Interpocket polarization model for magnetic structures in rare-earth hexaborides

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The origin of peculiar magnetic structures in cubic rare-earth (R) hexaborides RB$_6$ comes mainly from the rich structure in their ordered phases. The best studied example is CeB$_6$ which undergoes a quadrupole (orbital) order at 3.3 K and then a magnetic order at 2.4 K.$^{1}$ The magnetic ground state is characterized by double-$k$ structure with wave vectors (1/4, ±1/4, 1/2) in units of the reciprocal lattice parameter 2$\pi$/a. Since the orbital order is superimposed on the magnetic order, it has been suspected that the orbital degeneracy in the crystalline electric field (CEF) ground state $\Gamma_8$ plays an important role.$^{2}$ Recently, however, neutron scattering experiment on GdB$_6$ has detected an equivalent wave vector in the ordered phase below 15 K.$^{3}$ Since the trivalent Gd ion has a half-filled 4f shell without orbital degrees of freedom, the order at $k = (1/4, 1/4, 1/2)$ should have an origin which does not depend so much on the particular configuration of 4f electrons. It is known that PrB$_6$ also has the same wave number in the magnetically ordered ground state below 4.2 K, but the intermediate phase between 4.2 K and 6.9 K has an incommensurate structure.$^{4}$ On the other hand, the ground state of NdB$_6$ has a simple antiferromagnetic structure called the type I (or A-type) with alternating plane polarized along and against (0,0,1).$^{5,6}$

In this paper we propose a simple model to understand the origin of these structures from a unified point of view. The basic observation is that the Fermi surface of RB$_6$ consists of three nearly spherical pieces centered on the X points $X_x = (1/2, 0, 0)$, $X_y = (0, 1/2, 0)$, $X_z = (0, 0, 1/2)$ in the Brillouin zone. The RKKY interaction involves interpocket polarization, which has a new characteristic wave vector $K_3 = (1/2, 1/2, 0)$ which connects $X_x$ and $X_y$, and equivalent ones. Just like the ordinary RKKY interaction can bring about the antiferromagnetic ordering by halving the reciprocal lattice vector, the halving of the characteristic wave vector $(1/2, 1/2, 0)$ can bring about the ordering at (1/4, 1/4, 1/2).

Let us consider the case of GdB$_6$ where the 4f electrons have only the spin degrees of freedom. The exchange interaction between a 4f-spin $S_i$ at $R_i$ and conduction electrons is taken to be

$$H_{df} = \frac{J}{N} \sum_{k,p} \sum_i W_{k,p} \epsilon^{(p-k)}(R_i) S_i \cdot \sigma_{\alpha\beta} c^\dagger_{k\alpha} c_{p\beta}, \quad (1)$$

where $N$ is the number of lattice sites, and $JW_{k,p}$ is determined by the exchange integral involving 4f wave functions and the conduction states. We follow the previous argument$^7$ to derive $JW_{k,p}$. In analogy with the APW method we consider a muffin-tin sphere centered at the origin. The Bloch function $\psi_k(r)$ of the conduction band is expanded inside the sphere as

$$\psi_k(r) = \frac{1}{\sqrt{N}} \sum_\lambda R_{k\lambda}(r) \sum_\Gamma Y^{(\lambda)}_{\Gamma\gamma}(\hat{r}), \quad (2)$$

where $R_{k\lambda}(r)$ describes the radial part with orbital index $\lambda$ and $Y^{(\lambda)}_{\Gamma\gamma}(\hat{r})$ is the cubic harmonics for the point-group representation $\Gamma$ and its component $\gamma$. We neglect the $k$-dependence of $R_{k\lambda}(r)$ since the extent of 4f electrons is smaller than that of 5d electrons which contribute dominantly to the exchange. Because the orbital angular momentum is zero in Gd$^{3+}$, the exchange integral becomes diagonal with respect to the azimuthal quantum number of 4f states, and to $(\Gamma, \gamma)$. Thus the exchange interaction becomes isotropic with a factor

$$W_{k,p} = \sum_{\Gamma\gamma} d^{(5d)}_{\Gamma\gamma}(k) d^{(5d)}_{\Gamma\gamma}(p). \quad (3)$$

The RKKY interaction $I(q)$ is given by

$$I(q) = \frac{2J^2}{N} \sum_k |W_{k,k+q}|^2 \left( \frac{f(\epsilon_{k+q}) - f(\epsilon_k)}{\epsilon_k - \epsilon_{k+q}} \right)$$

with $f(\epsilon)$ being the Fermi function. The intrapocket contribution to $I(q)$ comes from such $k$ and $k + q$ that belong to the same pocket of the conduction band. In addition, there arises the interpocket contribution explained earlier. Let us take the free-electron-like dispersion and set $|W_{k,k+q}|^2$ constant in order to see the consequence of the interpocket contribution in the simplest manner.
In order to keep the lattice periodicity, we take summation over the reciprocal lattice vectors $G$ rather than restricting the $k$-summation within the Brillouin zone. The $G$-summation corresponds to inclusion of higher energy bands. Namely we introduce

$$\hat{\Pi}(q) = \sum_G F(q + G)\Pi(q + G),$$

where $F(q + G)$ is a form factor to be specified later, and $\Pi(q)$ is the Lindhard function multiplied by the partial density of states at the Fermi level. The Fermi wave number $k_F$ is given by $k_F a / \pi = 0.9656 / \sqrt{2}$, which means that the three spherical Fermi surfaces barely touch with one another. In the real RB$_6$ system, the Fermi surface also contains a fine structure along $(1, 1, 0)$ and equivalent directions $^8, ^9$

Adding both intrapocket and interpocket contributions we obtain for $q \in$ Brillouin zone:

$$I(q) = J^2 \left[ 3\hat{\Pi}(q) + 2 \sum_{i=1}^{3} \hat{\Pi}(q - K_i) \right] \equiv J^2 \chi(q),$$

where $3\hat{\Pi}(q)$ accounts for the three equivalent pockets, and $\hat{\Pi}(q - K_i)$ describes the interpocket polarization. The $K_i$‘s are given by $K_1 = (0, 1/2, 1/2), K_2 = (1/2, 0, 1/2), K_3 = (1/2, 1/2, 0)$ in units of $2\pi / a$. The factor 2 for the interpocket term enters because each pocket can be both starting and ending states of the transition. For simplicity we take the form factor such that $F(k) = 1$ if $|k_\alpha| < 6\pi / a$ for all components $\alpha = x, y, z$ and zero otherwise. The choice of the cut-off in the form factor hardly influences the $q$-dependence of the RKKY interaction, although it does influence the absolute value. Specifically with $F(q + G) = 1$ for all $G$, $\hat{\Pi}(q)$ diverges logarithmically by summation over $G$.

Figure 1 shows $\chi(q)$ in the $X$-$M$-$R$ plane of the Brillouin zone with $X = (0, 0, 1/2), M = (1/2, 0, 1/2)$ and $R = (1/2, 1/2, 1/2)$. The unit of ordinate is such that $\Pi(0) = 1$, and the large numerical value of $\chi(q)$ comes from summation over $G$. For the intersite interaction, only the variation in the $q$-space is relevant since the average of $\chi(q)$ represents the intra-site contribution.

We have also made a scan of $\chi(q)$ along $(1/4, 1/4, q_z)$ and found that the peak indeed occurs at $q_z = 1/2$. It is apparent that the interaction favors the magnetic order near the center of the $X$-$M$-$R$ plane, namely around $(1/4, 1/4, 1/2)$. Since the ridge extends more toward $M$ rather than $R$, an incommensurate structure with $q_z \neq q_x$ can be realized by slight change of the system parameters.

We now analyze in more detail the character of the conduction band, which consists mainly of $t_{2u}$ molecular orbitals of 2p electrons in B$_6$ clusters hybridized with $e_g$ orbitals of 5d electrons. One of the $t_{2u}$ orbitals has the angular dependence $z(x^2 - y^2)$ if seen from the center of the B$_6$ cluster, and hybridizes best with the 5d $x^2 - y^2$ orbital at neighboring rare-earth sites. Since $z(x^2 - y^2)$ changes sign below and above the $B_4$ plane, the wave number $(0, 0, 1/2)$ gains the bonding energy optimally. Therefore the bottom of the conduction band goes to $X_z$ and equivalent points. For $\Gamma = e_g$ we use a simplified notation $(\gamma | k) = \Delta^{(5d)}_\gamma (k)$ with $\gamma$ being either the state $x^2 - y^2$ or $3z^2 - r^2$. Then we have a large amplitude $(x^2 - y^2|X_z)$, while $(3z^2 - r^2|X_z)$ is negligible. At another point $X_x = (1/2, 0, 0)$, the wave function has the character of $y^2 - z^2$ which can also be represented by

$$|y^2 - z^2| = -\frac{1}{2}(x^2 - y^2) - \sqrt{3}/2(3z^2 - r^2),$$

with use of the basis set at $X_z$. Thus the orbital flip from $|x^2 - y^2| \rightarrow |y^2 - z^2|$ can take place even with the cubic symmetry. We note that the finite overlap does not contradict with the orthogonality of Bloch functions with different $k$.

The relative weight of the interpocket polarization against the intrapocket one should influence the detailed behavior of $I(q)$. We estimate from the above argument the weight factor $W_{k,p}$ for $k = X_z$ and $p = X_x$ relative to $W_{k,k}$ as

$$W_{k,p}/W_{k,k} \sim -1/2.$$  

These points $X_z$ and $X_x$, however, are not on the Fermi surface. In the region where two pieces of the Fermi sur-
face almost touch with each other, the interpocket con-
tribution connecting the nearby \( k \) states should have a
larger weight factor than the intrapocket one with remote
\( k \) and \( p \). We have made a tight-binding calculation tak-
ing the \( e_g \) and \( t_{2g} \) orbitals, and examined the character
of the wave functions at various points in the Brillouin
zone. It is found that 2p-electron weight is larger than the
5d-electron weight in general, and the latter changes gradu-
ally from \( |x^2 - y^2| \) to \( |y^2 - z^2| \) as \( k \) moves from
\( X_2 \) to \( X_3 \). In a future work, we shall evaluate \( W_{k,p} \) by
using realistic wave functions.

The presence of orbital degeneracy in rare-earth ions
other than Gd makes it necessary to consider more com-
plicated form of \( H_{df} \). Namely not only the spin exchange
interaction but multipole interactions also enter.\(^7,10,11\)
As long as the conduction band consists purely of \( e_g \)
for the 5d electron part, the wave-number dependence of the
multipole intersite interactions is the same as that of the
exchange interaction. Actually, however, \( t_{2g}(= \Gamma_5) \) also
enters into eq.(2). In the presence of orbital degener-
cy, \( W_{k,p} \) is no longer given by eq.(3) but with different
weights for each \( \Gamma_i \).\(^7\) Moreover, hybridization between 4f
electrons and boron 2p electrons may become important
in the open-shell case. The hybridization constitutes an-
other mechanism of the intersite interaction.

With these complications in mind we proceed to anal-
ysis of the exchange interaction in NdB\(_6\) where the spin-
wave spectrum has been measured. The dipole part of
\( H_{df} \) can be taken in the same form as eq.(1) except that
\( S_i^z \) is replaced by the angular momentum operator \( J_i \)
with \( J = 9/2 \). With only the magnetic intersite inter-
action, the easy axis of the magnetic moment should be
along \((1,1,1)\).\(^12\) Actually the moment is parallel or an-
tiparallel to \((0,0,1)\), which has been explained in terms of
ferroquadrupolar interaction.\(^13,14\) With inclusion of the
magnetic and \( \Gamma_3 \)-type quadrupolar interactions, we
consider the following model:

\[
H = - \sum_{i,j} I_{ij} J_i \cdot J_j - g_0^3 \sum_i \left( (O_2^0)^2 O_2^{0i} + 3(O_2^0 O_2^{0i}) \right),
\]

where we assume that the average of the quadrupole
moment does not depend on a site. Other interactions such
as the \( \Gamma_5 \)-type quadrupolar interaction\(^15\) are neglected
since they do not affect the spin-wave spectrum.

The CEF ground state is \( \Gamma_8^{(2)} \), which is four-fold de-
generate, and the first excited state lies 132-135 K
above.\(^13,16\) We introduce the Pauli matrix \( \sigma^\alpha (\alpha = \sigma \) 
\( x, y, z \) ) to describe the Kramers pair, and another Pauli
matrix \( \tau^\alpha \) to describe the orbital pair in the \( \Gamma_8^{(2)} \)
quarter. Then the angular momentum operator \( J^\alpha \) within the
\( \Gamma_8^{(2)} \) subspace is written as

\[
J^\alpha = \frac{1}{2} (\xi + \eta T^\alpha ) \sigma^\alpha ,
\]

where \( \xi = -0.883 \) and \( \eta = -4.712 \) are numerical con-
stants corresponding to the Lea-Leask-Wölfli\(^7\) parametrizer
\( x = -0.82 \).\(^13\) The orbital effect on the magnetic
moment is described by \( T^\alpha \) with \( T^2 = \tau^2 \) and

\[
T^{x,y} = -\tau^2/2 \pm \sqrt{3}\tau^2/2.
\]

In the Néel state the \( \Gamma_8^{(2)} \) quartet undergoes a Zeeman
splitting by the molecular field. This splitting induces a
finite quadrupole moment which is enhanced by
positive \( g_0^3 \). Then the lowest level is characterized by

\[
(+:\sigma^+) \rightarrow (\pm, -\sigma),
\]

with intensities \( I_+ \). Here \( \sigma = \uparrow, \downarrow \) in the A- and
B-sublayers, respectively. The intensity ratio \( I_+/I_- \) is
given by

\[
I_+/I_- = (2\xi/\eta - 1)^2/3 \sim 0.13.
\]

Thus we identify the observed branch as the inter-orbital
transition \((+,\sigma) \rightarrow (-, -\sigma)\), and assume that intra-
orbital branch was not detected because of the small
intensity.

By neglecting the small matrix elements for intra-
orbital magnetic excitations, we obtain a reduced model
which keeps only the two levels leading to \( I_+ \). Assuming
the A-type antiferromagnetic structure with \( Q = (0,0,1) \),
we obtain the excitation spectrum by the standard
spin-wave theory as

\[
\omega^2_q = [J(q) - \Delta] [J(q + Q) - \Delta],
\]

where \( J(q) \) is the Fourier transform of \( J_{ij} = (3\eta^2/16) I_{ij} \),
and

\[
\Delta = \frac{8\xi(\xi + \eta)}{3\eta^2} J(Q) + \frac{9}{2} \xi - \eta - 9)^2 g_0^3.
\]

The spectrum given by eq.(5) was also postulated in the
previous work, where \( \omega_q \) experimentally measured was
fitted by intersite interactions up to third neighbors. The
authors of ref.6 noted that the calculated Néel tempera-
ture was about half of the experimental one, \( 8-9 \) K. We
point out further that the substantial softening around
\((1/4,1/4,0)\) was not reproducible by the previous fit.

In view of the fact that the RKKY interaction has a
long range, we have included a sufficient number \((= 34)\)
of intersite interactions \( J_{ij} \). The comparison between
theory and experiment is shown in Fig.2. The experi-
mental spectrum is well reproduced by our fit. The fit
gives \( J(Q) = 1.16 \) meV and \( \Delta = 1.47 \) meV. Then we ob-
tain \( g_0^3 = 108 \) mK from eq.(6). This value is in excellent
agreement with experimental one, \( g_0^3 \sim 100 \) mK, deduced
from elastic constant.\(^13\) In the mean-field approxima-
tion the Néel temperature is not influenced by \( g_0^3 \), and is
given by

\[
T_N^{MF} = \frac{4\xi^2 + \eta^2}{3\eta^2} J(Q),
\]

which is 9.3 K with the fitted value of \( J(Q) \).

Figure 3 shows \( J(q) \) in the X-M-R plane. The maxi-
mum of \( J(q) \) occurs at \((0,0,1/2)\) in consistency with the
A-type order. In addition, there appears a local maxi-
mum near \((1/4,1/4,1/2)\). The latter indicates a ten-
dency toward the ordering with \( q = (1/4,1/4,1/2) \), and
brings about the softening of \( \omega_q \) near this wave num-
ber. We note that the overall behavior of \( J(q) \), and thus
\(I(q) = (16/3\eta)^2 J(q)\), is similar to the result of the inter-pocket polarization model shown in Fig. 1. This similarity supports relevance of the model to real RB₆ systems. The difference should mainly come from our simplification for \(W_{k,p}\) and \(\epsilon_k\), and partly from the presence of orbital degeneracy, hybridization, and correlation effect among conduction electrons.

In this paper we have concentrated on the \(q\)-dependence of the intersite interaction \(I(q)\). As the magnetization grows, the associated nonlinearity favors a commensurate structure in general. Then the maximum of \(I(q)\) does not necessarily give the ordering wave number at the ground state. We suggest that the incommensurate-commensurate transition in PrB₆ may be interpreted along this line. It should be worth investigating detailed features which depend on 4f-electron configurations of each rare-earth species.

Another feature to be addressed with finite order parameters is the direction of magnetic moment at each site. Even with the same \(q = (1/4,1/4,1/2)\), the moment patterns are rather different between CeB₆ and DyB₆. While in CeB₆ the nearest-neighbor moments are orthogonal to each other and within the (001) plane, the moments in DyB₆ point to \((1/2,1/2,1/2)\). The latter is consistent with the magnetic anisotropy in the paramagnetic region. In this connection it is interesting to inquire into the spin patterns of GdB₆ at low temperature, since the magnetic anisotropy in the paramagnetic region is extremely small.

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