

Evidence of Antiferromagnetic Order in the Green Phases $R_2\text{BaCuO}_5$ ($R = \text{Dy}, \text{Y}, \text{and Yb}$)

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Magnetic susceptibility measurements between 4.2 and 300 K for $R_2\text{BaCuO}_5$ compounds ($R = \text{Dy}, \text{Y}$ and Yb), also called "green phases," reveal the existence of antiferromagnetic ordering in the copper sublattice around 30 K. At lower temperatures χ vs. T plots show in all cases the existence of a sharp maximum, which can be attributed to the onset of antiferromagnetic ordering in the rare earth sublattice, probably induced by the polarization of Cu^{+2} ions. Experimental magnetic moments estimated from the Curie-Weiss region generally agree with the theoretical values expected for these R^{+3} ions. High-resolution transmission electron microscopy and electron diffraction experiments confirm the earlier proposed structures for the $R_2\text{BaCuO}_5$, and show the existence of a well ordered material. © 1990 Academic Press, Inc.

Introduction

The $R_2\text{BaCuO}_5$ oxides, where R is a trivalent lanthanide cation, were first prepared as a powder and characterized by Michel and Raveau in the early eighties (1). Schiffler and Müller-Buschbaum confirmed, from X-ray single crystal data, that these phases show orthorhombic symmetry, space group $D_{2h}^{16} - Pbnm$, $Z = 4$ (2). These oxides, which appear sometimes as impurities of the high-temperature superconducting oxides of composition $R\text{Ba}_2\text{Cu}_3\text{O}_{7-x}$, are usually called "green phases" (3, 4). The structure of these compounds (5) can be described as forming a framework built up from $[\text{RO}_7]$ monocapped trigonal prisms sharing a triangular face forming $R_2\text{O}_{11}$ groups. These $R_2\text{O}_{11}$ blocks then share edges to form a

three-dimensional network. The Ba^{+2} ions are coordinated by 11 oxygen atoms forming a very irregular polyhedron, while the Cu^{+2} ions are surrounded by five oxygen atoms giving rise to an isolated pyramidal coordination.

Neutron diffraction studies on Y_2BaCuO_5 have revealed the existence of antiferromagnetic ordering of the Cu^{+2} about 28 K (6). Also, previous work in the Ln_2NiO_4 oxides revealed the existence of antiferromagnetism in both the Ni^{+2} and the Ln^{+3} sublattices, the later induced by the polarization of the nickel (7, 8). It then appeared of interest to study the magnetic properties of the $R_2\text{BaCuO}_5$ where R is a paramagnetic lanthanide cation, in order to determine the possible magnetic interactions between the rare earth cations. A recent study appears

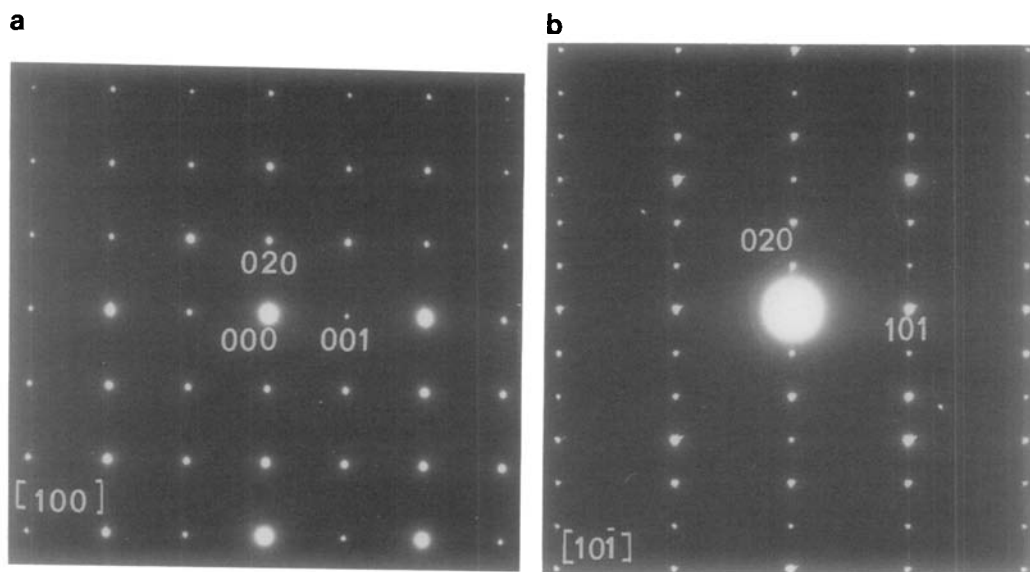


FIG. 1. Electron diffraction patterns for the $\text{Dy}_2\text{BaCuO}_5$; Zone axis: (a) $[100]$, (b) $[10\bar{1}]$.

to indicate that some kind of magnetic interactions are present for $\text{Dy}_2\text{BaCuO}_5$ at very low temperatures (9).

Experimental

The different $R_2\text{BaCuO}_5$ oxides were prepared by mixing the stoichiometric amounts of the high-purity oxides $R_2\text{O}_3$ (99.999%), CuO (99.999%), and BaCO_3 (R.A.). The homogenized mixture was fired in air at 950°C for 24 hr; then it was reground and reheated in air at 1000°C for 24 hr; the resultant products are green from which they take their common name.

The X-ray powder patterns were recorded using a Siemens Kristalloflex 810 diffractometer and D-500 goniometer with nickel filtered radiation ($\lambda = 1.54088145 \text{ \AA}$), selected with a graphite monochromator. Powder X-ray diffraction was used to verify that all the samples subjected to magnetic investigation were single phases. Lattice parameters were obtained from the Rietveld refinement (10).

Magnetic susceptibility measurements were made in the range 4.2–300 K using a DSM5 susceptometer described elsewhere (11): The apparatus, based upon the Faraday method, was calibrated with $\text{Hg}[\text{Co}(\text{SCN})_4]$ and $\text{Gd}_2(\text{SO}_4)_3 \cdot 8\text{H}_2\text{O}$, χ was independent of the field of in the temperature range of measurements. The maximum magnetic field was 14 KG with $H \cdot dH/dz \approx 30 \text{ KG}^2 \text{ cm}^{-1}$. The susceptibilities were corrected for ionic diamagnetism using the values of $-18 \times 10^{-6} \text{ emu gram-ion}^{-1}$ for R^{+3} , $-32 \times 10^{-6} \text{ emu gram-ion}^{-1}$ for Ba^{+2} , -11×10^{-6} for Cu^{+2} , and -12×10^{-6} for O^{-2} (12).

High-resolution transmission electron microscopy and electron diffraction experiments were made in a Jeol 4000EX electron microscope at 400 kV.

Results and Discussion

X-ray powder diffraction data for $\text{Dy}_2\text{BaCuO}_5$ were indexed on the basis of the orthorhombic $a = 7.1493(4) \text{ \AA}$, $b = 12.2168(6) \text{ \AA}$,

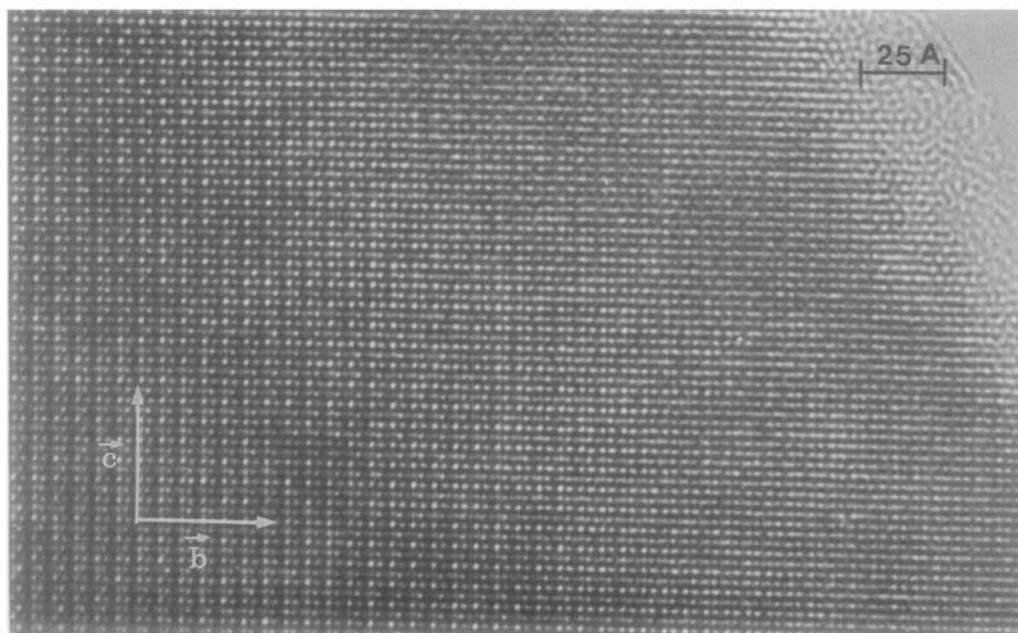


FIG. 2. Electron micrograph corresponding to $\text{Dy}_2\text{BaCuO}_5$ along the $[100]$ axis.

and $c = 5.6778(3)\text{\AA}$ unit cell. Figure 1 shows two electron diffraction patterns along the $[100]$ and $[101]$ zone axis for this sample. These results confirm the previous structural determination (1, 5). The presence of $[00l]$ and $[0k0]$ reflections with l and k equal to $2n + 1$ values, Figs. 1a and 1b respectively, which are forbidden in space group $Pbnm$, is likely to be due to multiple diffraction. The absence of streaking or split spots indicates that the material is well ordered. This is confirmed by the electron micrograph on Fig. 2, along the zone axis $[100]$ which shows a homogeneous contrast and no obvious defects.

In the case of the other $R_2\text{BaCuO}_5$ oxides X-ray and electron diffraction studies give similar results.

The temperature dependence of the reciprocal magnetic susceptibility for Y_2BaCuO_5 obeys Curie—Weiss behavior between 300 and 60 K, Fig. 3. The magnetic moment calculated from the linear part of the χ^{-1} vs.

T plot is 1.80 B.M., which agrees well with the expected value for a system with $S = \frac{1}{2}$. Below 60 K, upward deviations from linearity are observed, and a broad minimum centered at about 35 K is seen in the susceptibility; this is indicative of the existence of antiferromagnetic ordering in the copper

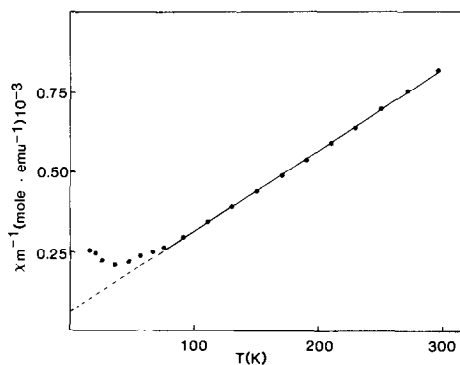


FIG. 3. Temperature dependence of the reciprocal molar susceptibility for Y_2BaCuO_5 .

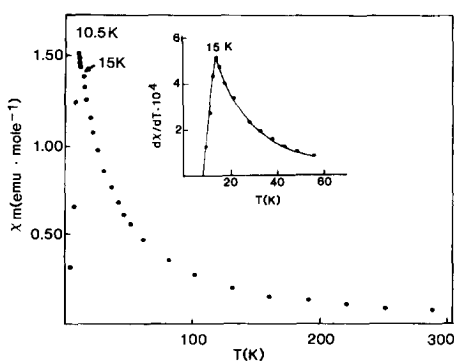


FIG. 4. Variation of the molar magnetic susceptibility with the temperature for $\text{Dy}_2\text{BaCuO}_5$. Inset shows the $d\chi/dT$ versus temperature plot.

sublattice. This is confirmed by the $\chi \times T$ value which is of the order of 3.41×10^{-3} emu mole $^{-1}$ K obtained at 8 K, 10 times smaller than that expected for the isolated copper ions.

Somewhat different results are obtained when Y is replaced by a paramagnetic cation such as Dy. The temperature variation of the molar magnetic susceptibility for $\text{Dy}_2\text{BaCuO}_5$ is shown on Fig. 4. It can be observed that the susceptibility shows a very clear maximum at 10.5 K; below this temperature the susceptibility sharply decreases, taking a value of only 3.494×10^{-1} emu mole $^{-1}$ at 4.2 K. This marked decrease in the susceptibility suggest an antiferromagnetic ordering of the dysprosium cations. A careful analysis of the χ vs T plot in Fig. 4 also shows an inflection point at about 15 K, which could be attributed to an antiferromagnetic ordering of the copper ions. This is a similar effect to that observed for Y_2BaCuO_5 , as shown above, in which the only paramagnetic cation is copper. These results agree with those very recently obtained from specific heat measurements by Levitin *et al.* (9). This latter effect is yet more noticeable when the $d\chi/dT$ vs T plot is obtained, (Fig. 4 inset). It can be observed that $d\chi/dT$ increases as the temperature decrease, reaching a maximum

at 15 K and then sharply decreases. It is obvious that at 10.5 K $d\chi/dT = 0$, as observed. This allows us to detect the presence of two different antiferromagnetic interactions corresponding to the copper and dysprosium sublattices. It is interesting to note that the ordering temperature of the copper appears to be half of that obtained in the case of Y_2BaCuO_5 .

Moreover the χ^{-1} vs T plot for the $\text{Dy}_2\text{BaZnO}_5$, isostructural with the copper compound (13), is in line with this reasoning, because, as experimentally observed (14), no antiferromagnetic interactions appear to be present down to 4.2 K. The absence of interactions is due to the presence of diamagnetic zinc, while, as proposed earlier (15), copper can induce the ordering on the dysprosium sublattice. The observed downward deviation of linearity in $\text{Dy}_2\text{BaZnO}_5$ from Curie-Weiss behavior, below 20 K, can be attributed to the crystal-field splitting of the ${}^6\text{H}_{15/2}$ ground isolated term. Since Dy^{+3} is a cation with an odd number of electrons, the lowest crystal-field term should be at least doubly degenerated and this can explain the small deviation at lower temperatures. The negative value of the Weiss constant θ for the zinc compound can be attributed to the crystal-field effect on the ground

TABLE I

MAGNETIC MOMENTS IN BOHR MAGNETONS (B.M.) OBSERVED (o) AND CALCULATED (c) FOR THE DIFFERENT $R_2\text{BaMO}_2$ OXIDES

Compound	μ_o^a	μ_c	θ	$T\chi_{\text{max}}$
$\text{Dy}_2\text{BaCuO}_5$	10.70	10.65	0.8	10.5
$\text{Dy}_2\text{BaZnO}_5$	10.70	10.65	-5.6	—
$\text{Yb}_2\text{BaCuO}_5$	4.52	4.54	-50.7	—
Y_2BaCuO_5	1.80	1.73	-33.9	35

Note. θ (K) is the Curie-Weiss constant and $T\chi_{\text{max}}$ (K) is the temperature for the maximum in the susceptibility.

^a Obtained taking into account the copper contribution.

term of Dy^{+3} (16), since antiferromagnetic interactions are not present.

For the homologous Dy_2BaCuO_5 oxide the upward deviation of the Curie–Weiss behavior about 20 K must be due to the copper ordering. The χ^{-1} vs T plot follows a Curie–Weiss law from 300 K to 20 K, and the obtained value for the magnetic moment of 10.70 B.M. is in good agreement with that expected for the dysprosium contribution (Table I). The fact that the susceptibility decreases below 20 K confirms the antiferromagnetic ordering of the copper, which seems to compensate the expected increase due to the crystal-field splitting always observed on the magnetically disordered dysprosium oxides.

Although the magnetic susceptibility data for Yb_2BaCuO_5 do not show a maximum as in the case of the homologous Y_2BaCuO_5 and Dy_2BaCuO_5 , the $\chi \times T$ vs T plot shows a marked decrease below 30 K. The $\chi \times T$ value obtained at 4.2 K is only 1.42 emu mol⁻¹ K. This is indicative that antiferromagnetic interactions are operative for both Cu^{+2} and Yb^{+3} sublattices at 4.2 K. This preliminary results show the influence of the rare earth element on the magnetic ordering in the green phase type compounds.

In an attempt to further develop this point, neutron diffraction and specific heat measurements are now in progress for all the series R_2BaCuO_5 in order to establish the Néel temperatures and to determine the magnetic structures of these oxides.

Acknowledgments

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