

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

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It is explained that the points raised by Whitehead, De'Bell, and Noakes in their Comment on our paper in *Phys. Rev. B* **46**, 11 033 (1992) are really not applicable.

Whitehead, De'Bell, and Noakes¹ argue in their Comment (preceding paper) on our paper on the low-temperature ordered states of $R\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$ (hereafter R 1:2:3) compounds that our calculations and resulting conclusions² are inconsistent with the crystal electric field (CEF) measurements in R 1:2:3 compounds. We discuss here the reasons why their arguments do not really apply in our case.

We have, indeed, used all the experimental g values reported in the literature for R 1:2:3 compounds. Specifically, for the compounds Dy 1:2:3 and Er 1:2:3 we did take into account the actual reported g values,² as estimated from the CEF parameters derived from inelastic neutron scattering (INS) data³ (Dy 1:2:3) and those determined from Mössbauer data (Er 1:2:3).⁴ Further, for Er 1:2:3, the values estimated from INS data were found to be quite close to those estimated from Mössbauer data.⁴ We found that the predicted orderings on the basis of these values did indeed agree with those predicted using the g values calculated for RRh_4B_4 compounds. This was clearly indicated in Table IV of our paper.² Furthermore, experimental g values for Nd 1:2:3 ($g_{\parallel}=3.60$; $g_{\perp}=2.13$) have also been reported recently,⁵ the predicted orderings on the basis of which are consistent with our previously predicted ordering.²

As for Ho 1:2:3, there was an error in our paper in quoting the experimental orderings determined by Birrer *et al.*⁶ In fact, our results show that even in Ho 1:2:3 the dipolar interaction correctly predicts the observed ordering, namely, z -axis antiferromagnetic ordering below 0.1 K. As for the tetragonal Ho 1:2:3, it is correct that a singlet state lies lowest, which in itself does not possess any magnetic moment. However, the admixture from adjacent excited states is responsible for the magnetic moment in this state, unless the temperature is too low to permit such an admixture. It should be noted that if this state is not magnetic then the exchange interaction would also not exist.

As for the relative orders of magnitudes of the second-, fourth-, and sixth-order CEF parameters, it is not true that the fourth- and sixth-order CEF terms dominate in R 1:2:3 whereas in RRh_4B_4 compounds the second-order parameters dominate, as mentioned in the Comment. The values quoted in Ref. 7 indicate larger numbers for

the fourth- and sixth-order CEF parameters than for the second-order CEF parameters in Ho 1:2:3, Nd 1:2:3, and Pr 1:2:3, because of the use of "tensor spin operators" rather than the usual Stevens spin operators commonly employed in CEF Hamiltonians. The corresponding members of these two sets of operators differ from each other by certain factors, resulting in larger values of the coefficients appearing in the fourth- and sixth-order CEF terms relative to that of the second-order CEF term used in Ref. 7. When the same Stevens spin-operator expressions are used as in the case of RRh_4B_4 ,⁸ the resulting coefficients in the second-order CEF parameters are, indeed, dominant over the coefficients in the fourth- and sixth-order CEF terms. This is further confirmed by comparing the values of the coefficients in the various CEF terms quoted by Furrer, Brüesch, and Unternährer⁹ using Stevens operators and the values of the coefficients in the corresponding CEF terms quoted by Solderholm *et al.*⁷ using the tensor operators.

Whitehead, De'Bell, and Noakes mention in the Comment that the difference between g_x and g_y values may be as large as 30% in the case of Er 1:2:3, without any supporting evidence. To the contrary, Hodges *et al.*,⁴ who reported experimental g values for this compound, do not find any significant difference in the g_x and g_y values. On the other hand, two of the authors of the Comment have themselves assumed equal values for the unit-cell parameters a and b in their Monte Carlo calculation of the transition temperatures,¹⁰ thus ignoring the a, b anisotropy.

In general, the ordering of the various R 1:2:3 compounds is expected to be the same on the basis of dipolar interactions for both the tetragonal and orthorhombic structures because their energies are about the same. Also, the transition temperatures are practically the same for the two structures except for Pr 1:2:3 and Nd 1:2:3. For $\text{Pr}_{0.925}\text{Gd}_{0.075}\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$ $T_N=16.5$ K for $x=0.1$ (orthorhombic) and $T_N=7.5$ K for $x=0.98$ (tetragonal).¹¹ On the other hand, for $\text{NdBa}_2\text{Cu}_3\text{O}_{7-x}$ $T_N=0.53$ K for $x=0.06$ (orthorhombic) and $T_N=1.5$ K for $x=0.7$ (tetragonal).¹² It may be because interactions other than dipolar also play important and decisive roles in Pr 1:2:3 and Nd 1:2:3. To this end, as for the anisotropy between the x and y axis orderings, an examination of Eqs. (3.3) in our paper² reveals that both the nearest- and

next-nearest-neighbor exchange interactions ($v_n, v_{n''}$) and the g_x, g_y values may become effective in determining which particular ordering has the lower energy to prevail at lower temperatures. There are other factors, also, which are important in this context. For example, as discussed by Lynn,¹³ the materials can get "confused" about what is the "correct" spin structure due to the influence of twin and grain boundaries, defects, intergrowths, variations in the O content, etc., which could alter the delicate balance of the dipolar energies. This leads, for both Er 1:2:3 and Dy 1:2:3, to similar dipolar energies for two different configurations, depending on the metallurgical state of the sample. Specifically, to describe them, these two configurations are such that they consist of chains of moments which are aligned ferromagnetically along the b axis, but while in one configuration the adjacent chains along the c axis are aligned antiparallel to form an overall antiferromagnetic configuration, in the other configuration the spins along the c axis are parallel, forming ferromagnetic sheets of spins.

Many experimental electron paramagnetic resonance (EPR) results on the Gd^{3+} ion have been published in the literature (see Ref. 14 for a review). It is evident that, despite being an S -state ion, the Gd^{3+} ion is characterized by a spin Hamiltonian consisting of second-, fourth-, and sixth-order spin operators (electron spin $\frac{7}{2}$), due to admixture of states with nonzero orbital angular momentum. In zero magnetic field the states $\pm\frac{7}{2}$ lie the lowest in Gd 1:2:3 because the absolute sign of the dominant second-order spin Hamiltonian parameter B_2^0 is negative, as reported by Causa *et al.*¹⁵ from a comparison of EPR and specific heat data. This lowest-lying state will then be characterized at low temperatures by an effective spin equal to $\frac{1}{2}$, associated with the g factors $g_z = 14, g_x = g_y = 0$. (Incidentally, this value as quoted in our paper² was not based on a private communication with Staveren and Andriessen but was rather based on the well-known reasoning presented here. We note also that two of the authors of the Comment have themselves referred to unpublished material¹⁶ in the context of screening of the dipolar interaction and the demagnetization correction.) The EPR measurements of Causa *et al.*¹⁵ indicate a CEF splitting of about 1.5 K in the ground state of the Gd^{3+} ion in dilute Gd_xEu_{1-x} 1:2:3. Further, an analysis of their measured CEF parameters indicates the existence of an easy axis of magnetization along the z direction. As the temperature is reduced toward the region where kT is comparable with the overall splitting (about 1.5 K) the population of the upper levels decreases, leading to an anisotropy in the g values, as well as a smaller effective spin. More details are discussed in the paper of Felsteiner¹⁷ dealing with the low-temperature ordering of Gd 1:2:3. The authors of the Comment seem to be unaware of the experimental results of Causa *et al.*,¹⁵ as their papers dealing with Monte Carlo and magnetic propagator calculations based on dipolar interactions^{10,16} do not take into consideration these experimental data.¹⁵

When there is coexistence of magnetic ordering and superconductivity, as, for example, in the case of RRh_4B_4

compounds,^{18,19} one should take into account the demagnetization correction to the energy of a ferromagnetic configuration, in accordance with the calculations on Chevrel compounds by Redi and Anderson,²⁰ who deal specifically with the case of $HoMo_6S_8$ mentioned by the authors of the Comment. In any case, even with the inclusion of the demagnetization correction which further lowers the energy of the ferromagnetically ordered states, none of the R 1:2:3 compounds has been found by us to have a ferromagnetic ordering lying lowest in energy on the basis of dipolar interactions. This is in accordance with the experimental results.

The R 1:2:3 system is very complicated, involving a large number of electrons, and not amenable to a detailed microscopic treatment. The simplifying assumptions used in our calculations have been well defined in Ref. 2. Further, the extrapolation of a single set of CEF parameters has often been made in the literature (for more details see Refs. 21–23), and is consistent with the other simplifying assumptions made in our calculations.

As for the remark in the Comment on the Monte Carlo calculations of the transition temperatures,¹⁰ we point out that while we have only attempted to predict which particular magnetic order prevails at low temperatures, the authors of Ref. 10, including two of the authors of the Comment, calculate transition temperatures in a manner contrary to their own concerns raised in the Comment. Specifically, they employ the Ising model, using the projection of the magnetic moment along the easy axis of magnetization. However, a more accurate approach would be to use the Heisenberg model, resulting in a value of the magnetic moment raised by a factor of $[(J+1)/J]^{1/2}$ from that used in the Ising model, which would in turn result in a transition temperature multiplied by a factor of $[(J+1)/J]$ ($=3$ for spin $\frac{1}{2}$) as discussed by Redi and Anderson.²⁰ This would, in effect, place greater importance on the role played by dipolar interactions in determining transition temperatures.

We point out the omission of the term $B_6^0O_6^4$ in the CEF Hamiltonian given in Refs. 2 and 18; see, e.g., Eq. (3.1) in Ref. 2, although this term was in fact taken into account in the calculation of the g factors for RRh_4B_4 compounds, which were also used for R 1:2:3 compounds.

Finally, we maintain that our calculations² establish beyond doubt that the dipolar interactions alone can account for all the observed orderings of the R 1:2:3 compounds. This does not mean that the dipolar interaction is necessarily dominant in all the R 1:2:3 compounds, since this interaction cannot alone account for all the observed transition temperatures, especially in the case of Pr 1:2:3 where the ordering occurs at a much higher transition temperature than in the other R 1:2:3 compounds, probably due to important roles played by other interactions. Of course, Eqs. (3.2) and (3.3) in Ref. 2 do take into account the exchange interactions in addition to the dipolar interactions.

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