \frac{9}{32u} \langle M | S_i^+ S_j^- S_k^+ S_l^- | M \rangle$$

$$\left. \times (\xi_{ij} + i\eta_{ij})^2 (\xi_{kl} - i\eta_{kl})^2 + \frac{9}{32u} \langle M | S_i^+ S_j^+ S_k^- S_l^- | M \rangle (\xi_{ij} - i\eta_{ij})^2 (\xi_{kl} + i\eta_{kl})^2 \right), \quad (19)$$

where

$$u = g \mu_B H + 2J |\sigma_0|. \quad (20)$$

The value of u corresponds to an increase in energy due to the change of the ζ component of a spin by one, and $\sum_{i>j}$, $\sum_{k>l}$ is a summation over the europium ion sites. In Eq. (19) the first, second, third and fourth, and the last two terms are, respectively, from the combination of the dipolar Hamiltonian $A-A$, $B-B$, $C-C$, and $E-E$, and all the cross terms, e.g., $A-B$, $A-C$, etc., vanish.

To illustrate the computational procedure, which we shall use to calculate K_2 from $\Delta F^{(2)}$, we consider the contribution to K_1 from the first term in Eq. (19). In this term, the part which is fourth order in ζ can only contribute to K_1 . If ζ is expressed in terms of its direction cosines α_1 , α_2 , and α_3 referred to the cubic axes, x , y , and z , and taking account of cubic symmetry, this term, denoted by $\Delta F^{(2)}(A-A)$, is written

$$\Delta F^{(2)}(A-A) = -9\beta \sum_M \frac{e^{-\beta E_M}}{Z_0} \sum_{i>j} \sum_{k>l} \langle M | S_{\zeta i} S_{\zeta j} S_{\zeta k} S_{\zeta l} | M \rangle$$

$$\times R(ij, kl) (\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2)$$

$$+ \text{constant term in } \alpha, \quad (21)$$

where

$$R(ij, kl) = D_{ij} D_{kl} (-x_{ij}^2 x_{kl}^2 + x_{ij}^2 y_{kl}^2$$

$$+ 2x_{ij} y_{ij} x_{kl} y_{kl}). \quad (22)$$

Since the total spin state $|M\rangle$ is expressed by a product of the individual spin states in the molecular-field approximation, the coefficient of $\alpha_1^2 \alpha_2^2 + \alpha_2^2 \alpha_3^2 + \alpha_3^2 \alpha_1^2$ in Eq. (21), $K_1(A-A)$, is written as

$$K_1(A-A) = -9\beta \left(\langle S_{\zeta} \rangle^4 \sum_{i>j} \sum_{k>l} R(ij, kl) \right.$$

$$\left. + 2 \langle S_{\zeta}^2 \rangle \langle S_{\zeta} \rangle^2 \sum_{i>j} \sum_l R(ij, il) + \langle S_{\zeta}^2 \rangle^2 \sum_{i>j} R(ij, ij) \right). \quad (23)$$

In Eq. (23), the sum \sum_l represents \sum_l with $l \neq i, j$, $\sum_{k,l}$ represents $\sum_{k,l}$ with $k, l \neq i, j$ while $\langle S_{\zeta} \rangle$ and $\langle S_{\zeta}^2 \rangle$ denote thermal averages in the molecular field. As seen from Eq. (22), the multiple sum of $R(ij, kl)$ vanishes when any one summation index includes all lattice points; we can write

$$\sum_{i>j} \sum_l R(ij, il)$$

$$= \sum_{i>j} \sum_l R(ij, il) - \sum_{i>j} R(ij, ij)$$

$$= -\frac{N}{2} \sum_j R(ij, ij) \quad (24)$$

and

$$\sum_{i>j} \sum_{k>l} R(ij, kl) = \sum_{i>j} \sum_{k>l} R(ij, kl)$$

$$- 2 \sum_{i>j} \sum_l R(ij, il) - \sum_{i>j} R(ij, ij)$$

$$= \frac{N}{2} \sum_j R(ij, ij). \quad (25)$$

With the use of the relations (24) and (25), Eq. (23) becomes

$$K_1(A-A) = -\frac{3}{2} N \beta (\langle S_{\zeta}^2 \rangle - \langle S_{\zeta} \rangle^2) \sum_j R(ij, ij). \quad (26)$$

This is the contribution to K_1 from the first term

in Eq. (19). Although other terms in Eq. (19) include ξ and η along with ζ , these terms are reduced to functions of only ζ and γ and thus the lattice sums for these terms yield the same form as that of the first term (see the Appendix). Therefore, the second term through the sixth term in Eq. (19) are calculated in the same way as the first term. Doing these calculations, we obtain the expression for K_1 as

$$\begin{aligned} K_1 = 9N & \left[-\frac{1}{2}\beta\{\langle S_c^2 \rangle - \langle S_c \rangle^2\}^2 \right. \\ & - \frac{1}{16}\beta\{[S(S+1) - \langle S_c^2 \rangle]^2 - \langle S_c \rangle^2\} \\ & - (1/u)\langle S_c \rangle\{\langle S_c^2 \rangle - \langle S_c \rangle^2\} + (1/8u)\langle S_c \rangle \\ & \left. \times \{S(S+1) - \langle S_c^2 \rangle\} \sum_j R(ij, ij) \right]. \quad (27) \end{aligned}$$

$$\begin{aligned} \Delta F_1^{(3)}(B-C-C) &= -\frac{27}{8u^2} \sum_M \frac{e^{-\beta E_M}}{z_0} \sum_{i>j} \sum_{k>l} \sum_{m>n} \langle M | \{S_i^+ S_{ej} S_k^+ S_l^- S_m^- S_n^-\} | M \rangle R(ij, kl, mn) \alpha_1^2 \alpha_2^2 \alpha_3^2 \\ &= -\frac{27}{8u^2} \left(2 \langle \{S^+ S^-\} \rangle^2 \sum_{i>j} \sum_{k \neq m} \bar{R}(ij, ki, mk) + 2 \langle S_c \rangle (\langle S^+ S^- \rangle \langle S^+ S^- S_c \rangle + \langle S^- S^+ \rangle \langle S^- S^+ S_c \rangle) \right. \\ & \left. \times \sum_{i>j} \sum_m \bar{R}(ij, ij, mi) + \langle \{S^+ S^- S_c\} \rangle^2 \sum_{i>j} R(ij, ij, ij) + 2 \langle \{S^+ S^-\} \rangle^2 \langle S_c^2 \rangle \sum_{i>j} \sum_k R(ij, ki, jk) \right) \alpha_1^2 \alpha_2^2 \alpha_3^2, \quad (28) \end{aligned}$$

where the curly brackets in the angular brackets $\langle \dots \rangle$ denote that $\{AB\} = AB + BA$ and $\{ABC\} = ABC + CBA$. The expression for $R(ij, kl, mn)$ is similar to that of Eq. (22) and is written

$$\begin{aligned} R(ij, kl, mn) &= 3D_{ij} D_{kl} D_{mn} [x_{ij}^2 x_{kl}^2 x_{mn}^2 \\ & - 3x_{ij}^2 x_{kl}^2 y_{mn}^2 + 2x_{ij}^2 y_{kl}^2 z_{mn}^2 \\ & + 16x_{ij} y_{ij} y_{kl} z_{kl} z_{mn} x_{mn} \\ & + 12x_{ij} y_{ij} x_{kl} y_{kl} (z_{mn}^2 - y_{mn}^2)]. \quad (29) \end{aligned}$$

The derivation of $R(ij, kl, mn)$ is given in the Appendix. In particular, it is shown that the other combinations yield the same form of $R(ij, kl, mn)$ as for $B-C-C$ except for the numerical factors.

In the derivation of Eq. (29), the fourth-order terms in the direction cosines α 's are neglected, since the contribution to K_1 from these terms is shown to be an order of magnitude smaller than

$$\begin{aligned} \Delta F_1^{(3)}(B-C-C) &= -\frac{27N}{16u^2} \left(2 \langle \{S^+ S^-\} \rangle^2 (\langle S_c^2 \rangle - \langle S_c \rangle^2) \sum_{j \neq k} \bar{R}(ij, jl, li) + \langle \{S^+ S^-\} \rangle^2 \langle S_c \rangle^2 - 2 \langle S_c \rangle \langle \{S^+ S^-\} \rangle \langle \{S_c S^+ S^-\} \rangle \right. \\ & \left. + \langle \{S_c S^+ S^-\} \rangle^2 \sum_j R(ij, ij, ij) \right) \alpha_1^2 \alpha_2^2 \alpha_3^2. \quad (32) \end{aligned}$$

From this equation, we see that there are two different types of contributions to K_2 . The difference is characterized by the configuration of the sum-

This result, first obtained by Van Vleck, has been given to illustrate the method used in calculating $\Delta F^{(3)}$.

B. K_2 Contribution from $\Delta F^{(3)}$

The third-order free energy $\Delta F^{(3)}$ is calculated by inserting the dipolar Hamiltonian Eq. (18) into Eq. (17). In this case the nonvanishing terms in Eq. (17) are the following combinations of the Hamiltonian [Eq. (18)]: $A-A-A$, $B-B-B$, $A-B-B$, $A-C-C$, $A-E-E$, $B-C-C$, $B-E-E$, and $C-C-E$. We now show the calculation of Eq. (17) for the combination $B-C-C$ as an example. If the summation over M' and M'' in Eq. (17) is carried out, we have for the first term in Eq. (17), similar to Eq. (21) for K_1 ,

that of K_1 from $\Delta F^{(2)}$. It can be seen from Eq. (29) that $R(ij, kl, mn)$ possesses the same property as $R(ij, kl)$, i. e., $R(ij, kl, mn)$ vanishes if any one of the indices is summed over all the lattice sites. Thus we have equations, which are derived in the Appendix, similar to Eqs. (24) and (25):

$$\sum_{i>j} \sum_m R(ij, ij, mj) = -\frac{1}{2}N \sum_j R(ij, ij, ij) \quad (30)$$

and

$$\begin{aligned} \sum_{i>j} \sum_{i \neq m} R(ij, il, mj) &= \frac{1}{2}N \left(\sum_j R(ij, ij, ij) \right. \\ & \left. - \sum_{j \neq l} R(ij, jl, li) \right). \quad (31) \end{aligned}$$

Using the above relations (30) and (31), $\Delta F_1^{(3)}(B-C-C)$ becomes

mation indices in R , i. e., $R(ij, ij, ij)$ and $R(ij, jl, li)$. However, we find that the contributions from the former type are negligibly small compared to

the latter at absolute zero of temperature: We neglect the contributions from the former type hereafter. Since the combinations $A-E-E$ and $A-B-B$ yield only the former type, we neglect these combinations accordingly. If we make the same calculations for the second term in Eq. (17), we have

$$\begin{aligned} \Delta F_2^{(3)}(B-C-C) &= \frac{27}{4u^2} \langle S^+ S^- \rangle \langle S^- S^+ \rangle \\ &\quad \times (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2) \sum_{j \neq l} R(ij, jl, li) \\ &\quad \times \alpha_1^2 \alpha_2^2 \alpha_3^2. \end{aligned} \quad (33)$$

The third sum in Eq. (17) vanishes for $B-C-C$ combination. Consequently, from Eqs. (32) and (33) the contribution to K_2 from the $B-C-C$ combination is obtained as

$$\begin{aligned} K_2(B-C-C) &= -\frac{27N}{2u^2} \langle S_\tau \rangle^2 \\ &\quad \times (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2) \sum_{j \neq l} R(ij, jl, li). \end{aligned} \quad (34)$$

Doing the same calculation as the $B-C-C$ combination mentioned above, we obtained the contributions to K_2 from the other combinations as follows:

$$\begin{aligned} A-A-A: & -9\beta^2 (\langle S_\tau \rangle - \langle S_\tau \rangle^2); \\ B-B-B: & \frac{9}{32} \beta^2 \\ & \{S(S+1) - \langle S_\tau^2 \rangle\} [\{S(S+1) - \langle S_\tau^2 \rangle\}^2 - \langle S_\tau \rangle^2]; \\ A-C-C: & -\frac{27}{u} \beta \langle S_\tau \rangle (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2); \\ B-E-E: & -\frac{27}{32u} \beta \langle S_\tau \rangle [\{S(S+1) - \langle S_\tau^2 \rangle\}^2 - \langle S_\tau \rangle^2] \\ & + \frac{27}{16u^2} \langle S_\tau \rangle^2 \{S(S+1) - \langle S_\tau^2 \rangle\}; \\ E-C-C: & -\frac{27}{2u^2} \langle S_\tau \rangle^2 (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2); \end{aligned} \quad (35)$$

with each term multiplied by the common factor

$$N \sum_{j \neq l} R(ij, jl, li).$$

Summing these contributions, we finally obtain

$$\begin{aligned} K_2 &= 9N \left(-\beta^2 (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2)^3 + \frac{\beta^2}{32} \{S(S+1) - \langle S_\tau^2 \rangle\} [\{S(S+1) - \langle S_\tau^2 \rangle\}^2 - \langle S_\tau \rangle^2] \right. \\ &\quad - \frac{3\beta}{u} \langle S_\tau \rangle (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2)^2 - \frac{3\beta}{32u} \langle S_\tau \rangle [\{S(S+1) - \langle S_\tau^2 \rangle\}^2 - \langle S_\tau \rangle^2] \\ &\quad \left. - \frac{3}{u^2} \langle S_\tau \rangle^2 (\langle S_\tau^2 \rangle - \langle S_\tau \rangle^2) + \frac{3}{16u^2} \langle S_\tau \rangle^2 \{S(S+1) - \langle S_\tau^2 \rangle\} \right) \sum_{j \neq l} R(ij, jl, li). \end{aligned} \quad (36)$$

At absolute zero, only the last term in large parentheses in Eq. (36) remains. We have

$$K_2(T=0) = \frac{27NS^3}{16u^2} \sum_{j \neq l} R(ij, jl, li). \quad (37)$$

For checking the arithmetical correctness of Eq. (36) we note that since u defined in Eq. (20) transforms like a vector, only terms in H^6 or higher-order terms can exhibit a dependence on the direction cosine of the form $\alpha_1^2 \alpha_2^2 \alpha_3^2$. If the thermal average values of spins included in Eq. (36) are expanded in terms of u , K_2 should vanish unless one goes to the sixth power of u . Equation (36) fulfills this condition.

III. TEMPERATURE DEPENDENCE OF DIPOLAR ANISOTROPY ENERGY

The anisotropy constants K_1 and K_2 as a function of temperature can be calculated from Eqs. (27) and (36), respectively. The results are plotted in

reduced units, $K(T)/K(0)$ versus T/T_C . Figure 1 shows $K_1(T)/K_1(0)$ for various spin values at zero external magnetic field. For $S = \frac{1}{2}$, the value of $K_1(T)/K_1(0)$ is almost constant until about $T/T_C = 0.3$ and decreases smoothly to zero at the Curie temperature, in agreement with the values calculated by Van Vleck. However, as the magnitude of spin increases, $K_1(T)/K_1(0)$ starts rising around $T/T_C = 0.1$, attains a broad maximum at about $T/T_C = 0.45$, and approaches zero at $T = T_C$. The value of $[K_1(T)/K_1(0)]_{\max}$ is roughly proportional to S , increasing about 10% for an increase in spin value of $\frac{1}{2}$. Figure 2 shows $K_2(T)/K_2(0)$ vs T/T_C . Essentially the same results are obtained for K_2 , except that K_2 increases more rapidly than K_1 and the maximum value occurs at a slightly lower temperature than that of K_1 . The value of $K_2(T)/K_2(0)$ near $T = T_C$ decreases as the sixth power of the magnetization as expected. Figures 3 and 4 indicate the effect of the external magnetic field on K_1

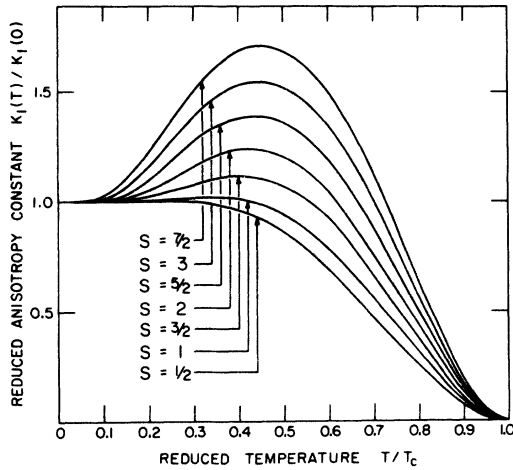


FIG. 1. Temperature dependence of reduced dipolar anisotropy constant $K_1(T)/K_1(0)$ for various spin values.

and K_2 for $S = \frac{1}{2}$. A reduced unit of $H_{\text{ext}}/(k_B T_C/g\mu_B)$ is used for the external magnetic field, and the values of K_1 and K_2 are normalized to those at $T=0$ and $H=0$. The increase of the anisotropy constants near the Curie temperature is due to the forced anisotropy caused by the induced magnetization from the external field.

The general behavior which characterizes the dipolar anisotropy energy in cubic crystals is that the anisotropy constants K_1 and K_2 increase with temperature to $T/T_C \sim 0.5$ and this increase in the anisotropy constants depends strongly on the value of S . When S is varied, the values of the anisotropy constants change due to the change in the quantization of spin. We shall see how the differ-

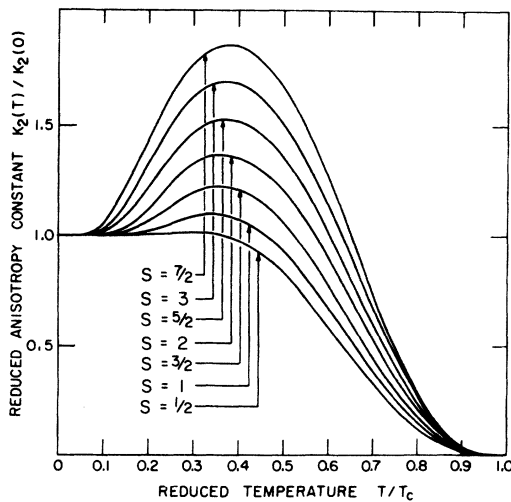


FIG. 2. Temperature dependence of reduced dipolar anisotropy constant $K_2(T)/K_2(0)$ for various spin values.

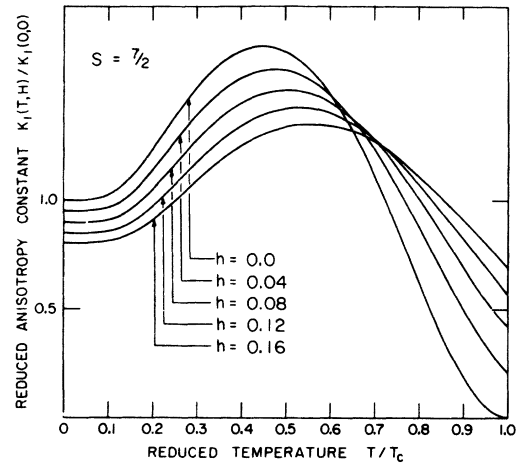


FIG. 3. Magnetic field dependence of the dipolar anisotropy constant $K_1(T,H)/K_1(0,0)$ for spin $\frac{7}{2}$. The reduced unit h is equal to $H/(k_B T_C/g\mu_B)$.

ence in the quantization leads to the difference in the temperature dependence of the anisotropy constants. We note here that when S is varied, there will also be a change in the magnitude of the magnetic moment $g\mu_B S$. However, this change will merely act as a multiplicative factor to the anisotropy constants and will not affect the temperature dependences. Therefore to see the essential difference in the temperature dependence of the anisotropy constants for different values of S , it is more appropriate to rewrite the expressions for the anisotropy constants where the magnitude of $g\mu_B S$ is kept constant. This is equivalent to treating the spins with different values of S as carrying

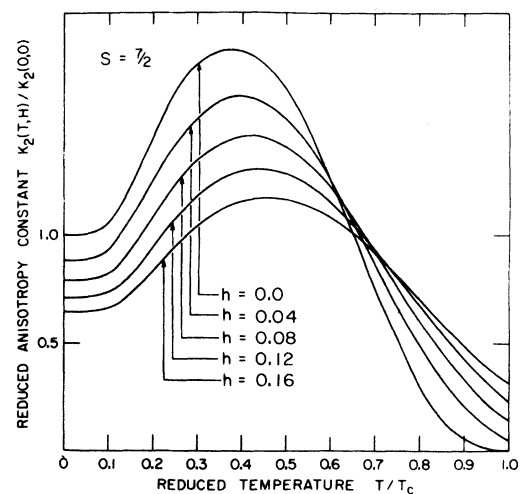


FIG. 4. Magnetic field dependence of the dipolar anisotropy constant $K_2(T,H)/K_2(0,0)$ for spin $\frac{7}{2}$.

the same magnetic moments but having different quantization. At $T=0$, only the last term in Eq. (27) remains and we rewrite the last term as

$$K_1(0) = (1/8u) \langle S_z \rangle \{ S(S+1) - \langle S_z^2 \rangle \} \\ \times \sum_j R_{ij, ij} \propto 1/S. \quad (38)$$

Here the quantity u , as defined in Eq. (20), is the change in the unperturbed energy when a spin is flipped by one unit. In the above equation, we must also let the unperturbed energy, the exchange, and the Zeeman be independent of the magnitude of S and thus we have let $u \propto 1/S$. Therefore we see that K_1 decreases as the value of S is increased. The above result is expected if we recall that the origin of the dipolar anisotropy energy at $T=0$ arises from the quantum fluctuation of spins. Since the quantum fluctuation decreases as the value of S is increased, we have a decrease in the value of K_1 . The above fact explains the effect of the external magnetic field on the anisotropy energy. Figures 3 and 4 show that at low temperatures anisotropy constants decrease as the magnetic field is increased. This is due to the suppression of the quantum fluctuation of spins by external magnetic field. In the limit of $S \rightarrow \infty$, K_1 vanishes as expected. Since we have treated the exchange energy being constant of S , if we let $S \rightarrow \infty$ and $\mu_B \rightarrow 0$ while keeping the magnitude of $g\mu_B S$ constant, it is equivalent to assuming classical spins in the expression of K_1 and there should be no anisotropy in this limit. At finite temperatures, Eq. (38) becomes

$$K_1(T) \propto \text{const in } S \text{ for large } S, \quad (39)$$

and the other three terms in the large square brackets of Eq. (27) also yield the same form as Eq. (39). Equations (38) and (39) indicate that at very low temperatures the value of K_1 decreases in going from small S to large S , while at intermediate temperatures the value of K_1 does not change much for different values of S . When S is of the order of unity, K_1 should not vary much over a wide range of temperature. For large S , however, the value of K_1 at low temperatures is reduced appreciably due to the decrease in the quantum fluctuation so that K_1 becomes smaller at low temperatures than at intermediate temperatures and thus K_1 increases with increasing temperature. This behavior is shown in Fig. 5, in which we have plotted K_1 vs T/T_C where the magnitude of the magnetic moment $g\mu_B S$ is kept constant. In Fig. 1 we note that the height of the broad maximum increases as the value of S is increased and one might suspect that our expression for K_1 would not yield a finite value at the classical limit. In Fig. 5 we see that when the limit is properly taken the

maximum value of K_1 approaches a finite value.

The above discussions lead to the following interpretation of the temperature dependence of the dipolar anisotropy energy in cubic crystals. Classically, all the spins in a cubic ferromagnet point in the same direction at absolute zero and the energy associated with dipolar interaction does not depend on the direction of the spins with respect to the cubic axes. However, when the dipolar interactions are considered quantum mechanically, because of the terms nondiagonal in $\sum_j S_{zj}$, the dipolar interaction causes the spins to fluctuate around the direction of the magnetization. The energy associated with this quantum fluctuation depends on the direction of the magnetization with respect to the cubic axes and thus gives rise to the anisotropy energy. Therefore the interaction involved in the anisotropy energy at $T=0$ is purely quantum mechanical so that the anisotropy energy depends strongly on the value of S . As the temperature is raised, the thermal fluctuation of the spins is introduced in addition to the quantum fluctuation. For small S , since only a few levels of the energy states are available between the ground state and the state of the complete reversal of the spin, raising of temperature does not introduce much the additional disturbance of the parallel arrangement of the spins. For large S , the anisotropy energy is very small at $T=0$. When the temperature is raised the spins begin to fluctuate thermally and tend less and less parallel to each other so as to minimize the total free energy. This fluctuation is larger for large S and thus gives additional contribution to the anisotropy energy.

Investigations of the spin-wave analysis for temperature dependence of the dipolar anisotropy energy have been done by several authors.¹⁰⁻¹² They

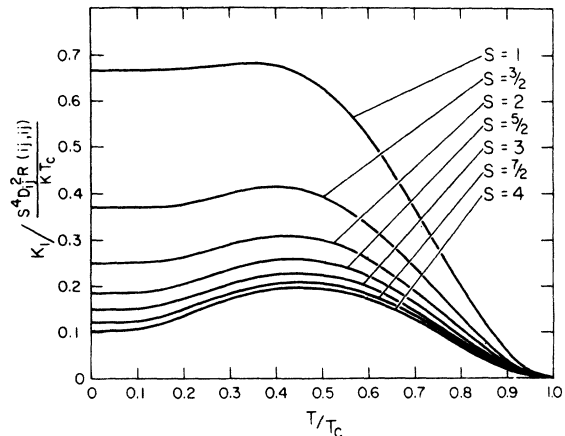


FIG. 5. Dependence of the dipolar anisotropy constant K_1 on spin values when the magnitude of the magnetic moment $g\mu_B S$ is held constant.

have carried out the analysis by assuming the strong correlation between the neighboring spins and shown that K_1 decreases with temperature as the tenth power of the magnetization when $T \ll T_C$, which seems to be contradicted by our results. We have used the molecular-field approximation to obtain the semiquantitative nature of the anisotropy energy in the whole temperature range and found that the temperature range in which the dipolar interaction gives the significant contribution is around $T/T_C = 0.5$. At this temperature range, still $\sim 90\%$ of the magnetization remains but the average angle of the spins with respect to the direction of the magnetization is already large ($\sim 25^\circ$), indicating a considerable departure of the spins from the parallel arrangement. It is also noted in our results that the tenth-power law does not seem to represent either quantitative or qualitative description of the temperature dependence of the dipolar anisotropy energy.

Comparing our expression of K_1 with that of the spin-wave results, we find that several terms, which are important at high temperatures ($T/T_C \sim 0.5$), are neglected in the spin-wave analysis. It would be interesting to investigate the contribution of these terms in the spin-wave analysis and compare with the molecular-field results.

IV. COMPARISON WITH EXPERIMENT

The temperature dependence of the anisotropy constants K_1 and K_2 in EuO,⁴ EuS,⁵ and EuSe⁶ has been measured by Everett and co-workers using ferromagnetic resonance. Miyata and Argyle³ determined K_1 in EuO from torque measurements and interpreted their results using the Wolf⁷ single-ion theory. They obtained good agreement using a single cubic crystal parameter b_4 . The ferromagnetic resonance determination of K_1 by Everett and co-workers essentially corroborated the torque measurements, while they determined, in addition, the temperature dependence of K_2 . These authors used the Wolf single-ion theory as extended by von Molnar¹³ to include the crystal-field term in b_6 in an attempt to fit the results obtained for K_2 . This analysis showed that a single-ion interaction alone was not sufficient to describe the experimental results. A similar situation exists in EuS and EuSe with evidence for a second contribution becoming more pronounced in progressing towards EuSe.

We have reanalyzed the results for K_1 and K_2 in EuO, EuS, and EuSe assuming that the dipolar contribution is important, in addition to single-ion terms. To obtain the values of K_1 and K_2 due to the dipolar interaction, the quantity u and the lattice sums, $R(ij, ij)$ and $R(ij, jl, li)$ in Eqs. (27) and (36), must be evaluated. For the quantity u , as defined in Eq. (20), the exchange constant J is estimated from the ferromagnetic Curie tempera-

ture for EuO and EuS, and from the paramagnetic Curie temperature (6 K) for EuSe.¹⁴ The g values are 2 in these compounds. For the lattice sums, since Eu^{2+} is an S-state ion we expect that the contributions of the pseudodipoles are small and about of the same order as the pure magnetic dipoles in the europium monochalcogenides. We define D_{ij} as

$$D_{ij} = (g^2 \mu_B^2 / r_{ij}^5)(1 + C_{ij}), \quad (40)$$

where C_{ij} indicates the contributions from the pseudodipole interaction. Considering the short-range nature of the pseudodipole coupling, we assume that C_{ij} are nonzero only between the nearest-neighbor and the next-nearest-neighbor pairs. We define

$$C_{ij} = \begin{cases} C_1 & \text{between nearest-neighbor pairs,} \\ C_2 & \text{between next-nearest-neighbor pairs,} \\ 0 & \text{otherwise.} \end{cases} \quad (41)$$

Since we have two independent experimentally measurable quantities, K_1 and K_2 , we can determine C_1 and C_2 independently. For the above definition of D_{ij} , Eq. (22) takes the form

$$\sum_j (1 + C_{ij})^2 (3x_{ij}^2 y_{ij}^2 - x_{ij}^4) / r_{ij}^{10}, \quad (42)$$

and we have a similar expression for the summation of $R(ij, jl, li)$ for K_2 . In the case where only the pure magnetic dipole is considered ($C_1 = C_2 = 0$), the numerical values of the above sums in units of $\frac{1}{2}a$ with a being the lattice constant are given in Table I for simple cubic, fcc, and bcc lattices.

For the crystalline field contribution, we have for the spin Hamiltonian appropriate for a $S_{7/2}$ ground state¹⁵

$$H = B_4[\hat{O}_4^0 + 5\hat{O}_4^4] + B_6[\hat{O}_6^0 - 21\hat{O}_6^4], \quad (43)$$

where \hat{O}_i^j are spin operators defined by Baker *et al.*,¹⁶ and B_4 and B_6 are related to the cubic crystal-field-splitting parameters b_4 and b_6 as

$$b_4 = 60B_4, \quad b_6 = 1260B_6.$$

Using this Hamiltonian with the molecular-field approximation, the free energy in terms of b_4 and b_6 is obtained in the form of Eq. (1) and therefore the temperature dependence of the anisotropy constants is calculated.^{7,13}

Since the temperature dependence of the dipolar

TABLE I. Lattice sum $R(ij, jl, li)$ for simple, body-centered, and face-centered cubic lattices.

sc	bcc	fcc
-0.005	0.046	-0.480

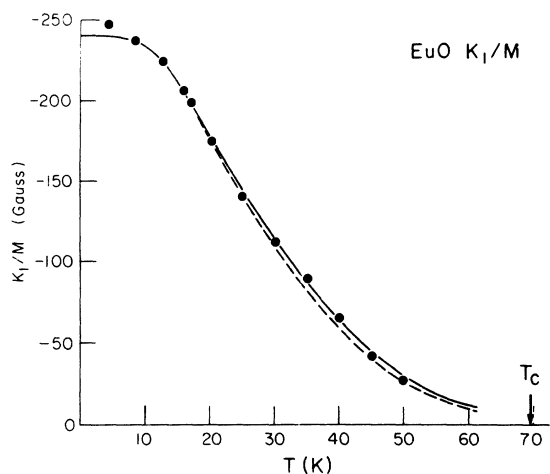


FIG. 6. Comparison with experiment for K_1 of EuO. The solid lines are the calculated values where the two contributions, dipolar and crystalline, are combined and the dashed lines are the calculated values where only the crystalline field anisotropy is assumed to exist. The experimental data are indicated by points.

interaction is quite different from that of the crystalline field effect, these contributions can be separated in the experimental data without difficulty. We first find the ratio of the two contributions by fitting the data for as wide a range of temperatures as possible. From this ratio and the observed values for K_1 and K_2 , the values of b_4 , b_6 , C_1 , and C_2 are determined independently. The results of the fittings for K_1 are illustrated in Figs. 6–8. Since the experimental results are obtained for K/M rather than K , we have plotted K/M versus temperature. For the theoretical expressions of K/M , the temperature variation of the magnetization M was calculated using the molecular-field approximation. The solid lines are the calculated values where the two contributions are combined and the dashed lines are the calculated values where the crystalline field anisotropy is assumed to be

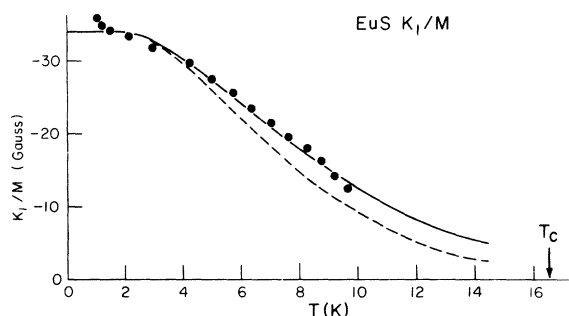


FIG. 7. Comparison with experiment for K_1 of EuS. (See caption to Fig. 6.)

the only mechanism. The experimental results^{4–6} are indicated by points. Negative values of K_1 were observed in all the compounds. In the case of EuO, the crystalline field anisotropy itself roughly explains the experimental results. This should be the case, since the observed values are too large to be accounted for by the dipolar anisotropy except in the temperature range 30–45 K where the dipolar anisotropy has its maximum effect. In the case of EuS, because of an increase in the lattice constant, both the exchange and dipolar interaction are decreased. However, the exchange interaction decreases with increasing lattice constant much faster than the dipolar interaction, the contribution to the anisotropy energy, which is the ratio of the square of the dipolar interaction to the exchange interaction, is effectively increased. Since the magnetic dipole interaction predicts negative values of K_1 , if the crystalline field effect also gives a negative contribution, as in the case of EuO, the two mechanisms contribute to K_1 additively. Recalling that the dipolar anisotropy energy increases with temperature up to $T/T_c \approx 0.45$, we now see why K_1 of EuS decreases more slowly than K_1 of EuO. This behavior of the temperature dependence is most pronounced in EuSe, where K_1 is almost constant until about the ordering temperature and then approaches zero asymptotically.

Figures 9–11 show the results of K_2 . We find that the dipolar anisotropy exhibits a more significant effect on K_2 so that even EuO cannot be described adequately by the crystalline field anisotropy. Since the values of K_2 predicted by the two mechanisms are opposite in sign, if they are combined, K_2 decreases very rapidly at low temperatures and goes through zero around $T/T_c = 0.5$, which is in contrast to K_1 where the two contributions are both negative, and therefore K_1 decreases very slowly at low temperatures. This temperature dependence explains well the observed behavior of K_2 in EuO and EuS. In the case of EuSe, the experimental results of K_2 are well described by

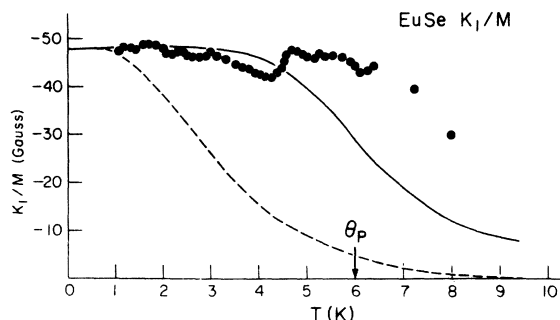


FIG. 8. Comparison with experiment for K_1 of EuSe. (See caption to Fig. 6.)

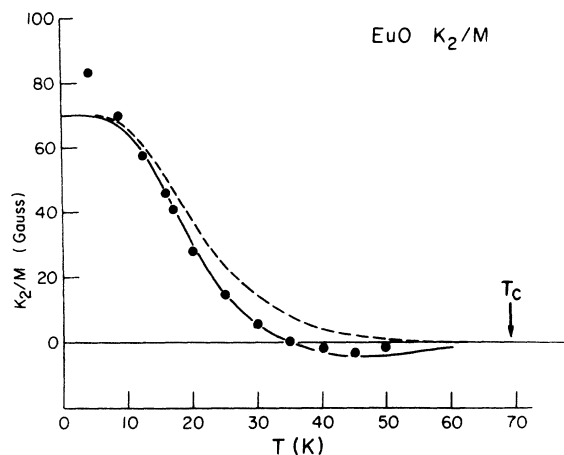


FIG. 9. Comparison with experiment for K_2 of EuO. (See caption to Fig. 6.)

the dipolar anisotropy alone and the contribution from the crystalline field must be negligibly small. The very pronounced minimum found in the experimental results at $T \approx 3.5$ K provides an evidence of the dipolar anisotropy. It is interesting to note that the net effect of the two competing mechanisms, a decrease in the crystalline field and increase in the dipolar interaction in going from EuO to EuS to EuSe, is clearly indicated in the experimental results of both K_1 and K_2 and we have fair agreement between theory and experiment.

The respective percentage contribution of the crystalline field, the pure magnetic dipole, and the pseudodipole for K_1 and K_2 for each compound are given in Table II. Table III includes the cubic crystal-field-splitting parameters b_4 and b_6 and the pseudodipole coupling constants C_1 and C_2 . Two sets of values are obtained for C_1 and C_2 for EuO and EuSe. The ratio of the crystalline field and

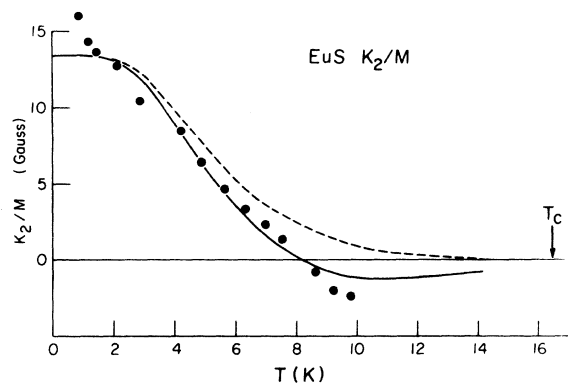


FIG. 10. Comparison with experiment for K_2 of EuS. (See caption to Fig. 6.)

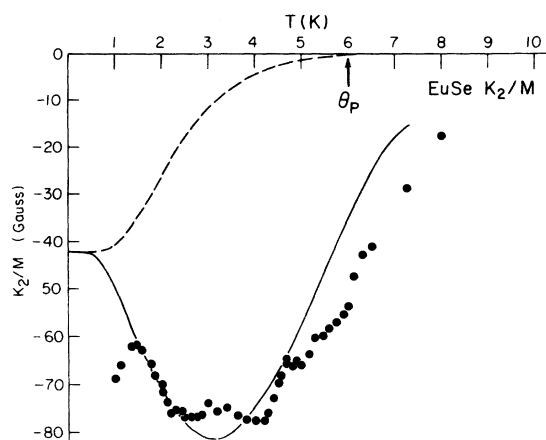


FIG. 11. Comparison with experiment for K_2 of EuSe. (See caption to Fig. 6.)

the dipolar contributions is determined by extending the theoretical calculations to $T=0$ after the best fit with the experiments is obtained. A few experimental points at the lowest temperature range are neglected. Sudden rises in K_1 and K_2 for EuS at this temperature range indicate some interference of another mechanism.

It is found that the cubic crystal-field parameters, both b_4 and b_6 , decrease monotonically with increasing lattice constant. The order of magnitude of b_4 and b_6 for EuO is in agreement with the values obtained from EPR measurements on Eu^{2+} -doped CaO¹⁷ and BaO.¹⁸ We do not find any pattern or trend among the pseudodipole coupling constants C_1 and C_2 for the compounds under consideration. The results of paramagnetic resonance linewidth measurements of Eastman,¹⁹ and von Molnar and Lawson²⁰ show that the pseudodipole interaction is about of the same order as the pure magnetic dipole interaction in EuO and negligibly small in EuS, which roughly supports our results. For EuSe the values of C_1 and C_2 are not in agreement with high-temperature linewidth measurements.⁶ Throughout our analysis we have assumed the spin system to be in the ferromagnetic state. However, EuSe may not be in a saturated state at 8.7 kOe, the applied field at which the anisotropy measurements were

TABLE II. Percentage contribution of the crystalline field, dipole, and pseudodipole.

	EuO		EuS		EuSe	
	K_1 (%)	K_2 (%)	K_1 (%)	K_2 (%)	K_1 (%)	K_2 (%)
Cryst.	98.3	94.0	93.9	91.9	62.5	0
Dipole	0.6	0.4	6.1	8.1	9.0	13.7
Pseudo-dipole	1.1	5.6	0	0	28.5	86.3

TABLE III. Estimated values for b_4 , b_6 , C_1 , and C_2 .

	EuO	EuS	EuSe
b_4	2.3 (10^{-3} cm $^{-1}$)	0.29 (10^{-3} cm $^{-1}$)	0.25 (10^{-3} cm $^{-1}$)
b_6	0.2 (10^{-3} cm $^{-1}$)	0.04 (10^{-3} cm $^{-1}$)	0
C_1	1.2	0	0.85
C_2	2.1	0	0

made; and thus further study at higher fields may be necessary to precisely determine the value of the pseudodipole coupling constants in this case.

ACKNOWLEDGMENTS

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APPENDIX

In this appendix, we shall derive the expression for $R(ij, kl, mn)$. As is mentioned in Sec. II B, each term of $\Delta F^{(3)}$ corresponding to each combination is expressed by a product of spin matrices and a function of ξ , η , ζ , and r . We list the form of the function for each combination:

$$\begin{aligned} A-A-A: & (r_{ij}^2 - 3\zeta_{ij}^2)(r_{kl}^2 - 3\zeta_{kl}^2)(r_{mn}^2 - 3\zeta_{mn}^2), \\ B-B-B: & \end{aligned} \quad (A1)$$

$$\begin{aligned} A-C-C: & (r_{ij}^2 - 3\zeta_{ij}^2)\zeta_{kl}(\xi_{kl}^2 - i\eta_{kl}^2) \\ B-C-C: & \times \zeta_{mn}(\xi_{mn}^2 + i\eta_{mn}^2) + \text{c. c.}, \end{aligned} \quad (A2)$$

$$\begin{aligned} B-E-E: & (r_{ij}^2 - 3\zeta_{ij}^2)(\xi_{kl} - i\eta_{kl})^2 \\ & \times (\xi_{mn} + i\eta_{mn})^2 + \text{c. c.}, \end{aligned} \quad (A3)$$

$$\begin{aligned} E-C-C: & (\xi_{ij} - i\eta_{ij})^2 \zeta_k(\xi_{kl} + i\eta_{kl}) \\ & \times \zeta_{mn}(\xi_{mn} + i\eta_{mn}) + \text{c. c.} \end{aligned} \quad (A4)$$

We have left out from each equation the coefficient $D_{ij}D_{kl}D_{mn}$ and also a numerical factor which is different for each combination. It is now desired to transform each equation, (A2) through (A4), into an equation which is only a function of r and ζ . Re-

calling the relation, $\zeta = \alpha_1 x + \alpha_2 y + \alpha_3 z$, we see that we need to retain only the terms which are sixth order in ζ . Using an identity,

$$\begin{aligned} \vec{r}_{kl} \cdot \vec{r}_{mn} &= \frac{1}{2}[(\xi_{kl} + i\eta_{kl})(\xi_{mn} - i\eta_{mn}) \\ &+ (\xi_{kl} - i\eta_{kl})(\xi_{mn} + i\eta_{mn})] + \zeta_{kl}\zeta_{mn}, \end{aligned} \quad (A5)$$

Eq. (A2) is transformed into

$$2(r_{ij} - 3\zeta_{ij})\zeta_{kl}\zeta_{mn}[(r_{kl}r_{mn}) - \zeta_{kl}\zeta_{mn}]. \quad (A6)$$

Similar transformations can be made for Eqs. (A3) and (A4) using identities which consist of $(\vec{r}_{kl} \cdot \vec{r}_{mn})^2$ and $(\vec{r}_{ij} \cdot \vec{r}_{kl})(\vec{r}_{ij} \cdot \vec{r}_{mn})$, respectively. Equation (A3) becomes

$$(r_{ij}^2 - 3\zeta_{ij}^2)(2\zeta_{kl}^2\zeta_{mn}^2 + \text{lower-order terms in } \zeta), \quad (A7)$$

and Eq. (A4) becomes

$$\zeta_{kl}\zeta_{mn}(2\zeta_{ij}^2\zeta_{kl}\zeta_{mn} + \text{lower-order terms in } \zeta). \quad (A8)$$

From Eq. (A1) and Eqs. (A6)–(A8), we see that all the combinations yield the same functional form so far as the terms sixth order in ζ are concerned. Therefore, when Eqs. (A1)–(A4) are summed over the lattice sites, we have the summation of the form

$$\begin{aligned} & \sum_{i>j} \sum_{k>l} \sum_{m>n} D_{ij}D_{kl}D_{mn}\zeta_{ij}^2\zeta_{kl}^2\zeta_{mn}^2 \\ &= \sum_{i>j} \sum_{k>l} \sum_{m>n} D_{ij}D_{kl}D_{mn}(\alpha_1 x_{ij} + \alpha_2 y_{ij} + \alpha_3 z_{ij})^2 \\ & \quad \times (\alpha_1 x_{kl} + \alpha_2 y_{kl} + \alpha_3 z_{kl})^2 (\alpha_1 x_{mn} + \alpha_2 y_{mn} + \alpha_3 z_{mn})^2 \end{aligned} \quad (A9)$$

which is the same, except for the numerical factors, for all the combinations. If the cubic symmetry of the crystal is taken into account, we obtain for Eq. (A9)

$$\begin{aligned} & \sum_{i>j} \sum_{k>l} \sum_{m>n} D_{ij}D_{kl}D_{mn}\zeta_{ij}^2\zeta_{kl}^2\zeta_{mn}^2 \\ &= \sum_{i>j} \sum_{k>l} \sum_{m>n} R(ij, kl, mn)\alpha_1^2\alpha_2^2\alpha_3^2 \\ & \quad + \text{lower-order terms in } \alpha, \end{aligned} \quad (A9')$$

where

$$\begin{aligned} R(ij, kl, mn) &= 3D_{ij}D_{kl}D_{mn}[x_{ij}^2 x_{kl}^2 x_{mn}^2 \\ & \quad - 3x_{ij}^2 x_{kl}^2 y_{mn}^2 + 2x_{ij}^2 y_{kl}^2 z_{mn}^2 + 16x_{ij}y_{ij}y_{kl} \\ & \quad \times z_{kl}z_{mn}x_{mn} + 12x_{ij}y_{ij}x_{kl}y_{kl}(z_{mn}^2 - y_{mn}^2)]. \end{aligned} \quad (A10)$$

For the derivation of Eqs. (30) and (31), following the derivation of Eqs. (24) and (25), we have

$$\begin{aligned} \sum_{i>j} \sum_m \bar{R}(ij, ij, mj) &= \sum_{i>j} \sum_m R(ij, ij, mj) - \sum_{i>j} R(ij, ij, ij) \\ &= -\frac{N}{2} \sum_j R(ij, ij, ij) \end{aligned} \quad (A11)$$

and

$$\begin{aligned}
\sum_{i>j} \sum_{i \neq m} \tilde{\tilde{R}}(ij, il, mj) &= \sum_{i>j} \sum_l \sum_m R(ij, il, mj) - 2 \sum_{i>j} \sum_m \tilde{R}(ij, il, mj) - \sum_{i>j} \sum_l \tilde{R}(ij, il, lj) - \sum_{i>j} R(ij, ij, ij) \\
&= \frac{N}{2} \sum_j R(ij, ij, ij) - \frac{N}{2} \sum_{j \neq l} \sum R(ij, jl, li) .
\end{aligned} \tag{A12}$$

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