# Dynamical Properties of Some Rare Earth-Intermetallic Compounds*

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Abstract

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The "band" structure which is discernable in the crystal level structure of the large J second half rare earth in cubic crystal fields is discussed. In the compounds which are considered the principal static and dynamic properties are determined by the properties of the low energy band. The spin waves in these substances consist of both longitudinal and transverse varieties, and expressions for their dispersion relations are obtained.



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## I. Introduction

A theoretical analysis (Trammell 1963) of the ground state properties of the rare earth intermetallic compounds (anion in the nitrogen column) (Child et al. 1963) led to the conclusion that in these materials the "exchange fields" responsible for their magnetic ordering are small relative to the crystalline fields acting on the rare earth ions. The analysis indicates that for the second half rare earths the exchange energy per ion is nearly an order of magnitude less than the crystalline field splitting. Satisfactory quantitative agreement with experiment was obtained upon assuming that the crystalline field exhibited cubic point symmetry. Possible experimental evidence for a small non-cubic component of the field is still inconclusive.

We intend to discuss certain general features of the low lying excitations which may be expected in these materials. More detailed theoretical treatments must await further experimental information.

In the notation of A we take for the Hamiltonian

$$H = \sum_i V_{ci} - \tfrac{1}{2}\sum_{i,j} J_{ij}\, \underline{J}_i \cdot \underline{J}_j \quad . \tag{1}$$

We break H into two parts, $H = H_0 + H_1$, where

$$H_0 = \sum_i \left[ V_{ci} - \sum_j J_{ij} \langle \underline{J}_j \rangle_0 \cdot \underline{J}_i \right] + \tfrac{1}{2}\sum_{i,j} J_{ij} \langle \underline{J}_i \rangle_0 \cdot \langle \underline{J}_j \rangle_0 , \tag{2}$$

and

$$H_1 = -\tfrac{1}{2}\sum_{ij} J_{ij} (\underline{J}_i - \langle \underline{J}_i \rangle_0) \cdot (\underline{J}_j - \langle \underline{J}_j \rangle_0) \, . \tag{3}$$

$H_0$ represents the effective field or self consistent approximation to the Hamiltonian, while $H_1$ represents the effect of correlations.

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The condition for the best product wave function approximation to the ground state of H, $\psi_0 \doteq \phi_0 = \prod_i w_0^i$ , leads to the Hartree-Fock self consistent field equations

$$(V_{ci} - \underline{B}_i \cdot \underline{J}_i) w_n^i = \epsilon_n^i w_n^i , \tag{4}$$

$$\underline{B}_i = \sum_j J_{ij} \langle \underline{J}_j \rangle_0 , \tag{5}$$

where in (5) the expectation value is that for the state $w_0^j$ which corresponds to the lowest eigenvalue $\epsilon_0^j$ of eq. (4). Hereafter, in order to simplify the discussion, we shall assume that the Hartree-Fock ground state is ferromagnetic so that the alignment of each ion is the same and eqs. (4) and (5) are independent of the index i.

## II. Crystal Field Bands

Before considering the effect of $H_1$ in determining the properties of the ground and excited states we must briefly recapitulate some of the results obtained in A concerning the eigenstates of $H_0$. We were there faced with the diagonalization of (eq. (4))

$$h_0(\underline{B}) = V_c - \underline{B} \cdot \underline{J} \ . \tag{6}$$

For the large J rare earths the full diagonalization of $h_0$ for a range of values of the effective field $\underline{B}$ and the parameters of $V_c$ calls for the use of high speed automatic computers, and White and Andeline (1959), and Ebena and Tsuya (1960) present tables and graphs of the results of such computations for the various rare earths in cubic crystal fields. However, simpler methods suffice to determine the low lying states for the small B's which are of principle concern to us.

The high and low lying states of $V_c$ form bands which for large J are well separated from the remaining states. The matrix of $\underline{J}$ in the representation which diagonalizes $V_c$ consists of large, low frequency components within the low energy band (say), and small high frequency components between a state in the band and one not in the band. The B's which occur in our compounds are such that BJ is of the order of or smaller than the low energy band width. The principal effect of such B's on the low states of $h_o$ is to only cause appreciable intermixture among the states of the low energy band, the effect of the other states of $V_c$ being ignorable or representing a small perturbation.

The physical significance of the band is best shown by an example. Suppose the cubic potential, $V_c$, is represented by just its fourth order component

$$V_4 = -K\ (J_z^4 + J_x^4 + J_y^4)\ . \tag{7}$$

Let $|m_x)$ represent the eigenstate of $J_x$ with eigenvalue m, and similarily define the quantities for the five other cartesian directions. In the classical limit of infinite J the states $|J_i)$ where i runs over the 6 cartesian directions obviously form the six fold degenerate ground states of (7) with energy

$$E_o = \langle J_z | V_4 | J_z) \doteq -K J^4\ . \tag{8}$$

For finite but large J's linear combinations of these six states still are the principal components of the ground state, but their degeneracy has been (partially) lifted by the non-vanishing "overlap integrals"

$$\langle J_z | V_4 | J_x \rangle \doteq -2K J^4 \langle J_z | J_x \rangle = -2K J^4 2^{-J}\ . \tag{9}$$

In our example, since each state overlaps four other states, the band width is of the order

$$\Delta E_0 \doteq 8 \cdot 2^{-J} E_0 . \tag{10}$$

On the other hand, the next higher "band" should be formed from the states with m = J-1, giving

$$E_1 - E_0 \doteq KJ^4 - K(J-1)^4 \doteq 4J^{-1} E_0 . \tag{11}$$

Thus for large J's the band width to level spacing ratio for the lowest band should be about

$$\Delta E_0 / (E_1 - E_0) \doteq (2J) \cdot 2^{-J} . \tag{12}$$

The interband spacing has, of course, a significance in the classical limit as a precessional frequency, while the intra band splittings are of purely quantum origin, representing the possibility of quantum mechanical tunneling between the various classical minima of $V_c$.

For the actual J's obtaining in the rare earths the above estimates serve only as rough quantitative guides. For holmium with J = 8 the right hand side of (12) (which represents the "jumping frequency" to "precessional frequency" ratio) is 1/16, whereas the actual ratio of the sextet band width to the spacing to the next level is about 1/10. According to A the sextet band width is about 5% of the overall crystalline field splitting for J = 8, and about 20% for J = 6. The octet band (corresponding to $\underline{J}$ in the body diagonal directions in the classical limit) width is about 20% of the overall crystalline splitting for J = 8, and about 30% for J = 6 (if we include only seven states in this "octet"). The band width increases with overlap, hence the increase in width as J decreases and in going from the sextet to the octet band.

As discussed above the band splitting is a purely quantum effect; similarly the actual level groupings within the band depend upon the value of J. Thus, if J is an even integer the sextet band consists of a singlet, a doublet, and a triplet; if J is odd, two triplets; and if J is half an odd integer, a doublet and a quartet. The spacings and ordering of the multiplets within the band are simply computed and depend upon the value of J (mod 4).

The utility of the band concept depends not only upon the smallness of the width to spacing ratio, but also upon the closeness of the identification of the band states with linear combinations of the $|J_1)$ functions. For $J \geq 6$ the sextet band in the $V_4$ potential contains only a few per cent admixture of other states. From the seven states composing the "octet" for $J = 6$ one may construct states for which $\langle J_{111} \rangle = 5.4$ (A), indicating about a 25% contamination of the $|6_1)$ states. Considerations concerning the octet band for $J = 6$ have only a rough quantitative significance.

III. Spin Waves

Exchange energies, $BJ$, which are of the order of or smaller than the low energy band width will yield ground state ordered moments of mean square magnitude

$$\sum_{n \neq 0} |(w_n, \underline{J}, w_0)|^2 = J(J+1) - |\langle \underline{J} \rangle_0|^2 . \qquad (13)$$

The inter-band states contribute roughly J to the sum in (13), while the intra-band matrix elements contribute the remainder. Interband excitations from the ground state correspond to spin waves which have the qualitative properties of ordinary spin waves in materials with axial anisotropy. On the other hand,

virtual intraband excitations give rise to a short range moment correlation in the ground state, and real intraband excitations give rise to "spin waves" whose properties are qualitatively different from the usual ones. We restrict our attention to the intra band excitations, which are of primary interest and importance in these materials.

The elementary excitations correspond to longitudinal oscillations of $\underline{J}$ parallel to $\langle \underline{J} \rangle_0$, and transverse oscillations perpendicular to $\langle \underline{J} \rangle_0$ which may be classified as clockwise and counter clockwise precessions about $\langle \underline{J} \rangle_0$ (we assume a ferromagnetic ground state).

In order to discuss the departures from the Hartree-Fock ground state we rewrite the Hamiltonian (1), (2), and (3) in the form

$$H = \sum_{i,n} \epsilon_n \bar{a}^i_n a^i_n - \tfrac{1}{2} \sum_{\substack{i,j,n,m \\ n',m'}} J_{ij} \, \underline{j}_{nm} \cdot \underline{j}_{n'm'} \, \bar{a}^i_n a^i_m \bar{a}^j_{n'} a^j_{m'}, \quad (14)$$

where $\bar{a}^i_n$ and $a^i_n$ are the usual Fermion creation and destruction operators for the states $w^i_n$ of eq. (4), and

$$\underline{j}_{nm} = (w_n, \underline{J} - \langle \underline{J} \rangle_0, w_m). \quad (15)$$

In order to obtain an approximate diagonalization of (14) we proceed in the familiar Bogoliubov manner (Bogoliubov 1957) retaining only those terms in the second sum of (14) which connect to $w_0{}^i$ and $w_0{}^j$, then replacing $\bar{a}_0$ and $a_0$ by one and interpreting the remaining creation and destruction operators as boson operators. Subtracting off the Hartree-Fock ground state contribution we obtain as an approximation to (14)

$$H' = \sum'_{i,n} e_n \bar{a}^i_n a^i_n - \tfrac{1}{2} \sum'_{i,j,n,m} J_{ij} (\underline{j}_{n0} \bar{a}^i_n + \underline{j}_{0n} a^i_n) \cdot (\underline{j}_{m0} \bar{a}^j_m + \underline{j}_{0m} a^j_m), \quad (16)$$

where $e_n = \epsilon_n - \epsilon_0$, and the prime on the summation signs indicate that n and m are restricted to non-zero values. H' can be diagonalized in a straight forward manner.

Longitudinal Modes. B, eq. (5), will be in one of the principal cubic directions. Calling this the z direction then the states $w_n$ having matrix elements of $J_z$ with $w_0$ will have zero matrix elements of $J_x$ and $J_y$ with this state. We may choose the phases of $w_n$ such that $(n|J_z|0)$ is real. Assume that there is only one such state which need be considered and let $(n|J_z|0) = m$. The part of H' determining the longitudinal oscillation now becomes

$$H'_{11} = \sum_i e\,\bar{a}_i a_i - \tfrac{1}{2}m^2 \sum_{i,j} \mathcal{J}_{ij}(\bar{a}_i + a_i)(\bar{a}_j + a_j),$$

$$= \sum_i \tfrac{1}{2}(p_i^2 + e^2 q_i^2 - e) - e m^2 \sum_{i,j} \mathcal{J}_{ij} q_i q_j \,, \qquad (17)$$

where we have deleted the subscript n from (17). In the second line of (17) we have expressed the a's and $\bar{a}$'s in terms of the usual p's and q's to show that the longitudinal vibrations obey the same equations of motion as spring coupled linear oscillators. Upon expressing $q_i$ as a sum of plane waves, $q_i = N^{-1/2}\sum_{\underline{K}} q_{\underline{K}} e^{i\underline{K}\cdot\underline{R}i}$, and similarly for $p_i$, (17) becomes

$$H'_{11} = \sum_{\underline{K}} \tfrac{1}{2}\left[p_{\underline{K}} p_{-\underline{K}} + (e^2 - 2em^2\mathcal{J}(\underline{K}))\, q_{\underline{K}} q_{-\underline{K}} - e\right]$$

$$= \sum_{\underline{K}} \left[\omega_{\underline{K}} \bar{A}_{\underline{K}} A_{\underline{K}} + \tfrac{1}{2}(\omega_{\underline{K}} - e)\right], \qquad (18)$$

where in the second line of (18) we have accomplished the diagonalization of $H'_{11}$. From (18) the dispersion relation for these waves is given by

$$\omega_{\underline{K}} = \left[e(e - 2m^2\mathcal{J}(\underline{K}))\right]^{1/2}. \qquad (19)$$

For the short range spin correlations in the ground state we have

$$\langle \Delta J_z^i \Delta J_z^j \rangle_0 = e m^2 \langle q_i q_j \rangle_0$$

$$= N^{-1} \sum_{\underline{K}} \left( \frac{e m^2}{2 \omega_K} \right) e^{i \underline{K} \cdot \underline{R}_{ij}} \quad . \qquad (20)$$

Transverse Modes. If the sextet band lies lowest (holmium or dysprosium for the second half rare earths) then the two circularly polarized transverse oscillations are nearly degenerate in frequency and may be replaced by two linearly polarized modes.

Thus for holmium the sextet band consists of a singlet, $8_z + 8_{-z} + 8_x + 8_{-x} + 8_y + 8_{-y}$; a doublet, $8_z + 8_{-z} - 1/2(8_x + 8_{-x} + 8_y + 8_{-y})$, $8_x + 8_{-x} - (8_y + 8_{-y})$; and a triplet, $8_z - 8_{-z}$, $8_x - 8_{-x}$, $8_y - 8_{-y}$. Under the influence of an exchange field, $\underline{B}$, along the z axis say, these states are mixed, the ground state taking the form

$$w_0 = a\, 8_z + b\, 8_{-z} + c\,(8_x + 8_{-x} + 8_y + 8_{-y}) \, .$$

The two transverse modes represent transitions between $w_0$ and the states $8_x - 8_{-x}$, $8_y - 8_{-y}$. The degeneracy of these latter states are lifted by the exchange, however, their splitting is only $B(8_x, J_z 8_y) = B/32$, which is negligible compared to their distance from the ground state $= B \langle J_z \rangle_0$.

The dispersion relations and other properties of these modes may be obtained from the expressions of the last section for the longitudinal modes.

If the lowest band is the octet then the right and left hand circularly polarized transverse modes may differ appreciably in frequency.

We put $(w_2, J_+ w_0) = m_2$, $(w_3, J_- w_0) = m_3$ for the two states to which the transitions take place (we suppose that only two states make appreciable contributions) $m_1$ and $m_2$ may be taken to be real. We obtain for the Hamiltonian governing these motions

$$H'_\perp = \sum_i (e_2 \bar{a}_2^i a_2^i + e_3 \bar{a}_3^i a_3^i) - \frac{1}{4} \sum_{ij} J_{ij} [(m_2 \bar{a}_2^i + m_3 a_3^i)(m_2 a_2^j + m_3 \bar{a}_3^j) + c.c.] \quad (21)$$

Eq. (21) may be diagonalized in a straight forward manner and one obtains for the dispersion relation

$$\omega_K = \left[\frac{1}{4}\{e_2 + e_3 - J(K)(m_2^2 + m_3^2)\}^2 - (J(K) m_2 m_3)^2\right]^{\frac{1}{2}} \pm \frac{1}{2}[e_2 - e_3 - J(K)(m_2^2 - m_3^2)]. \quad (22)$$

Upon transforming (22) to the plane wave representation the hamiltonian is diagonalized upon making the canonical transformation $(A_{2K}, A_{3K}) \rightarrow (A'_{2K}, A'_{3K})$ where

$$A_2 = u A'_2 - v \bar{A}'_3,$$
$$\bar{A}_3 = v A'_2 - u \bar{A}'_3, \quad (23)$$

with $u^2 - v^2 = 1$, and letting $u = \cosh x$

$$\tanh 2x = m_2 m_3 [e_2 + e_3 - J(K)(m_2^2 + m_3^2)]^{-1}. \quad (24)$$

As a final comment we notice that in general the frequencies of these osicllations do not vanish when $k \rightarrow 0$. There is an exception to this however. The lowest states in the octet band are a singlet and a triplet. If the exchange field is weak enough such that only these states need be considered (as is the case for thullium in these compounds) then the susceptibility is isotropic, and the frequency of the long wave length transverse spin waves vanishes.

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