Crystal Field, Magnetic Anisotropy and Excitations in Rare-Earth Hexaborides

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We clarify the role of crystalline electric field (CEF) induced magnetic anisotropy in the ground state and spin-wave spectrum of cubic rare-earth materials with dominating isotropic magnetic exchange interactions. In particular we study the hexaboride NdB₆ which is shown to exhibit strong spin-quadrupolar coupling. The CEF scheme is analyzed and a non-collinear magnetization response is found. The spin orientation in the antiferromagnetically ordered ground-state is identified. Moreover, the spin excitations are evaluated and in agreement with inelastic neutron scattering a suppression of one of the two magnetic modes in the strong-coupling regime is predicted.

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Introduction

Over the last two decades cubic rare-earth hexaborides, REB₆ (RE, rare-earth element), with CaB₆-type crystal structure have been at the center of numerous studies of materials with crystalline-electric-field (CEF) driven, non-trivial ordering phenomena. Among these compounds, CeB₆ (e.g., []) serves as a prototypical system which exhibits an impressively complex phase diagram. In this material the CEF of cubic symmetry selects the Γ₈ quartet to be the ground state of the Ce³⁺ ions (J = 5/2). The latter quartet is well separated from the next-highest Γ₇ doublet by an energy gap of order 540K [3]. Thus, on a low-energy scale, the physics of CeB₆ is reasonably well described by projecting onto the Γ₈ subspace. Similar systems with Γ₈ ground states can be realized starting from the right side of the rare-earth series, i.e., invoking compounds of cubic symmetry with Yb³⁺ or Tm²⁺ ions, whose incomplete f-shell contains 13 electron, or one f-hole. In accordance with Hund’s rule and contrast to the Ce-case however, the Γ₈ basis has to be constructed from a J = 7/2 multiplet, breaking direct electron-hole symmetry thereby.

In this brief note we will focus on the hexaboride NdB₆. Although investigated in detail experimentally by inelastic neutron scattering (INS) [3], the anisotropy of the magnetically ordered state below the temperature Tₘ of order Tₘ ≈ 8.6K [4] remains unclear as well as the existence of only a single magnetic mode as observed by INS. The aim of our work is to consider these open issues.

Crystalline electric field

The CEF level scheme of the Nd³⁺ multiplet (three f-electrons, J = 9/2, S = 3/2, L = 6) is consistent with the sequence Γ₈⁽²⁾(0 K) - Γ₈⁽¹⁾(135 K) - Γ₆(278 K) [3]. Similar to CeB₆ the energy gap separating the lowest quartet is large enough to restrict the Hilbert space to Γ₈⁽³⁾ only. The basis states of the latter sub-manifold can be represented by the linear combinations [3]:

\[ ψ_+ ≈ v_1 |+9/2⟩ + v_2 |+1/2⟩ + v_3 |−7/2⟩, \]
\[ ψ_- ≈ w_1 |+5/2⟩ + w_2 |−3/2⟩, \]
\[ ψ_+ ≈ v_1 |−9/2⟩ + v_2 |−1/2⟩ + v_3 |+7/2⟩, \]
\[ ψ_- ≈ w_1 |−5/2⟩ + w_2 |+3/2⟩. \]

The coefficients v₁ and w₁ depend on the respective ratios of the CEF splittings. For NdB₆ one finds [3]:

\[ v_1 = 0.1437, \quad v_2 = -0.3615, \quad v_3 = 0.9212; \]
\[ w_1 = -0.9223, \quad w_2 = 0.3865. \]

The states in [1] and [2] have been labeled such that the 2nd index denotes a "spin"-like projections, whereas the 1st index stands for two "orbital"-like components which reflect the different shapes of the electron wave-functions. This leads to a description of the quartet in terms of two Pauli matrices, σ and τ [5]:

\[ \sigma^± \psi_± = \pm i/2 \psi_±, \quad \sigma^± \psi_± = \psi_±, \]
\[ \tau^± \psi_± = \pm 1/2 \psi_±, \quad \tau^± \psi_± = \psi_±. \]

where the magnetic-moment operator can be represented in terms of σ and τ by:

\[ M_α = μ_B (ξ + 2ηT_α) σ_α, \quad (α = x, y, z). \]

Here T is a vector with components

\[ T_x = -1/2 \tau_x + \sqrt{3}/2 \tau_z, \quad T_y = -1/2 \tau_x - \sqrt{3}/2 \tau_z, \quad T_z = \tau_z, \]

which transforms according to the Γ₈ representation.

Note, that for NdB₆, ξ and η depend on the parameters of CEF splitting [3] with:

\[ ξ = -0.661, \quad η = -6.857. \]

This identifies NdB₆ to be a system with strong coupling of the magnetic and quadrupolar degrees of freedom. In the 1f-electron(hole) cases ξ and η are universal and do not depend on the CEF splitting parameters.
For Ce$^{3+}$ $\xi = 2$ and $\eta = 8/7$, for Yb$^{3+}$ $\xi = -8/3$ and $\eta = -32/21$. Therefore CeB$_6$ and YbB$_6$ exhibit rather weak spin-quadrupolar coupling with a characteristic parameter $\eta/(2\xi) = 2/7$.

Exchange anisotropy

In this section we clarify the spin orientation in the magnetically ordered ground state. Most likely, the dominant interaction in NdB$_6$ is of isotropic magnetic exchange type $\hat{H}$[54x352-]. However, due to the $\Gamma_8$ ground state a CEF induced magnetic anisotropy exists which depends on the ratio $\xi/\eta$. This can be understood easily by considering the single-ion Zeeman interaction, i.e., $-\vec{H} \cdot \vec{M}$ in an external magnetic field $\vec{H}$. The eigenvalues $\lambda$ in the $\Gamma_8$-space are

$$\lambda = \pm \sqrt{\frac{2}{7} + \frac{8}{7} \frac{\eta^2}{\xi^2} \pm \frac{4}{7} \frac{\eta^2}{\xi^2} \frac{4}{2 - 2\xi} - 3F(n) \left( \frac{\eta^2}{2 - 2\xi} \right), \quad (7)$$

measured in units of $g\mu_B H/2$. This clearly manifests a cubic anisotropy through the function $F(n)$:

$$F(n) = n_x^4 + n_y^4 + n_z^4, \quad n = \frac{\vec{H}}{H}. \quad (8)$$

The anisotropy results in a non-collinearity of the magnetic field and the magnetization for any general orientation of $\vec{H}$. Exceptions are the directions [111], [110], [001], and their crystallographic equivalents. Energetically favorable states are related either to the cubic axes ([001]-type), if $|\eta| < 2|\xi|$, or to the cubic diagonals ([111]-type), if $|\eta| > 2|\xi|$. The anisotropy caused by the CEF disappears, if $|\eta| < 2|\xi|$. Therefore, we may conclude that Ce$^{3+}$, Yb$^{3+}$ and Tm$^{3+}$ $\Gamma_8$ compounds tend to exhibit "easy axis" anisotropy ($\eta/(2\xi) = 2/7$), whereas for Nd$^{3+}$ in NdB$_6$ we have $\eta/(2\xi) \approx 5.19$ which results in "easy diagonal" anisotropy.

Within a mean-field treatment of the exchange interaction

$$- \sum_{\vec{R},\vec{R}'} J_{\vec{R}\vec{R}'} \mathbf{S}_R \cdot \mathbf{S}_{R'} \quad (9)$$

where $J_{\vec{R}\vec{R}'}$ is the exchange integral and $\mathbf{S}_R$ the spin at site $\vec{R}$ the magnetic field in $\hat{H}$ and $\hat{S}$ has to be replaced by the Weiss field $J_0(\mathbf{S})/(g\mu_B)$ with $J_0 = \sum_{\vec{R},\vec{R}'} J_{\vec{R}\vec{R}'}$ if ferromagnetic exchange is dominant. The Landé factor in NdB$_6$ is $g = 8/11$. For bipartite antiferromagnetism (AFM), the Weiss field on sublattice $A$ is proportional to $-J_0(\mathbf{S}_A) + J_0(\mathbf{S}_B)$ with $J_{0(1)} = (-) \sum_{\vec{R},\vec{R}'} J_{\vec{R}\vec{R}'}$ for $\vec{R}$ and $\vec{R}'$ on equal(opposite) sublattices. On sublattice $B$, one should replace $A \leftrightarrow B$. Therefore, in conclusion, we expect [111] orientational ordering in the ground state of NdB$_6$ if isotropic exchange interactions are dominant $\hat{H}$[54x352-].

Magnetic excitations

In this section we focus on the spin dynamics by considering the time-dependent magnetic susceptibility

$$\chi_{\alpha\beta}(\mathbf{k}, t) = i\Theta(t)[\langle S_{\alpha k}(t), S_{\beta - k} \rangle]. \quad (10)$$

Lower Greek indices of $\chi$ and the spin operator refer to $x, y, z$ and boldfaced vectors $\mathbf{k}$ denote the momentum. We use a spin operator rescaled by $\eta^{-1}$, i.e., $S_{\alpha k} = A_{\alpha k} / (g\mu_B \eta)$. Therefore the dependence of the magnetic spectrum on the CEF can be expressed solely in terms of the ratio $\xi/\eta$. To evaluate (10) we proceed via a mean field analysis consistent with AFM ordering $\hat{S}$ on a bipartite lattice. Rather than employing the Pauli-matrix representation $\mathbf{S}_\alpha$ of (11) we perform this analysis using a dyadic basis to express the spin operator within the $\Gamma_8$ manifold $\hat{S}$:

$$S_{\alpha k} = \frac{1}{\sqrt{2}} S_{\alpha}^{\mu
u} (a_{\mu k}^{\nu} + b_{\mu k}^{\nu})$$

$$a_{\mu k}^{\nu} = \sqrt{\frac{2}{N}} \sum_{\vec{R}} e^{-i\mathbf{k} \cdot \mathbf{R}} \hat{a}_{\mu \nu}^{\vec{R}}$$

$$b_{\mu k}^{\nu} = \sqrt{\frac{2}{N}} \sum_{\vec{R}'} e^{-i\mathbf{k} \cdot \mathbf{R}'} \hat{b}_{\mu \nu}^{\vec{R}'} \quad (11)$$

where a summation over repeated indices is implied for the remainder of this paper and

$$\hat{a}_{\mu \nu}^{\vec{R}} = |\mu \vec{R}\rangle \langle \nu \vec{R}|, \quad \hat{b}_{\mu \nu}^{\vec{R}'} = |\mu \vec{R}'\rangle \langle \nu \vec{R}'| \quad (12)$$

are the dyadics on sites $\vec{R}(\vec{R}')$ of the magnetic $\Lambda(B)$-sublattice. $|\mu \rangle$ are the eigenstates of the $z$-component of the spin in the $\Gamma_8$-manifold $S_{\alpha z} = s_{\mu} |\mu\rangle$. The spin should be quantized along(against) the [111] direction of the Weiss-field on the $\Lambda(B)$-sublattice sites. $S_{\alpha}^{\mu\nu}$ are the matrix elements of the spin corresponding to the latter quantization direction. The dyadic transition operators $a_{\mu k}^{\nu}$ and $b_{\mu k}^{\nu}$ with $\mu, \nu = 1 \ldots 4$ can be recast into a 32-component operator $A_{\kappa}^{\mu\nu} = 1 \ldots 32 = \{a_{1}^{\mu\nu}, \ldots, a_{4}^{\mu\nu}, b_{1}^{\mu\nu}, \ldots, b_{4}^{\mu\nu}\}$ with a corresponding $32 \times 32$ matrix-susceptibility of the $A_{\kappa}^{\mu\nu}$ operators

$$\chi^{\mu\nu}(\mathbf{k}, t) = i\Theta(t)[\langle A_{\kappa}^{\mu}(t), A_{\kappa}^{\nu \dagger} \rangle]. \quad (13)$$

The original magnetic susceptibility $\chi_{\alpha\beta}(\mathbf{k}, t)$ can be obtained from this by projecting the dyadics onto the momentum

$$\chi_{\alpha\beta}(\mathbf{k}, t) = \frac{1}{2} \chi^{\mu\nu}(\mathbf{k}, t) C_{\beta\alpha}^{\mu\nu} \quad (14)$$

where $C_{\beta\alpha}^{\mu\nu} = v_{\beta}^{\mu\nu} \cdot v_{\alpha}^{\mu\nu}$ with $v_{\alpha}^{\mu\nu} = 1 \ldots 32 = \{s_{1}^{\mu\nu}, \ldots, s_{4}^{\mu\nu}, s_{1}^{\mu\nu}, \ldots, s_{4}^{\mu\nu}\}$ is 32-component vector for each spin component $\alpha$.

To proceed we evaluate the equation of motion (EJM) of the dyadic susceptibility

\[ \chi^{\mu\nu}(\mathbf{k}, t) = i\Theta(t)[\langle A_{\kappa}^{\mu}(t), A_{\kappa}^{\nu \dagger} \rangle] \]
\[ i \partial_t \chi^{\mu \nu}(k, t) = -\delta(t) \left( [A^{\mu \nu}_k, A^{\nu \mu}_k] \right) \]
\[ + i \Theta(t) \left( [A^{\mu \nu}_k(t), H], A^{\nu \mu}_k \right) . \]  

(15)

In this brief report we concentrate on the spin dynamics for next-neighbor (NN) AFM exchange-couplings \( J \) only. The effects of longer-ranged couplings will be discussed elsewhere. Therefore, setting \( J \eta^2 / g^2 \) to unity the Hamiltonian in terms of the dyads reads

\[ H = \sum_{R \in \mathbf{R}} S^{\mu \nu} S^{\lambda \sigma} a^{\mu \nu \lambda \sigma}_R b^{\mu \lambda \sigma}_R \]

(16)

where \( I \) runs over the NN sites of \( \mathbf{R} \). The real-space representation of the commutator on the r.h.s of the EQM is evaluated using the algebra of the dyads, yielding

\[ [a^{\mu \nu}_R, H] = \sum_{1} \left( S^{\mu \omega} a^{\omega \nu}_R - S^{\omega \mu} a^{\omega \nu}_R \right) S^{\lambda \alpha}_R b^{\lambda \alpha}_R \]  

(17)

An analogous expression results on the B sub-lattice. On the mean-field level the EQMs are closed by factorizing all quadratic terms in (17) according to the scheme

\[ a^{\mu \nu}_R = (a^{\mu \nu}_R)_R + a^{\mu \nu}(b^{\nu \mu}_R) . \]

Moreover, ‘up’(‘down’) \([111]-\)polarization on the A(B) sub-lattice is enforced by setting

\[ \langle d^{\mu \nu}_R \rangle = \delta^{\mu 1} \delta^{\nu 1} \]

(18)

In momentum space the linearization results in

\[ [a^{\mu \nu}_k, H] = z S^{\mu \lambda}_\alpha S^{\nu \lambda}_\alpha - S^{\lambda \mu}_\alpha S^{\lambda \nu}_\alpha a^{\lambda \sigma}_k + \gamma_k \left( d^{\mu \nu}_k - S^{\lambda \mu}_\alpha S^{\lambda \nu}_\alpha b^{\lambda \sigma}_k \right) \]

(19)

where \( z \) is the coordination number and \( \gamma_k = \sum_i e^{ik_1} \). A similar equation arises for \([b^{\mu \nu}_k, H] \) introducing two additional 16x16 matrices \( L^{\mu \lambda \alpha \beta}_k \) and \( L^{\mu \lambda \alpha \sigma}_k \). Switching to frequency space the EQMs can be solved as

\[ \chi^{\alpha \beta}_\omega(k, \omega) = -\left( \omega I - zL_k \right)^{-1} \chi_0 \mathbf{C}_{\alpha \beta} \]  

(20)

where boldfaced symbols refer to matrix notation in a 32x32 space. \( L_k \) is set by \( L^{\mu \lambda \alpha \beta}_k \) with \( i, j = 1, 2 \) labeling four 16x16 sub-blocks. Similarly \( \chi_0 \) consists of four sub-blocks \( \chi^{\mu \nu \lambda \sigma}_{0,ij} \) with \( \chi^{\mu \nu \lambda \sigma}_{0,01} = 0 \) and \( \chi^{\mu \nu \lambda \sigma}_{0,11} = \delta^{\sigma \delta} \delta^{\mu \lambda (4)} \delta^{\lambda \mu (4)} - \delta^{\mu \lambda} \delta^{\sigma \lambda (4)} \delta^{\nu \mu (4)} \). Eqn. (20) allows for substantial simplifications. First, all diagonal dyads, i.e. \( a(b)_k^{\mu \mu \nu \nu} \), commute with \( H \). Second, the linearized form of (17) for the non diagonal dyads, i.e. for \( a(b)_k^{\mu \nu} \) with \( \mu \neq \nu \), is diagonal with respect to \( \mu \nu \) and remains local for nearly all pairs \( \mu \nu \). This follows from the identity

\[ S^{11(4)} \rightarrow S^{\mu \nu} = 0 . \]  

(21)

The only set of dyads which couple dispersively via the EQMs is

\[ B_\gamma^2 = \{ a^{(1, 2)}, a^{(1, 3)}, b^{(3, 4)}, b^{(4, 2)} \} \]  

(22)

and the corresponding hermitian conjugate set \( B_\gamma^2 = \{ a^{(1, 2)}, a^{(1, 3)}, b^{(3, 4)}, b^{(4, 2)} \} \). From the preceding discussion it is conceivable that the complete spin dynamics can be expressed in terms of the physically relevant dyads \( B_\gamma^2 = \{ a^{(1, 2)}, a^{(1, 3)}, b^{(3, 4)}, b^{(4, 2)} \} \) only. In fact, after some elementary rearrangements of the matrix-EQM \( 22 \), the longitudinal spin susceptibility, which, due to cubic symmetry, is identical to the three-trace \( \chi^{\alpha \beta}_\omega(k, \omega) \) simplifies to

\[ \chi^{\alpha \beta}_\omega(k, \omega) = -Tr[D^{-1} N] \]  

(23)

where the dynamical matrix \( D \) and the static susceptibility-matrix \( N \) are identical to \((\omega/\xi)(1-L_k) \) and \( \chi_0 \mathbf{C}_{\alpha \beta}/\omega \) restricted to within the 4 dimensional subspace spanned by eqn. (22). The complex conjugate dyads \( B_{\gamma}^2 \) introduce an overall prefactor of 2 only. After some algebra we find that \( D \) and \( N \) are determined by five parameters \( a, b, c, d, e \) and \( w = \omega/\xi \) through

\[ D = \begin{pmatrix}
  w - a & 0 & -c\gamma_k & -e\gamma_k \\
  0 & w - b & -c\gamma_k & -d\gamma_k \\
  -c\gamma_k & -e\gamma_k & w + a & 0 \\
  -d\gamma_k & -e\gamma_k & 0 & w + b \\
\end{pmatrix} \]

(24)

with \( w = \omega/\xi \) and

\[ a = S^{44}_\alpha (S^{22}_\alpha - S^{11}_\alpha) \], \[ b = S^{44}_\alpha (S^{11}_\alpha - S^{33}_\alpha) \]

\[ c = S^{21}_\alpha S^{34}_\alpha \], \[ d = -S^{13}_\alpha S^{32}_\alpha \], \[ e = -S^{13}_\alpha S^{34}_\alpha = \sqrt{cd} \].  

(25)

With this the longitudinal spin susceptibility of eqn. (23) is obtained readily as

\[ \chi^{\alpha \beta}_\omega(k, \omega) = \frac{Z(k, w)/\omega}{(w^2 - w_1^2)(w^2 - w_2^2)} \]  

(26)

where the weight factor \( Z(k, w) \) given by

\[ Z(k, w) = 2(ac - bd - (c-d)^2 \gamma_k)w^2 + (ad - bc)(ab + (ad - bc)\gamma_k) \]  

(27)

and the excitation energies \( \pm w_{1,2}(k) \) are being set by the roots of the biquadratic equation

\[ w^4 + w^2((c - d)^2 \gamma_k - (a^2 + b^2)) + a^2b^2 - (ad - bc)^2 \gamma_k = 0 \].  

(28)

In fig. (1) the dispersion as well as the weight \( R_{1,2}(k) = \chi^{\alpha \beta}_\omega(k, \omega) - \omega_1,2(k) \) are depicted along a path in the Brillouin zone (BZ) ranging from \( k = (1, 1, 1) \) to \((0, 0, 0) \) to \((1, 0, 0) \) for various values of the anisotropy ratio \( \xi/\eta \). This figure clarifies the concluding issue aimed at in this brief note,
i.e. the observation of only a single excitation mode in NdB₆. Based on the eigenvalues two excitations of comparable energy are expected in the Weiss field of the AFM state at $\xi/\eta \ll 1$. However, fig. (1) shows that only a single mode carries significant weight at small $\xi/\eta$. We have shown this feature to remain valid for arbitrary range couplings. Furthermore, in agreement with the spectrum of a single-ion pseudo-spin $J = 3/2$, the system exhibits a single-mode spin-wave like excitation at the isotropic point $2\xi = \eta$. Only for intermediate anisotropy both modes show sizeable weight at any given point in the BZ.

Conclusion

In summary we have considered rare-earth compounds of cubic symmetry with a $\Gamma_8$-quartet ground-state of the RE ions. Particular emphasis has been put on the hexaboride NdB₆. Analyzing the CEF splitting we have identified NdB₆ to be a genuine example of a system with strongly coupled magnetic and quadrupolar degrees of freedom.

We have studied the CEF induced intrinsic magnetic anisotropy superimposed onto an isotropic exchange interaction revealing that NdB₆ should display magnetic anisotropy of a different type, i.e. 'easy diagonal', as compared to Ce or Yb compounds which show 'easy axis' anisotropy.

The magnetic anisotropy leads to a non-collinear $\mathbf{M}$ vs. $\mathbf{H}$ behavior and is tempting to speculate that angular-dependent magnetization measurements on the corresponding RE cubic compounds, as well as diluted systems, e.g. La$_{1-x}$Ce$_x$B₆, should be able to detect this behavior.

We have evaluated the magnetic excitations in the AFM state of an 'easy diagonal' type using a dyadic operator approach. For systems with strong spin-quadrupolar coupling this method is superior to less controlled pseudo-particle descriptions which are applicable to the weak-coupling system CeB₆ and are based on the conventional $\sigma$-$\tau$ Pauli-matrix representation. In accordance with the number of independent Pauli matrices ($\sigma$ and $\tau$), we find two branches of spin excitations. However, the spectral weights in the two magnetic channels are very different in a strongly coupled spin-quadrupolar system. In fact, in the $\xi = 0$ limit one channel disappears completely. This is reminiscent of the INS data on NdB₆ which display only one branch of spin excitations. Although derived by a linearization of the EQMs we believe that our results are quite robust against nonlinear corrections since the spin-wave spectrum in non-isotropic case is gapful. This should diminish the relevance of quantum fluctuations.

Finally, regarding a direct comparison to experimental data we note that NdB₆ displays a [0, 0, 1/2] wave vector of the AFM modulation. This requires the inclusion of longer-range exchange interactions which have been neglected in this paper. These and the physical nature of the branch unobservable by INS will be studied elsewhere.

Fig. 1. Dispersion and weight of spin excitations.

[1] J.M. Effantin et al, J. Magn. Magn. Mater. 47/48, 145 (1985).
[2] E. Zirngiebl et al, Phys. Rev. B 30, 4052 (1984).
[3] M. Loewenhaupt and M. Prager, Z. Phys. B 62, 195 (1986).
[4] W.A.C. Erkelens et al, J. Physique Colloque C8, 457 (1988).
[5] P. Burlet, et al., Proc. ICM’88 (Paris).
[6] G. Uimin and W. Brenig, unpublished.
[7] F.J. Ohkawa, J. Phys. Soc. Jpn. 54, 3909 (1985).
[8] G. Uimin, Y. Kuramoto, and N. Fukushima, Solid State Commun. 97, 595 (1996).
[9] R. Shina, H. Shiba, and P. Thalmeier, J. Phys. Soc. Jpn. 66, 1741 (1997).
[10] This has to be contrasted against claims of [001] polarization in [4] which deserve additional confirmation.
[11] see eg.: K.W. Becker, P. Fulde, and J. Keller, Z. Phys. B 28, 9 (1977).