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Spin structures of europium selenide

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Europium selenide undergoes a series of magnetic transitions among antiferromagnetic (↑↑↓↓ and ↑↓↑↓) and ferrimagnetic (↑↑↓) phases. We propose that these phases are stabilized by lattice distortions induced by the differential dependence of the two exchange constants on the interplane distance. The corresponding change in dipolar energy is computed and is shown to be relatively small. In the induced distortion neighboring planes of parallel spins converge, and neighboring planes of antiparallel spins diverge. This model predicts macroscopic dilatations in general agreement with data of Griessen, Landolt, and Ott. A molecular-field theory is given and the results and limitations of the theory are discussed.

I. INTRODUCTION

The europium monochalcogenides (EuO, EuS, EuSe, EuTe) constitute perhaps the simplest known system of magnetic insulators,[1–3] yet the magnetic structures of EuSe remain unexplained. We propose an explanation based on interactions of the spin structure with internal lattice distortion modes. The relevance of spin-lattice interactions has been suggested before, notably by the experiments of Griessen, Landolt, and Ott[4] and by the consequent theory of Janssen.[5] Janssen, however, invoked a homogeneous lattice dilatation, whereas we shall show that the appropriate strain mode is associated with the particular spin structure, and it may or may not result in a net lattice dilatation along the [111] spin symmetry axis. The effect arises physically from the distance dependence of exchange integrals and it is associated with a contraction of the distance between planes of parallel spins, and an expansion of the distance between planes of antiparallel spins.

It is generally accepted that the europium chalcogenides have only first- and second-neighbor exchange interactions[1,3,6] (but see Ref. 3 for a dissenting suggestion). The nearest-neighbor interaction J_1 is a positive direct exchange which decreases in magnitude as increasing anion size increases the Eu-Eu distance (Fig. 1). In contrast J_2 is an indirect exchange integral. At least for the sulfide, selenide, and telluride it is negative and only weakly dependent on lattice constant; for the oxide there is some uncertainty as to the sign of J_2, and both Kasuya[7] and Swendsen[8] have presented evidence that its value is positive (see Fig. 1). The positive exchange dominates in EuO and EuS which therefore are simple ferromagnets, whereas the negative J_2 dominates in EuTe which is a simple antiferromagnet. In EuSe, the first- and second-neighbor exchanges are approximately equal in magnitude and opposite in sign,[6–8] leading to the sequence of more elaborate phases observed[3,9–11] (principally, by NMR and Mössbauer experiments) in EuSe.

All the observed magnetic structures of the europium chalcogenides can be considered to be composed of (111) planes such that within each (111) plane all spins are parallel to each other and to the plane itself. The anisotropy which constrains the spins to lie parallel to the planes arises from dipolar interactions.[1,3,5]

The experimental osbservations of spin configurations in EuSe have been interpreted and summarized by Bykovetz,[3] as follows. At a temperature of 4.6 °K there is a first-order transition from paramagnetic to ↑↑↓↓. As the temperature decreases the ↑↓↑↓ phase appears (coexistent with ↑↑↓↓) at roughly 2.8 °K (this temperature is structure-sensitive and varies from sample to sample). Further decrease in temperature is accompanied by continuous further conversion of ↑↑↓↓ to ↑↓↑↓.

As the temperature is increased again the behavior is slightly more complicated. One starts at low T with a mixture of ↑↑↓↓ and ↑↓↑↓. At approximately 1.9 °K the ↑↑↓↓ phase undergoes a sharp transition to ↑↑↓ (a ferrimagnetic phase) which then persists to higher temperature, gradually converting to ↑↑↓↓ and becoming depleted a half-degree or so below the critical temperature (4.6 °K). The initial ↑↓↑↓ phase meanwhile undergoes a sharp transition to ↑↑↓↓ at roughly 2.5 °K (again a structure-sensitive temperature).

Finally, we briefly note that, as emphasized by Bykovetz,[3] the theoretical interest in EuSe is enhanced by a kind of pseudo-two-dimensionality. The spins

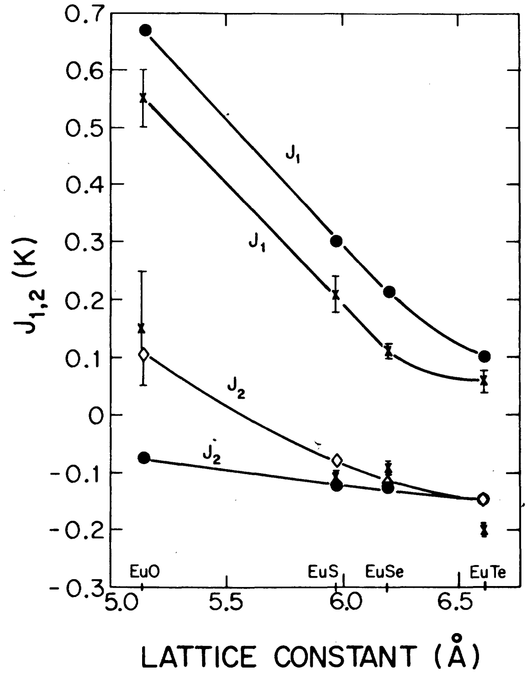

FIG. 1. Exchange integrals for europium chalcogenides. The upper curve for J_1 and the lower curve for J_2 (circles) are the early estimates of McGuire and Shafer (Ref. 6). The upper curve for J_2 (diamonds) is the recent suggestion of Kasuya (Ref. 7). The crosses, with error bars, are the weighted averages of various measurements as analyzed by Zinn (Ref. 2).

within a plane are strongly coupled (each spin has six nearest neighbors in the same plane), but neighboring planes are very weakly coupled (each spin has three nearest neighbors and three next-nearest neighbors in the neighboring plane, so that the mean interplane exchange cancels if $J_2 = -J_1$).

The dipolar interaction provides a residual interplane coupling. In a previous paper[12] we found that the dipole interaction does stabilize the $\uparrow\uparrow\downarrow\downarrow$, $\uparrow\downarrow\uparrow\downarrow$ and $\uparrow\uparrow\downarrow$ configurations over a very narrow range of J_2 in the vicinity of $J_2 = -J_1$, and that the $\uparrow\uparrow\downarrow\downarrow$ phase is the dominant phase in the region. However the first-order transition and the dimensional changes[4] indicate that the lattice-coupling mechanism is dominant, augmented by the dipolar interaction.

II. LATTICE COUPLING MECHANISM

The decrease of J_1 with increasing Eu-Eu distance, as exhibited in Fig. 1, has been validated further by observations on mixed crystals[3,13] and by pressure experiments.[11,14] On the basis of magnetization measurements under pressure by Busch *et al.*,[15] Schwob[16] has inferred that 8 kbar of pressure would convert EuSe to a simple ferromagnet; this pressure would decrease the lattice constant by only one-tenth[17] of the change required to make it equal to that of EuS. In contrast, the variation of J_2 through the chalcogenide series, experiments with EuSe-EuS mixtures,[3,13] and pressure experiments[14] all support the inference that J_2 is a slowly varying function of lattice constant in the neighborhood of EuSe; presumably because of a compensating hybridization of the electronic wave functions involved in the indirect exchange.

Consider EuSe in the $\uparrow\uparrow\downarrow\downarrow$ configuration. The net exchange energy of all spins is lowered if the distance between parallel planes is decreased and that between antiparallel planes is increased. This decrease in magnetic energy is linear in the elastic strain, whereas the increase in elastic energy is quadratic, so that the (free) energy is minimized by a nonzero strain.

The lattice distortion of the $\uparrow\uparrow\downarrow\downarrow$ phase corresponds to a positive displacement of odd-numbered planes and a negative displacement of even-numbered planes (or vice-versa), and therefore, it produces no macroscopic lattice dilatation. This is in agreement with the observations of Griessen, Landolt, and Ott,[4] who found no dimensional anomaly at the 4.6° transition temperature (although a change in slope indicates the phase transition); see Fig. 2. In contrast, the sublattice magnetization undergoes a first-order jump[3,9] of approximately 60%.

Consider now the $\uparrow\downarrow\uparrow\downarrow$ phase, which exists below $\simeq 2.8$ °K (for decreasing temperature) or below $\simeq 2.5$ °K (for increasing temperature). In this case the repulsion of antiparallel planes leads to a homogeneous lattice expansion. The corresponding dimensional anomaly is seen in Fig. 2.

Finally, consider the $\uparrow\uparrow\downarrow$ phase, which exists above $\simeq 1.9$ °K. The repulsion of antiparallel planes and the

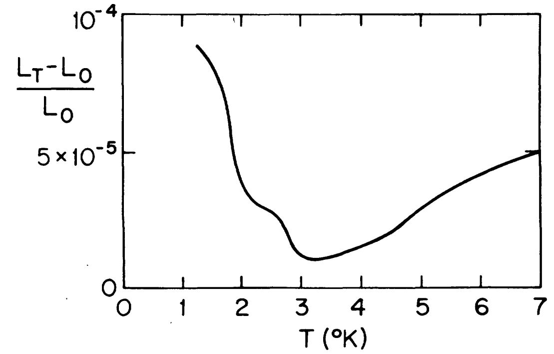

FIG. 2. Linear dimension (in [100] direction) of EuSe as a function of temperature. From Griessen, Landolt, and Ott (Ref. 1). L_T is the length at temperature T, with no applied magnetic field. The reference length L_0 is at $T = 0$, with an applied field of 100 Oe.

attraction of parallel planes expands two-thirds of the interplane distances and contracts one-third of the interplane distances. Hence, the lattice dilatation in this phase should be approximately one-third of that in the $\uparrow\downarrow\uparrow\downarrow$ phase. A dilatational anomaly at $\simeq 1.9$ °K can reasonably be ascribed to the data of Fig. 2. And the steeper character of the curve below 1.9 °K is consistent with the absence of the $\uparrow\uparrow\downarrow$ phase below that temperature.

The distortions can be understood in terms of the formalism of spin-phonon coupling. The relevant term in the Hamiltonian is $-J_{ij}\vec{S}_i\cdot\vec{S}_j$, with $J_{ij} = J_{ij} + xJ_{ij}'$, where x denotes a lattice displacement and J_{ij}' is the spatial derivative of J_{ij}. Thus we obtain a spin-phonon interaction $(a_{k_1}^{\pm}S_{k_2}^{+}S_{k_3}^{-})$ which is first order in phonon operators and second order in magnon operators. It is necessary that $\vec{k}_1 + \vec{k}_2 + \vec{k}_3 = \vec{K}$, a vector of the reciprocal lattice. We can corroborate that this is so in each of the phases described. The planes form an effective one-dimensional system along the [111] direction, with an interplane distance $d(=a/\sqrt{3})$. The spin structure in the $\uparrow\uparrow\downarrow\downarrow$ phase has $\lambda = 4d$ (or $k_{\text{spin}} = 2\pi/4d$), whereas the lattice distortion has $\lambda = 2d$ (or $k_{\text{spin}} = 2\pi/2d$); thus, $2k_{\text{spin}} + k_{\text{lat}} = 2\pi/3d = K$. Similarly, for $\uparrow\uparrow\downarrow$ the spin structure has $\lambda = 3d$ (or $k_{\text{spin}} = 2\pi/3d$) and the lattice distortion also has $\lambda = 3d$, so that $2k_{\text{spin}} + k_{\text{lat}} = 2\pi/d = K$. Finally, for $\uparrow\downarrow\uparrow\downarrow$, $k_{\text{spin}} = 2\pi/2d$ and $k_{\text{lat}} = 0$ and again $2k_{\text{spin}} + k_{\text{lat}} = K$. In all cases the spin structure and the lattice distortion can be considered as the growth to finite amplitude of a coupled spin-lattice soft mode.

III. MOLECULAR-FIELD THEORY OF ELASTICALLY DISTORTED SPIN STRUCTURES

We briefly indicate a molecular-field theory of the spin phases of EuSe, primarily to illustrate the mechanism. In the strained crystals, the distortions can be described by a parameter ξ, where the distance between neighboring parallel (111) planes is $(a/\sqrt{3})(1-\xi)$ and the distance between neighboring antiparallel (111) planes is $(a/\sqrt{3})(1+\xi)$. The elastic free energy of the strained lattice is taken to be

$$F = \tfrac{1}{2}N\kappa(T)\xi^2 \ , \tag{1}$$

where $\kappa(T)$ is an elastic stiffness parameter and N is the number of Eu ions in the sample. We apply molecular-field theory to the (111) planes as sublattices. Let i be an index which numbers planes, with $i=0$ taken as a "$\uparrow$" plane. Let $\vec{J}_{ji}$ be the sum of the exchange interactions between one spin on the jth plane with all spins on the ith plane, so that $(N/n)\vec{J}_{ji}$ is the total exchange interaction constant between the jth and ith planes. Here n is the number of (111) planes in the sample, and N/n is the number of spins in one plane. Similarly let $\vec{D}_{ij}$ be the (tensorial) dipolar interaction between planes, so that the total energy of spin interaction is

$$E_{\text{spins}} = \frac{N}{n}S^2 \sum_{i,j} \vec{\sigma}_i\cdot(\vec{J}_{ij} + \vec{D}_{ij})\cdot\vec{\sigma}_j \ , \tag{2}$$

where $\vec{\sigma}_i$ is the normalized spin of the ith plane

$$\vec{\sigma}_i = \langle\vec{S}\rangle/S \tag{3}$$

for any spin on plane i. Then minimizing the sum of the spin energy [Eq. (27)] and the elastic energy [Eq. (1)] gives

$$\xi = \frac{S^2}{n}\sum_{i,j}\vec{\sigma}_i\cdot(\vec{j}_{ij} + \vec{d}_{ij})\cdot\vec{\sigma}_i \times \left\{\kappa - \frac{S^2}{n}\sum_{i,j}\vec{\sigma}_i\cdot(\vec{j}_{ij}{}' + \vec{d}_{ij}{}')\cdot\vec{\sigma}_i\right\}^{-1} \ , \tag{4}$$

where the expansion coefficients of J_{ij} and D_{ij} in powers of ξ are defined by

$$\vec{J}_{ij} = \vec{J}_{ij}^{0} + \xi\vec{j}_{ij} + \tfrac{1}{2}\xi^2\vec{j}_{ij}{}' \ , \tag{5}$$

$$\vec{D}_{ij} = \vec{D}_{ij}^{0} + \xi\vec{d}_{ij} + \tfrac{1}{2}\xi^2\vec{d}_{ij}{}' \ . \tag{6}$$

One might perhaps expect that minimizing the *free* energy of the spins [rather that the energy as given by Eq. (2)] would alter this result, but as shown explicitly by Janssen[5] the entropy term in the free energy does *not* contribute to Eq. (4) in molecular-field theory.

The remaining equation of molecular-field theory is of the familiar form

$$\vec{\sigma}_i = B_S\left\{\frac{2S^2}{k_BT}\sum_j(\vec{J}_{ij} + \vec{D}_{ij})\cdot\vec{\sigma}_j\right\} \ . \tag{7}$$

Simultaneous solution of Eqs. (4)–(7) gives $\vec{\sigma}_i$ and ξ as a function of temperature.

As a specific illustration we apply this formalism to the $\uparrow\uparrow\downarrow\downarrow$ phase. If we define the "signature" of the j th plane to be

$$s_j = \begin{cases} +1 & \text{if the } j\text{th plane is "}\uparrow\text{"}, \\ -1 & \text{if the } j\text{th plane is "}\downarrow\text{"}, \end{cases} \tag{8}$$

then the $\uparrow\uparrow\downarrow\downarrow$ phase is characterized by

$$s_j = \sqrt{2}\cos[\tfrac{1}{4}(2j+1)\pi] \ . \tag{9}$$

The symmetry of the $\uparrow\uparrow\downarrow\downarrow$ phase simplifies the analysis considerably. All planes are equivalent except for simple reversal of spins, so that

$$\sigma_j = s_j\sigma \tag{10}$$

and the problem reduces to two unknowns: σ and ξ. Furthermore, the dipolar interaction is an odd function of ξ, so that $d_{ij}' = 0$ in Eq. (6). And we take $j_{ij}' = 0$ in Eq. (5), as the curvature in Fig. 1 is small relative to the contribution of the linear slope. Then, Eqs. (4)–(7) can be summarized in a single equation for σ:

$$\sigma = B_S[(T_0/T)\sigma + (T_1/T)\sigma^3] \ , \qquad (11)$$

where T_0 is proportional to the critical temperature in a rigid lattice [see Eq. (18)],

$$T_0 = \frac{2S^2}{k_B} \sum_j (J_{0j} + D_{0j}) s_j \ , \qquad (12)$$

and where T_1 is a measure of the "feedback" effect of the lattice strain,

$$T_1 = \frac{4S^4}{k_B \kappa} \left[\sum_j (j_{0j} + d_{0j}) s_j \right]^2 \ . \qquad (13)$$

In Eq. (12) the exchange contribution arises only from the six nearest neighbors in the $j=0$ plane (because $s_1 = -s_{-1}$); with J_1/k_B taken[4] as$\simeq$0.11 °K the exchange contribution to T_0 is therefore 12 $S^2 J_1/k_B \simeq 16$ °K. The dipolar term has been calculated[3,5] to be$\simeq$2 °K. Hence the sum of the two contributions to T_0 gives $T_0 \simeq 18$ °K. The value of T_1 is more difficult to estimate. A rough approximation of j_{ij}, interpolated from the dependence of J_1 on lattice constant is $j_{ij}/k_B \simeq 5$ °K (if $j = \pm 1, 0$ otherwise); thus $\sum_j j_{0j} s_j / k_B \simeq 10$ °K. The dipolar contribution in Eq. (13) can be evaluated by direct differentiation of the dipolar energy, giving

$$N^{-1} \frac{dE_D}{d\xi} = 16 g^2 \mu_B^2 S^2 a^{-3} \times \sum_{(nml)} \frac{s_\upsilon \nu}{r^5} \left[2 - \frac{5(n-m)^2}{r^2} \right] \ , \qquad (14)$$

where $r = (n^2 + m^2 + l^2)^{1/2}$ and where the summation is over all integral values of n, m, and l such that $n + m + l$ is even and υ is odd. We have evaluated this summation numerically for the ↑↑↓↓ phase, finding the value $-0.2N$ for the summation, whence

$$\sum_j{}' d_{0j} \sigma_j = 16 g^2 \mu_B^2 a^{-3}(-0.2) = -0.03 \text{ °K} \ . \qquad (15)$$

Hence, for our purposes we simply absorb the d_{0j} contribution into our estimate above of j_{0j}. We still must estimate κ, in the denominator of Eq. (13). A crude estimate is $\kappa \simeq \frac{1}{4} E a^3$, where E is Young's modulus; compressibility measurements[17] suggest $\kappa \simeq 10^{-11}$ ergs, whence $T_1 \approx 0.1$ °K. Then Eq. (11) is easily solved by iteration with a hand calculator, inserting $\sigma = 1$ in the argument of the Brillouin function as the zeroth iterate.

Alternatively, the result can be analyzed by a graphical construction that reveals the shortcoming of molecular-field theory. We write Eq. (11) as

$$\sigma = B_S \left(\frac{\sigma}{t} \right), \quad \frac{t}{t_{\text{crit}}} = \frac{T}{T_c^0} (1 + a\sigma^2)^{-1} \ , \qquad (16)$$

where

$$t_{\text{crit}} \equiv (S+1)/3S = \tfrac{3}{7} \ \text{ for } S = \tfrac{7}{2} \ , \qquad (17)$$

$$T_c^0 \equiv [(S+1)/3S] T_0 = \tfrac{3}{7} T_0 \ \text{ for } S = \tfrac{7}{2} \ , \qquad (18)$$

and

$$a = T_1/T_0 \ . \qquad (19)$$

We now plot t/t_c as a function of σ^2, obtaining two such graphs from the first and second of Eqs. (16). The graph of t/t_c *vs* σ^2 from the first of Eqs. (16) is given in Fig. 3; by expansion of the Brillouin function we find that the initial slope is $(-\frac{13}{27})$, or, more generally,

$$\frac{t}{t_c} = 1 - \frac{3}{10} \frac{(S+1)^2 + S^2}{(S+1)^2} \sigma^2 + \cdots$$

$$= 1 - \tfrac{13}{27} \sigma^2 + \cdots \quad \text{for } S = \tfrac{7}{2} \ . \qquad (20)$$

For $T = T_c^0$ the second of Eqs. (16) is

$$t/t_c = 1 - a\sigma^2 + \cdots \quad (T = T_c^0) \ . \qquad (21)$$

Hence, to have a nonzero intersection at $T = T_c^0$ we must have $a\,(\equiv T_1/T_0) > \frac{13}{27}$. Such an intersection is clearly necessary in order to have a first-order transition, so that it is evident that our theory predicts only a second-order transition (for our estimated values of T_1 and T_0), a matter to which we shall return in a moment.

In Fig. 3 we plot the second of Eq. (16) for three values of a. The plots are given for $T/T_c^0 = 1$, but for any other temperature the curves are merely to be multiplied by the factor T/T_c^0. The intersection of

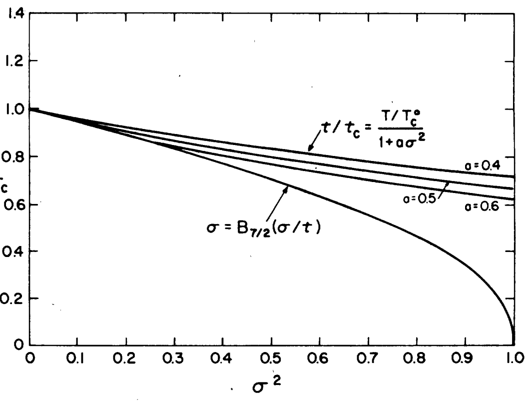

FIG. 3. Graphical analysis of Eqs. (16). The single curve is the first of Eqs. (16). The triplet are the second of Eqs. (16), for $T/T_C^0 = 1$, and for $a = 0.4$, 0.5, and 0.6. For $T/T_C^0 \neq 1$ these latter curves must be multiplied by T/T_C^0.

such curves with the "Brillouin curve" in Fig. 3 gives σ as a function of T, for any given T_0 and T_1.

Returning now to the second-order nature of the transitions, we identify its source in molecular-field theory. The theory of critical phenomena requires that the "Brillouin curve" should satisfy $\sigma \sim (t - t_c)^{1/3}$, or $t/t_c = 1 - \text{const}\,\sigma^3$. *That is, the correct initial slope of the "Brillouin curve" in Fig. 3* (in a t/t_c −vs $-\sigma^2$ plot) *should vanish.* Then any nonzero value of a would give a nonzero intersection of the two curves, and hence a first-order transition. We conclude that the molecular-field theory is strongly suggestive of a first-order transition, but a more adequate theory requires that we analyze the magnon-phonon coupling as described in Sec. II.

The deficiencies of molecular-field theory can be looked at from another perspective, which relates to the pseudo-two-dimensionality referred to in Sec. II. If $J_2 = J_1$ the molecular field acting on a given spin arises only from the six nearest neighbors in the same plane (and from the weak dipole interaction, which we temporarily neglect), so that the crystal is effectively a collection on noninteracting two-dimensional planes. It is well known that such two-dimensional structures cannot order (although molecular-field theory does predict two-dimensional order). In the real crystal, the planes are weakly coupled by fluctuations and strongly coupled by the lattice distortion (which makes $J_2 \neq -J_1$), restoring effective three dimensionality and stabilizing the spin ordering.

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