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No Giant Two-Ion Anisotropy in the Heavy-Rare-Earth Metals*

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A new Bose-operator expansion of tensor operators is applied to the heavy-rare-earth metals. The Er data for the cone phase have been analyzed successfully with *single-ion anisotropy* and *isotropic exchange interaction*. The Tb data can be understood on the same basis. The previously found large two-ion anisotropy was due to an inadequate treatment of the large single-ion anisotropy leading to an incorrect expression for the spin-wave energy.

Recently very accurate and detailed experiments of spin-wave spectra in the heavy-rare-earth metals[1-3] revealed that the magnetic interactions might be exceedingly complex. It is in particular difficult to understand the origin of the reported large two-ion anisotropy. Nicklow *et al.*[2] pointed out that this might be due to an inadequate model Hamiltonian. I shall show for the first time that the complexity is nonphysical and arises from an inadequate traditional treatment of the model Hamiltonian.

The previous analysis of the spin-wave data has been done on the basis of the theory of Niira[4] for the ferromagnet and by Cooper *et al.*[5] for the more general case including the spiral and cone phases. They included an anisotropic exchange interaction and the crystal field in the model Hamiltonian. Several subsequent theories added finer details and extra interactions, such as the magnetoelastic effect.[6] However, all theories are based either on the Holstein-Primakoff[7] (HP) transformation or on random-phase-approximation decoupled-spin Green's functions.[8] The anisotropy is treated incorrectly to lowest order by these theories.

A new transformation of spin (tensor) operators in terms of Bose operators has been developed. This makes it feasible to treat a strongly anisotropic magnetic system consistently to a given order of perturbation in the crystal field versus the exchange interaction. In terms of Bose operators, the Hamiltonian can generally (when neglecting higher-order terms) be written as[9,10]

$$\mathcal{H}=N^{-1}\sum_q [A_q \tfrac{1}{2}(a_q^{\dagger}a_q + a_q a_q^{\dagger}) + B_q \tfrac{1}{2}(a_{-q}a_q + a_q^{\dagger}a_{-q}^{\dagger})], \quad (1)$$

where A_q and B_q are wave-vector–dependent functions. The spin-wave energy is then[5,10]

$$E_q = \tfrac{1}{2}(A_q - A_{-q}) + [\tfrac{1}{4}(A_q + A_{-q})^2 - B_q^2]^{1/2}. \quad (2)$$

It is therefore not possible[10] from a measurement of E_q alone to determine A_q and B_q uniquely. The neutron scattering intensity contains sufficient extra information in principle[10]; however, in practice it is difficult to measure with sufficient accuracy. Experimental information about A_q and B_q separately has been obtained for two types of structure. For the cone structure $E_q \neq E_{-q}$ so that two functions are available to determine A_q and B_q from (2). This was done for Er by Nicklow *et al.*[2] For a ferromagnet the effect of an external magnetic field H is (predominantly) to change A_q to $A_q + g\mu_B H$. It is therefore possible, although less direct to find A_q and B_q separately by studying the field dependence of (2). This was done for Tb by Houmann and co-workers.[3] Both experiments revealed a strongly q-dependent B_q. On the basis of the existing theories[4-6,8] this could only be understood as a re-

sult of a giant two-ion anisotropy of the same order of magnitude as the isotropic exchange interaction or larger. This is at least an order of magnitude larger than that expected from theory[11] and also than the observed symmetry-breaking two-ion anisotropy.[12]

The new consistent transformation is obtained using the method of matching of matrix elements.[13] It is related to, but different from, the HP and the pseudo Bose transformation.[14] The transformation for any tensor operator $\tilde{O}$ is given by

$$\langle\psi_{n'}|\tilde{O}|\psi_n\rangle=\langle n'|f(a^\dagger,a)|n\rangle, \tag{3}$$

where $|\psi_n\rangle$ is an eigenstate of the single-site part of the Hamiltonian including the crystal field V_c, $|n\rangle$ is the corresponding Bose state, and $f(a^\dagger, a)$ is a well-ordered infinite Bose-operator expansion.[15] For the HP transformation $|\psi_n\rangle$ is the eigenstate of the single-site part of the exchange interaction: $H_{ex}S_i^z=2S\mathcal{J}(0)S_i^z$; in the pseudo Bose transformation a finite expansion is used. We shall here consider the effect of the crystal field to first order in V_c/H_{ex}. The perturbation approach makes it feasible to maintain the useful concept of anisotropy.

Given an isotropic exchange interaction and an axial crystal field,

$$\mathcal{H}=\mathcal{H}_{ex}+\sum_i V_{ci},\quad \mathcal{H}_{ex}=-\sum_{ij}\mathcal{J}_{ij}\vec{S}_i\cdot\vec{S}_j,$$
$$V_c=\begin{cases}\sum_l B_{l0}\tilde{O}_{l0}\ (c\text{ axis})\\ \sum_l\sum_{m=-l}^{l}\left(\frac{(l-m)!}{(l+m)!}\right)^{1/2}P_l^m(\cos\theta)B_{l0}\tilde{O}_{lm}\ (\theta\text{ axis}),\end{cases} \tag{4}$$

we find the spin-wave functions in (1) and (2) for a cone structure characterized by the cone angle θ and the wave vector $\vec{Q}$:

$$A_q=H_{ex}+D_0-\Delta_q-A_q^{ex}+B_q^{ex}D_2/H_{ex},$$
$$B_q=-B_q^{ex}+A_q^{ex}D_2/H_{ex}. \tag{5}$$

The exchange interaction enters via

$$H_{ex}=H(\vec{Q},\theta)=2S[\mathcal{J}(0)\cos^2\theta+\mathcal{J}(\vec{Q})\sin^2\theta],$$
$$A_q^{ex}=A_{-q}^{ex}=S\{\mathcal{J}(\vec{q})\sin^2\theta+\tfrac{1}{2}[\mathcal{J}(\vec{Q}+\vec{q})+\mathcal{J}(\vec{Q}-\vec{q})](\cos^2\theta+1)\},$$
$$B_q^{ex}=B_{-q}^{ex}=S\{\mathcal{J}(\vec{q})\sin^2\theta+\tfrac{1}{2}[\mathcal{J}(\vec{Q}+\vec{q})+\mathcal{J}(\vec{Q}-\vec{q})](\cos^2\theta-1)\}, \tag{6}$$
$$\Delta_q=-\Delta_{-q}=S[\mathcal{J}(\vec{Q}+\vec{q})-\mathcal{J}(\vec{Q}-\vec{q})]\cos\theta.$$

The anisotropy enters via

$$D_0=-\sum_l B_{l0}(S_l/S_1)P_l^0(\cos\theta)l(l+1)/2,$$
$$D_2=\sum_l B_{l0}(S_l/S_1)P_l^2(\cos\theta)/2 \tag{7}$$
$$=D_0\text{ for }\cos\theta=0,$$

where $S_l=S(S-\frac{1}{2})\cdots[S-\frac{1}{2}(l-1)]$ and $P_l^m(\cos\theta)$ are the Legendre polynomials. Since Δ_q is antisymmetric in q, A_q is asymmetric.

If the HP transformation is used neglecting the higher-order terms, which contain important contributions from the anisotropy, one obtains[4-6]

$$A_q=H_{ex}+D_0-\Delta_q-A_q^{ex}$$

and

$$B_q=D_2S_1/\sqrt{S_2}-B_q^{ex}. \tag{8}$$

This is clearly different from (5). However, both expressions (5) and (8) give the same energy difference $E_{-q}-E_q=\Delta_q$. The condition which determines the equilibrium cone angle θ_{eq} is when ($x\equiv\cos\theta_{eq}$)

$$2Sx^2[\mathcal{J}(Q)-\mathcal{J}(0)]=D_0-D_2\left(\frac{1-x^2[\mathcal{J}(Q)-\mathcal{J}(0)]}{\mathcal{J}(Q)}\right)^{-1}. \tag{9}$$

Except for the last term this is identical to that obtained by Cooper *et al.*[5] The last term is a ground-state correction which was not considered in Ref. 5.

Equations (5)–(7) contain as limiting cases spin-wave expressions for the spiral structure for $\cos\theta=0$, $\vec{Q}\neq0$, and the ferromagnetic structure for $\vec{Q}=0$. For the ferromagnetic structure $A_q^{ex}=2S\mathcal{J}(q)$ and $B_q^{ex}=0$. We notice using (2), (5), and (7) that $A_0=B_0$ or $E_{q\to0}$ is exactly zero for $\cos\theta=0$. This shows that the new transformation satisfies the Goldstone theorem exactly for planar anisotropy. This is not the case for (8) which

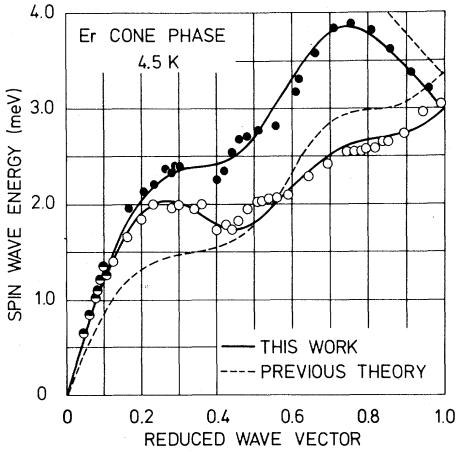

FIG. 1. The spin-wave data for Er by Nicklow *et al.* (Ref. 2). The full line is the fit by the present theory using six parameters and a q-independent anisotropy. The dashed line is the best fit of the previous theories using eight parameters (Ref. 2). By introducing a q-independent anisotropy a curve almost identical to the full line was obtained by Nicklow *et al.* (Ref. 2) with ten parameters.

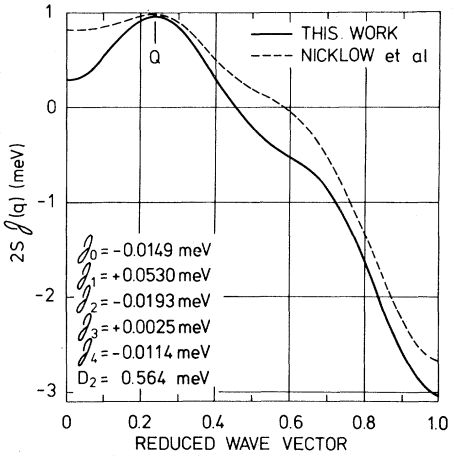

FIG. 2. The deduced exchange interaction $2S\mathcal{J}(q)$. The full line is the present fit and the dashed line that obtained by Nicklow *et al.* (Ref. 2) by fitting to Δ_q. The dashed curve is shifted to give the same $\mathcal{J}(Q)$. The exchange and anisotropy parameters are given in meV.

gives an imaginary energy, $E_{q\to 0}=D_0[1-(1-1/2S)^{-1/2}]$.

The spin-wave data[2] for Er at 4.5 K for q along the ΓA direction were analyzed on the basis of (5) using one *q-independent* anisotropy parameter and the Fourier expansion of the exchange interaction

$$\mathcal{J}(q)=2\sum_{l=0}^{n}\mathcal{J}_l\cos(lq\pi),$$

identical to that used by Nicklow *et al.*[2] except for the inclusion of the $l=0$ term and the reduced units for q. We notice that the q dependence of $\Delta_q=(E_{-q}-E_q)/2$ is given by $2S\sum_l \mathcal{J}_l\sin(Ql\pi)\times\sin(ql\pi)$. Since $Q=0.238$[16] is very close to $\frac{1}{4}$, in particular $\mathcal{J}_4$ is ill determined from Δ_q alone. The fit is therefore made directly to the energies and the result is shown in Fig. 1. The parameter values are given in Fig. 2. Since the fit did not improve significantly by including more parameters I limited the number of exchange constants to $\mathcal{J}_0$ and four interplanar exchange constants. Nicklow *et al.*[2] used seven interplanar exchange constants; see the caption of Fig. 1. The resultant $\mathcal{J}(q)$ is shown in Fig. 2 (full line). It has a sharper maximum at $q=Q$ than that obtained by Nicklow *et al.*[2] (dashed line). We notice that (5) permits a determination of $\mathcal{J}(q)$ on an absolute scale, whereas (8) only gives $\mathcal{J}(0)-\mathcal{J}(q)$. The maximum, $\mathcal{J}(Q)$, gives a mean-field $T_N^0=\frac{2}{3}S(S+1)\mathcal{J}(Q)$ of 32 K which compares reasonably well with that obtained from the high-temperature susceptibilities, $T_N^0=53$ K, with the ordering wave vector $Q(T_N)=0.28$.[16] Using (9), $\mathcal{J}(q)$, and the cone angle $\theta_{eq}=28.5°$ we find the single-ion anisotropy constants $D_2=0.564$ meV and $D_0=1.74$ meV. This only permits a unique determination of two crystal-field parameters B_{l0} from (7). Using $B_{20}=-0.029$ meV, $B_{40}=6.0\times10^{-5}$ meV, and $B_{60}=1.8\times10^{-6}$ meV determined from measurements on dilute alloys of Er,[17] we find $D_0=0.40$ meV, mainly determined by B_{20}, and $D_2=0.57$ meV, mainly determined by B_{40}. B_{20} depends strongly on the c/a ratio and may therefore be different in the pure element and in the alloys.

I conclude that within the experimental accuracy the spin waves in the cone phase in Er are excellently described by an isotropic exchange interaction and an axial single-ion anisotropy. The previously found large two-ion anisotropy was based on an incorrect expression (8) for the spin-wave energy. On the other hand the presence of a small genuine two-ion (exchange) anisotropy cannot be excluded.[11,12] For a ferromagnet we find from (5) $B_q=D_2\mathcal{J}(q)/\mathcal{J}(0)$, which is strongly q dependent, with the property that $A_0-A_q=[D_2/2S\mathcal{J}(0)](B_0-B_q)$. This is in accordance with the experimentally found A_q and B_q (Ref. 3, p. 315, Fig. 5) from which we find $D_2\simeq\frac{1}{3}2S\mathcal{J}(0)\sim kT_c/(S+1)\simeq 2.7$ meV. This is the magnitude to be expected for the $m=2$ contribution to anisotropy for Tb. I therefore expect that the same conclusion

applies to the result for Tb.[3] The discussed effects are also important for other strongly anisotropic systems. A comprehensive analysis of the spin waves in the heavy-rare-earth metals on the basis of the systematic Bose operator expansion will be published elsewhere.

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Observation of Pyroelectricity in Chiral Smectic-*C* and -*H* Liquid Crystals*

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Pyroelectricity has been observed in the smectic-*C* and smectic-*H* phases of *l*-*p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate after the material is poled in a dc field. The observed pyroelectric coefficient is consistent with an estimate of its theoretical value.

Recently Meyer *et al.*[1] have presented both theoretical arguments and some experimental evidence that *p*-decyloxybenzylidene-*p'*-amino-2-methylbutylcinnamate (DBC), when prepared as a pure enantiomer (using *l*-amyl alcohol), is ferroelectric in the smectic-*C* and smectic-*H* phases. It occurred to us that an indication of spontaneous polarization in these phases would be the presence of a *pyroelectric* effect. We have succeeded in measuring a pyroelectric current in the smectic-*C* and smectic-*H* phases of the *l*-enantiomer of DBC after aligning the phases in a dc electric field, and verified that no pyroelectric effect is observed in the racemic form of DBC.

l- and *dl*-DBC were synthesized in the following manner[2]: *p*-nitrocinnamic acid was converted to the acid chloride via treatment with thionyl chloride; *l*-amyl alcohol or *dl*-amyl alcohol was then added to form the *p*-nitrocinnamate ester,