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R–M interactions in R_2BaMO_5 (R = Y or Gd; M = Cu or Zn)

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Abstract. R_2BaMO_5 (R = Gd or Y; M = Cu or Zn) oxides have been studied using the specific heat, DC magnetic susceptibility and electron paramagnetic resonance (EPR). For one member of the series without a magnetic moment at M, namely Gd_2BaZnO_5 , measurements reveal long-range antiferromagnetic order at $T_N(Gd_2BaZnO_5) = 2.3 \pm 0.1$ K, much lower than the Curie–Weiss temperature Θ of 15.9 ± 0.3 K. This indicates the existence of competing interactions that introduce a large degree of magnetic frustration in the system. For Y_2BaCuO_5 the Cu–Cu interactions are responsible for the broad maximum in the magnetic contribution to the specific heat centred at 18.5 ± 0.01 K that stretches beyond the instrumental limit of 25 K. The strong Cu–Cu interactions also present in Gd_2BaCuO_5 , combined with the Gd–Cu interaction, polarize the Gd sublattice, giving measurable contributions to the specific heat in the same temperature range. In addition, they broaden the Gd EPR line and saturate its integrated intensity. The ordering temperature of Gd ions is raised to $T_N(Gd_2BaCuO_5) = 12.0 \pm 0.1$ K.

1. Introduction

Magnetic interactions in the R_2BaMO_5 family of ternary oxides (R = rare earth or Y; M = 3d transition metal) have been analysed in recent papers [1–3]. Attention to these systems has been driven by the different crystalline and magnetic structures of the members that change according to the nature of the R and M elements, providing in some cases examples of low-dimensional magnetism [3–5].

Additional interest arises because structural and electron difference density measurements [6] have shown that the Cu at Cu(2) sites of the high- T_c superconductor $YBa_2Cu_3O_{7-\delta}$, which mediates the superconducting mechanism, has a similar site geometry and electronic configuration to Cu in the insulating ‘green-phase’ Y_2BaCuO_5 .

Specific heat and magnetic susceptibility measurements reported for most R_2BaCuO_5 compounds, when R is a magnetic ion, have been interpreted in terms of two separate magnetic transitions [7, 8] associated with the magnetic ordering of the R and Cu sublattices (T_{N1} and T_{N2} , respectively). These temperatures vary with the different R ions involved, lying within the range $T_{N1} \lesssim 12$ K and $15 \text{ K} \lesssim T_{N2} \lesssim 23$ K. On the other hand, recent neutron diffraction experiments suggest [9] that magnetic order appears simultaneously in the R and Cu sublattices. Below T_{N2} , the magnetic ordering of the Cu spins partially polarizes the R spins due to the magnetic R–Cu coupling. Further cooling causes saturation

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of the R moments at a lower temperature T_{N1} . Although the microscopic interaction between the two magnetic subsystems has not been fully analysed, it has been suggested [2] that the presence of Cu at M sites is necessary to induce magnetic ordering at the R site.

In the presence of two interacting magnetic subsystems, namely the R and M ions, it seems necessary to investigate first the R–R and M–M interactions in order to clarify the nature of the coupling of the R and M subsystems. To clarify this question, we have performed magnetic susceptibility, specific heat and EPR measurements on the same set of samples of the isomorphous compounds: $\text{Gd}_2\text{BaZnO}_5$ with magnetic Gd ions at R sites and non-magnetic Zn at M sites; Y_2BaCuO_5 with non-magnetic Y and magnetic Cu; $\text{Gd}_2\text{BaCuO}_5$ with both magnetic species present simultaneously.

2. Experimental details

Samples of R_2BaMO_5 , with $\text{R} = \text{Y}$ or Gd and $\text{M} = \text{Zn}$ or Cu , were prepared by standard solid state reaction of R_2O_3 (99.99%), BaCO_3 (99.99%) and MO (99.999%) powders, mixed in stoichiometric amounts. The homogenized mixture was first fired in air at 500°C , then reground and reheated three times at 900°C for 24 h. Powder x-ray diffraction characterization was performed using $\text{Cu K}\alpha$ radiation. Data were refined by Rietveld profile analysis [10] showing in all cases a single phase in the $Pnma$ group, according to previous structural data on these systems [11, 12]. DC magnetic susceptibility was measured with a SQUID magnetometer in the temperature range 1.7–300 K. In all cases, susceptibilities were corrected for core diamagnetism from the ions. EPR data were obtained with a Bruker ESP300 spectrometer for the X band ($\nu \approx 9.4$ GHz) between 2.5 and 300 K, and at room temperature for the Q band ($\nu \approx 35$ GHz). The powder EPR spectra were processed by comparison with simulated spectra. We have included the necessary corrections [13] to superposition of resonant lines at positive and negative fields when the peak-to-peak linewidth ΔH_{pp} was comparable with the resonance field H_R . Specific heat measurements were obtained by a pulsed method in a semiadiabatic calorimeter up to 25 K. In order to subtract the non-magnetic contributions to C_p in Y_2BaCuO_5 , we performed specific heat measurements on the isomorphous compound Y_2BaZnO_5 , including corrections for the small difference in molar mass.

Table 1. Néel temperature T_N , magnetic moment μ_{eff} , Weiss temperature Θ , EPR peak-to-peak linewidth ΔH_{pp} and gyromagnetic factor g_{eff} -values for the powder samples.

Compound	T_N (K)	μ_{eff} (μ_B)	Θ (K)	ΔH_{pp} (mT)	g_{eff}^a
Y_2BaCuO_5	^b	1.87(1)	−43(4)	24.5(9)	2.126(3)
$\text{Gd}_2\text{BaZnO}_5$	2.3(1)	7.99(1)	−15.9(3)	260(10)	1.99(2)
$\text{Gd}_2\text{BaCuO}_5$	12.0(1)	8.12(2)	−23.2(3)	109(3)	2.017(3)

^a This value corresponds to polycrystalline samples and is therefore an average over the components of the \mathbf{g} tensor.

^b No ordering temperature is observed from the susceptibility data.

3. Results and discussion

The magnetic susceptibility of $\text{Gd}_2\text{BaZnO}_5$ was found to be independent of the applied field H . Figure 1 shows the data measured between 1.8 and 300 K, with $H = 50$ mT. The

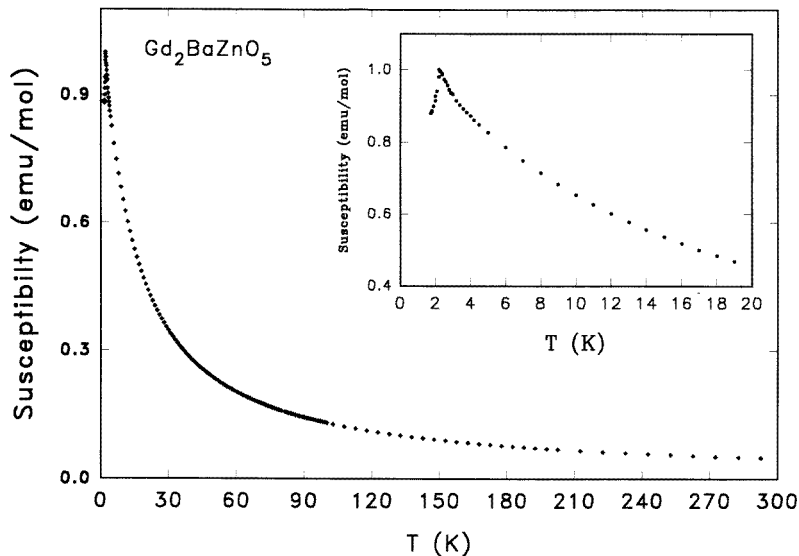


Figure 1. Magnetic susceptibility for $\text{Gd}_2\text{BaZnO}_5$ versus T , measured with $H = 50$ mT. The inset shows the peak at $T_N = 2.3(1)$ K.

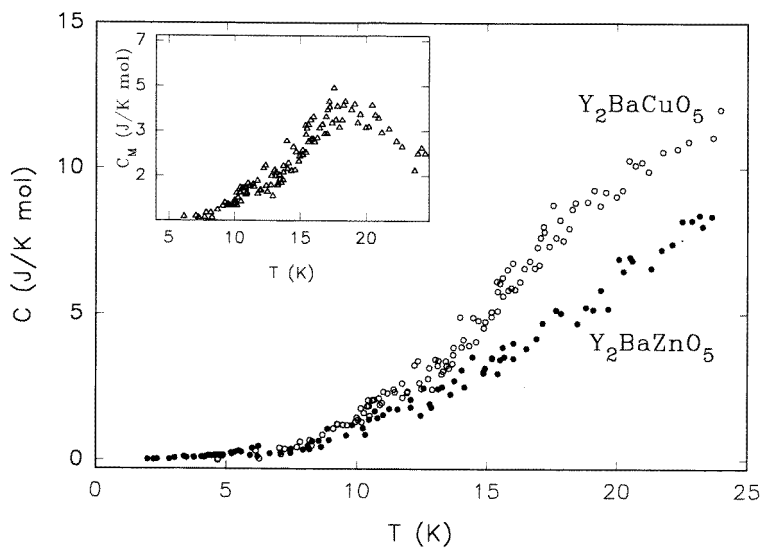


Figure 2. Specific heat of magnetic Y_2BaCuO_5 and non-magnetic Y_2BaZnO_5 . The inset displays the Cu magnetic contribution, as obtained from the $C_p(\text{Y}_2\text{BaCuO}_5) - C_p(\text{Y}_2\text{BaZnO}_5)$ difference.

high-temperature data (100–300 K) were fitted to a Curie–Weiss law, $\chi(T) = C/(T - \Theta)$, with $C = 8.00 \pm 0.03$ emu K mol $^{-1}$ and $\Theta = -15.9 \pm 0.3$ K (table 1). This value of C yields a calculated effective moment $\mu_{eff} = (7.99 \pm 0.01)\mu_B$ close to the expected value for free Gd^{+3} ions ($S = 7/2$; $g_{eff} = 1.991$). Since the effect of the crystalline field on the

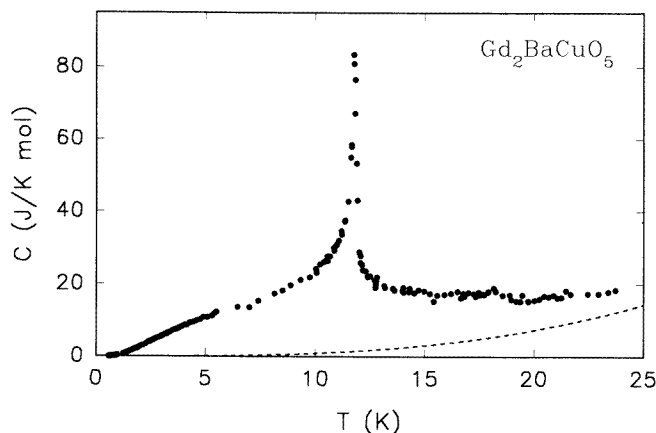


Figure 3. Specific heat of $\text{Gd}_2\text{BaCuO}_5$: ---, lattice contribution.

ground S state is usually very small, it gives no measurable contributions to $\chi(T)$ in the temperature range of our experiment. The negative value of Θ indicates antiferromagnetic interactions between Gd ions. A peak at $T_N(\text{Gd}_2\text{BaZnO}_5) = 2.3 \pm 0.1$ K is clearly noticed, indicating long-range ordering of the Gd ions.

Susceptibility measurements on Y_2BaCuO_5 show a paramagnetic regime at high temperatures (100–300 K), following a Curie–Weiss law with $\mu_{eff} = (1.87 \pm 0.01)\mu_B$ and $\Theta = -43 \pm 4$ K (table 1), in agreement with previous results [14, 15]. Below 55 K, DC susceptibility deviates from paramagnetic behaviour and exhibits a broad maximum at $T(\chi_{max}) \approx 32$ K, well above the ordering temperature determined from neutron diffraction experiments [16], $T_N(\text{Y}_2\text{BaCuO}_5) = 16.5$ K. Our data display non-linearity of the M versus H curves in the region $T \lesssim 15$ K, in agreement with this ordering temperature.

DC susceptibility data of $\text{Gd}_2\text{BaCuO}_5$ display a peak at $T_N(\text{Gd}_2\text{BaCuO}_5) = 12.0 \pm 0.1$ K, and follows a Curie–Weiss law [8, 17] at high temperatures (100–300 K). The fitted parameters are shown in table 1. The value of the Curie constant corresponds to the sum of contributions from Gd and Cu ions. The $\chi^{-1}(T)$ versus T curves show deviations from the Curie–Weiss law for $T \lesssim 35$ K. This kind of deviation is not observed in $\text{Gd}_2\text{BaZnO}_5$ down to $T \approx 3$ K.

The specific heat for Y_2BaCuO_5 and non-magnetic Y_2BaZnO_5 are shown in figure 2. The magnetic contribution estimated from the difference between the two curves presents a broad maximum at $T_{max} \approx 18.5$ K. This maximum corresponds to the change in slope and the rounded anomaly reported in [7] and [18], respectively. Non-negligible contributions are observed well above T_{max} , up to our experimental limit ($T \approx 25$ K). Only 35% of the magnetic entropy is removed below T_{max} , and 57% below 25 K.

Specific heat measurements in $\text{Gd}_2\text{BaCuO}_5$, shown in figure 3, present a λ -type anomaly at $T_{N1}(\text{Gd}_2\text{BaCuO}_5) = 11.8 \pm 0.1$ K, in coincidence with the DC susceptibility peak. The entropy removed below T_{N1} corresponds to about 69% of the value expected for $S = 7/2$: $\Delta S(\text{Gd}) = 2R \ln 8$. Above T_{N1} the magnetic contribution is still significant. The magnetic entropy removed up to the small bump observed at $T_b = 18.0 \pm 0.5$ K, $\Delta S = 3.6R$, is about 87% of $\Delta S(\text{Gd})$. If the magnetic entropy associated with the Cu moments is included, the entropy removed is about 75% of the total value.

Figure 4 shows the X-band EPR spectra for Y_2BaCuO_5 , $\text{Gd}_2\text{BaCuO}_5$ and $\text{Gd}_2\text{BaZnO}_5$,

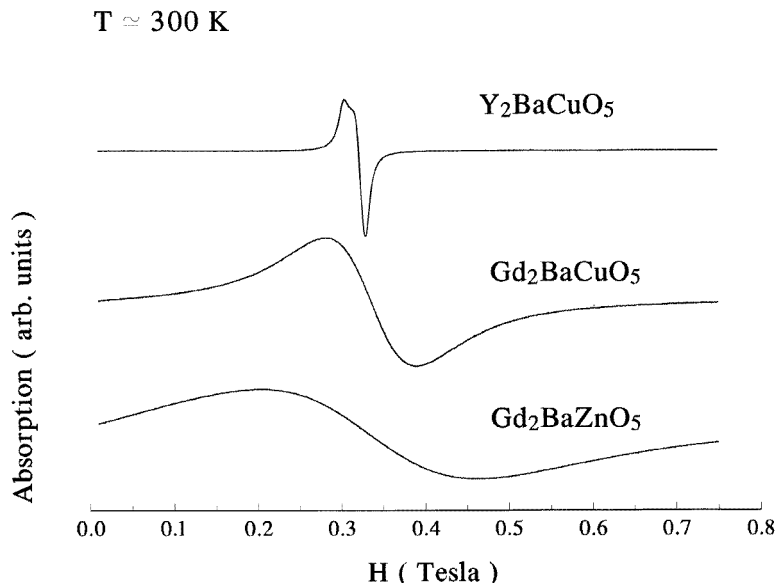


Figure 4. Room-temperature X-band EPR spectra of Y_2BaCuO_5 , $\text{Gd}_2\text{BaCuO}_5$ and $\text{Gd}_2\text{BaZnO}_5$.

measured at room temperature. For Y_2BaCuO_5 the Cu ions give a resonance line with a structure that reflects the g -factor anisotropy. At the Q band this structure is completely resolved into its three components that correspond to the rhombic symmetry of the \mathbf{g} -tensor [19]. The fit of the powder spectrum with computer-simulated profiles gives $g_x = 2.229 \pm 0.003$, $g_y = 2.096 \pm 0.003$ and $g_z = 2.054 \pm 0.003$, in close agreement with previous results [19]. The intrinsic linewidth was also obtained from the fit. At room temperature we determined, for both the X and the Q band, $\Delta H_{pp}(300 \text{ K}) = 8.0 \pm 0.5 \text{ mT}$, which is slightly larger than the values found for single crystals [20]. The observed full width, $\Delta H_{pp}(300 \text{ K}) = 24.5 \pm 0.9 \text{ mT}$ for the X band and $97.5 \pm 0.9 \text{ mT}$ for the Q band, is much larger than the intrinsic linewidth due to the anisotropy of the g -factor. To examine the exchange interaction near the ordering temperature we have determined the variation in the EPR linewidth and the integrated intensity versus temperature, shown in figure 5. The integrated intensity reaches a maximum around 20 K, above the ordering temperature of the Cu ions [16]. Below T_N the intensity of the resonance line is expected to decrease as a consequence of the development of a field-dependent energy gap in the frequency–field diagram. For antiferromagnetically coupled moments this gap is usually anisotropic [21] and, for a powder sample, antiferromagnetic resonance would only be observed for a fraction of the microcrystals. Thus, the maximum at 20 K indicates the presence of short-range antiferromagnetic order above T_N . Note that the broad peak reported at around 54 K in [17] may be a consequence of estimating the intensities as the peak-to-peak amplitude multiplied by the square of the measured linewidth [22]. In this case the procedure would be incorrect, because the observed peak-to-peak linewidth is due to the g anisotropy and numerical integration is required.

For $\text{Gd}_2\text{BaZnO}_5$, EPR measurements show a single broad line associated with the Gd ions, centred at $g = 1.99(2)$ and with a room-temperature linewidth $\Delta H_{pp}(300 \text{ K}) = 0.26(1) \text{ T}$. Figure 6 shows that the linewidth increases slowly with decreasing temperature,

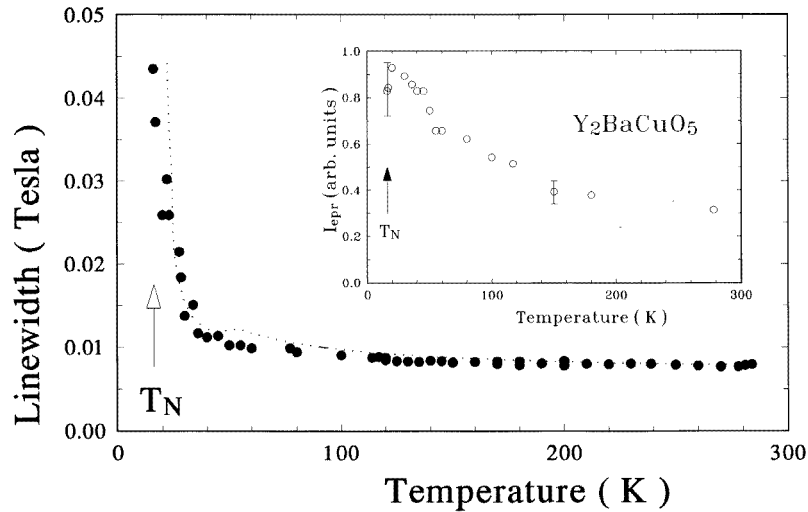


Figure 5. Temperature dependence of ΔH_{pp} for Y_2BaCuO_5 : \cdots , $\Delta H_{pp}(T) = \Delta H_{pp}(\infty)/T\chi(T)$. The inset shows the integrated intensity versus T .

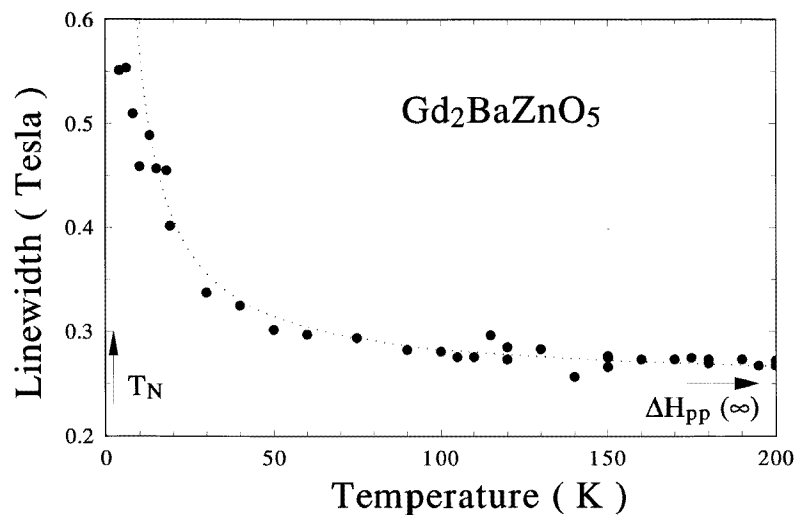


Figure 6. Temperature dependence of ΔH_{pp} for $\text{Gd}_2\text{BaZnO}_5$. \cdots , $\Delta H_{pp}(T) = \Delta H_{pp}(\infty)/T\chi(T)$.

following approximately an expression $\Delta H_{pp}(T) \propto \Delta H_{pp}(\infty)/T\chi(T)$ in accordance with the behaviour found in other magnetic compounds [23, 24]. This expression gives a constant linewidth for paramagnetic Curie-law systems. In the case of antiferromagnetic compounds, where the susceptibility obeys a Curie–Weiss law, the expression $\Delta H \propto (1 + \Theta/T)$ predicts a monotonic broadening of the linewidth when the temperature decreases. This broadening is observed in an extended region of T ($3 \text{ K} \lesssim T \lesssim 200 \text{ K}$) because the system orders at $T_N \approx \Theta/7$ due to its high degree of frustration.

In the case of $\text{Gd}_2\text{BaCuO}_5$, where two magnetic species are present, the EPR line is expected to correspond mainly to the Gd^{3+} moments, owing to their much larger DC susceptibility. A single line, with no structure, is observed in this case. A value of $g = 2.017 \pm 0.003$ was determined from Q-band data. The linewidth $\Delta H_{pp}(300 \text{ K}) = 109 \pm 3 \text{ mT}$ for the X band and $124 \pm 3 \text{ mT}$ for the Q band is about a third of that in the case of $\text{Gd}_2\text{BaZnO}_5$ and reflects the exchange coupling of the Cu and Gd sublattices. The $\text{Gd}_2\text{BaCuO}_5$ linewidth, unlike that of $\text{Gd}_2\text{BaZnO}_5$, decreases slightly with decreasing T , reaching a shallow minimum at $\Delta H_{pp}(70 \text{ K}) \approx 92 \pm 3 \text{ mT}$, as shown in figure 7. The fast increase in ΔH_{pp} due to each interaction is observed below about 30 K, in agreement with [17]. This linewidth increase produces a rapid diminution in the peak-to-peak amplitude and the signal is not longer observed below $T \approx 12 \text{ K}$. The integrated intensity, in turn, increases up to 20 K, where it reaches its maximum value.

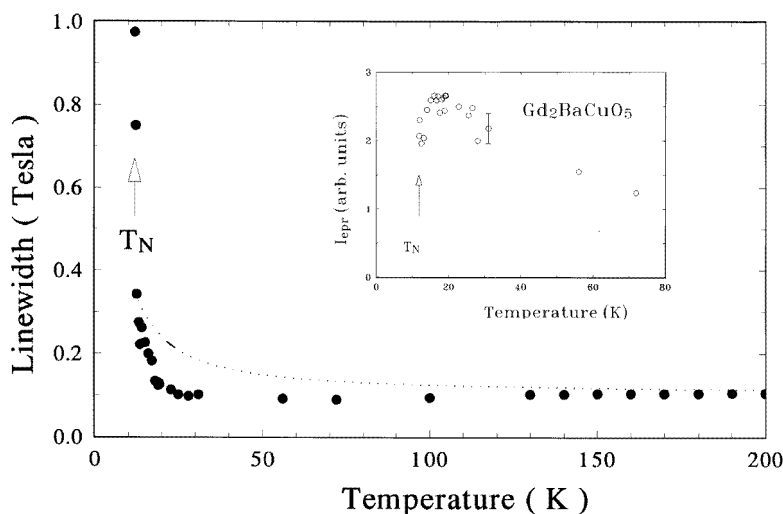


Figure 7. Temperature dependence of ΔH_{pp} for $\text{Gd}_2\text{BaCuO}_5$: \cdots , $\Delta H_{pp}(T) = \Delta H_{pp}(\infty)/T\chi(T)$. The integrated intensity versus T of the EPR line is shown in the inset.

The crystalline structure of $Pnma$ $R_2\text{BaMO}_5$ consists of distorted monocapped trigonal prisms of RO_7 , which form a three-dimensional framework. Isolated MO_5 pyramids are located in cavities delimited by the RO_7 framework [6, 12]. This complex structure makes possible the existence of several exchange pathways between magnetic ions, even in $\text{Gd}_2\text{BaZnO}_5$ and Y_2BaCuO_5 , where only one magnetic species is present. This observation may explain the high value of Θ/T_N for these compounds, indicative of a strong degree of magnetic frustration. On the other hand, the presence of Cu moments, with a large Cu–Cu antiferromagnetic interaction (see table 1) reduces the Θ/T_N ratio from 7 in the case of $\text{Gd}_2\text{BaZnO}_5$ to 2 for $\text{Gd}_2\text{BaCuO}_5$.

Based on the neutron diffraction results for other $R_2\text{BaCuO}_5$ compounds ($R = \text{Y}, \text{Dy}, \text{Ho}, \text{Er}, \text{Tm}$ or Yb) [9, 16] we can suggest the following picture for $\text{Gd}_2\text{BaCuO}_5$; at a temperature around $T_N(\text{Y}_2\text{BaCuO}_5) = 16.5 \text{ K}$, the Cu moments are expected to order antiferromagnetically. The saturation of the EPR intensity at about 20 K, and the small bump at 18 K in the specific heat of $\text{Gd}_2\text{BaCuO}_5$ might signal this temperature. The Cu ordering would in turn polarize the Gd moments, as they do in other $R_2\text{BaCuO}_5$ and $R_2\text{BaNiO}_5$

compounds [5, 9]. As the temperature of the coupled system is lowered, the Gd polarization increases. The large peak of C_p at $T_{N1}(\text{Gd}_2\text{BaCuO}_5) = 12$ K indicates the temperature of maximum increase in the Gd sublattice magnetization with T . The fact that the entropy removed between 12 and 18 K, $\Delta S/R = 0.8 \pm 0.1$, is much larger than the value measured in Y_2BaCuO_5 for the ordering of Cu ions up to the same temperature, also suggests that the Gd ions start to order above $T_{N1}(\text{Gd}_2\text{BaCuO}_5)$, thus contributing to the total specific heat. It seems therefore possible that, in $\text{Gd}_2\text{BaCuO}_5$, the exchange coupling between Gd and Cu moments helps to overcome the magnetic frustration of the Gd subsystem (observed in $\text{Gd}_2\text{BaZnO}_5$) at a much higher temperature than $T_N(\text{Gd}_2\text{BaZnO}_5) = 2.3$ K. The likelihood of this description is also supported by the saturation of the Gd EPR intensity at 20 K, well above the ordering temperature.

In summary, we have observed long-range magnetic order for $\text{Gd}_2\text{BaZnO}_5$, a compound of the $Pnma$ R_2BaMO_5 family with no magnetic moments at the M sites. Contrary to previous indications [2], this result establishes that the existence of a magnetic M sublattice is not necessary to induce magnetic ordering of the R lattice. Nonetheless, the relevance of the Gd–Cu interactions can be noticed since they raise the ordering temperature by a factor of 6, from $T_N(\text{Gd}_2\text{BaZnO}_5) = 2.3$ K to $T_N(\text{Gd}_2\text{BaCuO}_5) = 12.0$ K, in spite of the similarity between Gd–Gd interactions suggested by the corresponding Curie–Weiss temperatures. Moreover, the EPR results indicate that magnetic order in this compound extends well above 12 K. A large tail in the specific heat and a small feature at 18 K suggest that the Néel temperature of the coupled Gd–Cu system may be higher than 12 K, the temperature where the specific heat and the magnetic susceptibility reach their maximum value. Additionally, our data show that short-range order in Y_2BaCuO_5 extends above the Néel temperature $T_N = 16.5$ K determined from neutron scattering experiments, although not as high as the 54 K estimated previously [17].

Acknowledgments

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References

- [1] Ditusa J F, Cheong S W, Broholm C, Aeppli G, Rupp L W and Batlogg B 1994 *Physica B* **194** 181
- [2] Sáez-Puche R and Hernandez-Velasco J 1994 *Adv. Mater. Res.* **1** 65
- [3] Sachan V, Buttrey D J, Tranquada J M and Shirane G 1994 *Phys. Rev. B* **49** 14
- [4] Batlogg B, Cheong S W and Rupp L W 1994 *Physica B* **194** 173
- [5] Butera A, Causa M T and Tovar M 1995 *J. Magn. Magn. Mater.* **140–4** 1681
- [6] Buttner R H and Maslen E N 1993 *Acta Crystallogr. B* **49** 62
- [7] Burriel R, Castro M, Piqué C, Salinas-Sánchez A and Sáez-Puche R 1992 *J. Magn. Magn. Mater.* **104–7** 627
- [8] Levitin R Z, Mill B V, Moshchalkov V V, Samarin N A, Snegirev V V and Zoubkova J 1990 *J. Magn. Magn. Mater.* **90–1** 536
- [9] Golosovskii I V, Plakhtii V P, Kharchenkov V P, Zoubkova J, Mill B V, Bonnet M and Roudaut E 1992 *Sov. Phys.–Solid State* **34** 782
- [10] Skthivel A and Young R A 1991 *DBWS-9006PC, Program for Rietveld analysis of X-ray powder diffraction patterns, Georgia Institute of Technology, Atlanta, GA*
- [11] Michel C and Raveau B 1982 *J. Solid State Chem.* **43** 73
- [12] Michel C and Raveau B 1983 *J. Solid State Chem.* **49** 150

- [13] Causa M T and Passeggi M C G 1983 *Phys. Lett.* **98A** 291
- [14] Causa M T, Dutrús S M, Fainstein C, Salva H R, Steren L B, Tovar M and Zysler R D 1988 *J. Appl. Phys.* **63** 4164
- [15] Goya G, Stewart S, Goeta A, Grunfeld G, Punte G and Mercader R 1994 *J. Magn. Magn. Mater.* **138** 147
- [16] Golosovsky I V, Böni P and Fischer P 1993 *Solid State Commun.* **87** 1035
- [17] Mehran F, Barnes S, Giess E A and McGuire T R 1988 *Solid State Commun.* **67** 55
- [18] Eckert D, Junod A, Bezinge A, Graf T and Muller J 1988 *J. Low Temp. Phys.* **73** 241
- [19] Ong E W, Ramakrishna B L and Iqbal Z 1988 *Solid State Commun.* **66** 171
- [20] Kobayashi T, Katsuda H, Hayashi K, Tokumoto M and Ihara H 1988 *Japan. J. Appl. Phys.* **27** L670
- [21] After this work was submitted, a submillimetre wave (100–300 GHz) study was performed by Ohta H, Kimura S and Motokawa M 1995 *J. Phys. Soc. Japan* **64** 3934. These authors determined that the zero-field energy gap at 1.8 K for Y₂BaCuO₅ varies from 0 to 80 GHz
- [22] Mehran F, Barnes S E, McGuire T R, Gallagher W J, Sandstrom R L, Dinger T R and Chance D A 1987 *Phys. Rev. B* **36** 740
- [23] Causa M T, Tovar M, Obradors X, Labarta A and Tejada J 1991 *Phys. Rev. B* **44** 4455
- [24] Dorman E and Jaccarino V 1974 *Phys. Lett.* **48A** 81