Comment on "Low-temperature ordered states of RBa$_2$Cu$_3$O$_{7-\delta}$ due to dipole-dipole and exchange interactions"

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In a recent paper Misra and Felsteiner calculate the low-temperature ordered states of certain RBa$_2$Cu$_3$O$_{7-\delta}$ compounds, using the Luttinger-Tisza method. Based on the results of these calculations the authors conclude that dipolar interactions alone can account for all the observed orderings of these materials. However, the calculations and the conclusions drawn from these calculations are based on assumptions that we believe are inconsistent with many crystal electric field measurements in the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds.

Misra and Felsteiner recently presented an analysis of the magnetic ground-state spin configurations of the RBa$_2$Cu$_3$O$_{7-\delta}$ series of compounds.[1] On the basis of the results from their analysis they claim that the dipole interaction is sufficient to explain the observed orderings of all these materials. Their analysis is based on the assumption that the magnetic properties of the ground state of the RBa$_2$Cu$_3$O$_{7-\delta}$ compounds may be described in terms of an effective spin-1/2 Hamiltonian in which the interaction between two spins is given by

$$J_{ij}^{\mu\nu} = \frac{\langle S^2 \rangle}{2} \mu_B^2 \left(g_{\mu\mu} g_{\nu\nu} \frac{r_{ij}^2 \delta\mu\nu - 3 r_{ij}^{\mu} r_{ij}^{\nu}}{r_{ij}^5} + v_{ij} \Delta_{ij} \delta\mu\nu \right), \tag{1}$$

where $S = 1/2$ represents the effective ionic spin, $\mathbf{r}_{ij}$ denotes the vector joining the ith and jth lattice site, v_{ij} represents the nearest-neighbor and the next-nearest-neighbor interaction, assumed to be isotropic, with $\Delta_{ij} = 1$ if i and j are nearest or next-nearest-neighbors and 0 otherwise, and $g_{\mu\nu}$ denotes the g tensor, assumed diagonal in the particular choice of coordinate axis.

The assumption that we can adequately describe the magnetic ground state of these compounds in terms of a spin-1/2 Hamiltonian requires that the $2J+1$ degeneracy of the free-ion ground state is lifted by the crystal electric field (CEF) interactions, and the resultant ground state of the rare earth ion is a doublet. Moreover it requires that the energy of the first excited state of the rare earth ion be much larger than the characteristic energy scale of both the dipolar and the exchange interactions. If such criteria are satisfied then the dipolar and exchange interaction between the rare earth ions may be treated as a perturbation to the CEF Hamiltonian. To leading order the ground-state wave function of the rare earth lattice may be written as a linear superposition of the 2^N-fold manifold of states constructed from the doublet ground states of the N rare earth ions and the energy spectrum obtained by diagonalizing the interaction Hamiltonian within this manifold, thus removing, in part, the degeneracy of the unperturbed ground state. In such a way the system is reduced to an $S=1/2$ spin system with an effective interaction which may be represented in terms of the interaction given in Eq. (1).

In such a representation, the effect of the CEF is entirely contained within the form of the g tensor. Denoting by $|+\rangle$ and $|-\rangle$ two orthonormal wave functions of the ground-state doublet of the unperturbed rare earth ion that diagonalize J_z, and assuming that the g tensor is diagonal then we define g_x, g_y, and g_z as[2]

$$g_J \begin{bmatrix} \langle +|J_i|+\rangle & \langle +|J_i|-\rangle \\ \langle -|J_i|+\rangle & \langle -|J_i|-\rangle \end{bmatrix} = g_i \sigma_i, \tag{2}$$

where $i = x$, y, z, and σ_i denotes the corresponding Pauli spin matrices. It is important to note that despite the above simplifications the spin system is still quantum mechanical and any analysis of the ground-state properties will, in general, involve further approximations.

The splittings induced by the CEF in these compounds have been studied extensively by a variety of techniques, most notably inelastic neutron scattering (INS), and there exists a considerable body of experimental data in the literature. In particular, based largely on the INS data, explicit values for the CEF parameters are presented for Dy,[3] Ho,[4,5] and Er.[6,7] However, Misra and Felsteiner base their analysis of the RBa$_2$Cu$_3$O$_{7-\delta}$ on the CEF parameters determined some years earlier for the RRh$_4$B$_4$ compounds[8] instead of using presently available data on RBa$_2$Cu$_3$O$_{7-\delta}$. Their justification for this is that the value of the largest CEF parameter estimated by Simuzu *et al.*[9] for orthorhombic HoBa$_2$Cu$_3$O$_7$ is comparable in magnitude to the corresponding parameter estimated for ErRh$_4$B$_4$,[10] which has tetragonal symmetry. This assertion allows Misra and Felsteiner to use the g

factors listed by them in an earlier publication.[8]

This approach, however, creates certain difficulties in the context of the present analysis. In particular, while the CEF interactions in $HoRh_4B_4$ yield a Γ_5 doublet ground state for the Ho ions,[11] the orthorhombic D_{2h} symmetry of the $HoBa_2Cu_3O_7$ lattice completely lifts the 17-fold degeneracy of the free Ho ion. Specific heat measurements on orthorhombic $HoBa_2Cu_3O_{7-\delta}$ show a singlet ground state with a first excited state at around 7 K.[12] This is consistent with CEF splittings obtained from inelastic neutron scattering which show a singlet Γ_3 ground state with a first excited state Γ_4 at around 6.4 K.[5] In the tetragonal phase the first excited state merges with the second excited state in the orthorhombic phase to form a Γ_5 doublet at approximately 14 K.[13] It should be noted, however, that even in the absence of the orthorhombic distortion, all the experimental evidence indicates that the ground state of the Ho ion remains singlet. The singlet ground state of the Ho is consistent with the low magnetic-ordering temperature of orthorhombic $HoBa_2Cu_3O_{7-\delta}$. The reason for the difference in the CEF level positions between RRh_4B_4 and $RBa_2Cu_3O_{7-\delta}$ compounds may be attributed to the fact that the fourth- and sixth-order CEF parameters in the RRh_4B_4 compounds are sufficiently small that the second-order parameter dominates the CEF effects,[14] while in the case of the $RBa_2Cu_3O_{7-\delta}$ compounds the fourth- and sixth-order parameters dominate, and the second-order parameters only cause small perturbations on the higher-order effects. This suggests that the approach of Misra and Felsteiner does not properly represent the ground state of the Ho ion, and hence is not applicable to the results of Ref. 15.

Another difficulty associated with the assumption that the CEF parameters for the $RBa_2Cu_3O_{7-\delta}$ compounds may be approximated by those obtained for the RRh_4B_4 compounds is that the difference between g_x and g_y is ignored in the analysis. While the orthorhombic distortion of $RBa_2Cu_3O_7$ is small, this difference is not insignificant and may be as large as 30% in the case of $ErBa_2Cu_3O_7$, and will be of some importance in distinguishing between the various magnetic configurations in which the spins are constrained to lie in the x-y plane. It has also been argued that this anisotropy may account for the differences between the magnetic behavior of the erbium in the orthorhombic and tetragonal phases of $ErBa_2Cu_3O_7$.[16]

Aside from the subtleties arising from the use of the CEF parameters associated with RRh_4B_4 compounds in the analysis of the magnetic properties of $RBa_2Cu_3O_{7-\delta}$, the value of the g tensor listed by Misra and Felsteiner for the Gd compounds also presents some difficulties. It is well known that, as an S-state ion, the Gd ion retains, at least to leading order, the eightfold degeneracy and magnetic moment of the free ion. This is consistent with both specific heat[16–18] and neutron scattering[19,20] results on $GdBa_2Cu_3O_{7-\delta}$. It is difficult therefore to see how the magnetic properties of $GdBa_2Cu_3O_{7-\delta}$ may be analyzed on the basis of a spin-1/2 Hamiltonian. In particular, it is not clear how the g tensor may be calculated for Gd, and the only reference given is to a private communication. The matter is of some importance in resolving the role of the exchange interaction in these compounds since, in the absence of any CEF splitting, a mean-field analysis of the magnetic ground-state of $GdBa_2Cu_3O_{7-\delta}$ with a purely dipolar interaction yields a ground state ordering in which the spins are aligned in the basal plane.[21,22] The fact that the magnetic moments of the rare earth ions in the observed ground state are aligned perpendicular to the basal plane,[19,20] not only suggests that the exchange interaction does indeed contribute to the magnetic interaction between the Gd ions in $GdBa_2Cu_3O_{7-\delta}$, but also places some bounds on its value.[23,24] While such an argument admittedly ignores the potentially important role played by quantum fluctuations in determining the magnetic structure of the ground state, if the direction of the Gd moment is not constrained by CEF interactions to lie along a single axis, we, nevertheless, remain unconvinced that the observed ground state can be accounted for solely in terms of the dipolar interaction.

It should also be noted that extrapolating a single set of CEF parameters across a particular isostructural series provides only a qualitative estimate of the splittings and the ground-state wave function of the rare earth ions. This is particularly so in the case of the light rare earth ions, as it is generally believed that in these ions the $4f$-electron wave function is less well isolated and consequently interacts less trivially with the other electrons and the nearest-neighbor ions.

One final point we would like to make concerns the comment that in calculating the magnetic interaction energy of various spin configurations, the demagnetization contribution should be included. While the rare earth ions in all of the $RBa_2Cu_3O_{7-\delta}$ compounds order antiferromagnetically and therefore the demagnetization energy does not contribute, it is nevertheless well established that in the case of magnetic superconductors the long-range character of the dipolar interaction is screened by the persistent current.[25–27] Consequently the demagnetization factor does not contribute to the interaction energy, even in the case of ferromagnetic ordering. The screening of the dipolar interaction is of some importance in properly interpreting the magnetic properties of the reentrant superconductors $ErRh_4B_4$ and $HoMo_6S_8$.

While a mean-field analysis of the magnetic ground states of the $RBa_2Cu_3O_{7-\delta}$ compounds can provide some insight into the relative magnitude of the exchange interaction, we believe that a more careful treatment of the CEF interaction is called for. Certainly the assumption that the CEF parameters in the $RBa_2Cu_3O_{7-\delta}$ compounds may be approximated by those given by the RRh_4B_4 compounds is far from adequate. Moreover, the fact that Misra and Felsteiner argue that the CEF interaction plays a role in determining the ground state of $GdBa_2Cu_3O_{7-\delta}$, for which they provide no details (referring to an apparently unpublished private communication referred to in an earlier publication), is difficult to accept. Finally we would like to point out that results from Monte Carlo simulations indicate that the dipolar interaction of itself does not yield the experimentally observed transition temperature for either $DyBa_2Cu_3O_{7-\delta}$ or $ErBa_2Cu_3O_{7-\delta}$.[28] Estimates of the exchange interaction obtained from these calculations, when extrapo-

lated to Gd, indicate that the exchange interaction is sufficiently large to stabilize the observed ground-state ordering.[23,24]

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