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# Complex magnetic structures of the rare-earth cuprates $R_2Cu_2O_5$ ($R$ = Y,Ho,Er,Yb,Tm)

J. L. García-Muñoz and J. Rodríguez-Carvajal
*Institut Laue-Langevin, 38042 Grenoble CEDEX, France*

X. Obradors
*Institut de Ciencia de Materials de Barcelona, Martí i Franqués s/n 08028 Barcelona, Spain*

M. Vallet-Regí, J. González-Calbet, and M. Parras
*Laboratorio de Magnetismo Aplicado, REd Nacional de Ferrocarriles Españoles-Universidad Complutense Madrid, Las Matas, Madrid, Spain*

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The magnetic structures at $T=1.5$ K of several members of the $R_2Cu_2O_5$-type compounds ($R$ = Y,Ho,Er,Yb,Tm) have been determined by means of neutron diffraction. All of them appear to be commensurate with the crystal lattice having propagation vectors $\mathbf{k}=(0,0,0)$ for Y, Er, and Tm, $\mathbf{k}=(0,\frac{1}{2},0)$ for Ho, and $\mathbf{k}=(0,\frac{1}{2},\frac{1}{2})$ for Yb. In all cases, except for Yb, we found that both copper and rare-earth sublattices order simultaneously. The easy axis of the magnetic moments for the two copper sites is along [010] for Y, Er, and Yb, whereas it is along [100] for Ho and Tm, conserving in all the cases the same type of arrangement $[A^{(1)}+A^{(2)}=(+--+)^{(1)}+(+--+)^{(2)}]$. The arrangement of magnetic moments in the rare-earth sublattices strongly differs between the different compounds indicating the existence of a strong competition between crystal-field and exchange interactions. From the determined magnetic structures, we propose models concerning the metamagneticlike transitions observed in the magnetization curves.

One important issue to be investigated in high-$T_c$ superconductivity is the magnetic behavior of the heavy rare-earth ions ($R$) in $RBa_2Cu_3O_7$ (or in $R_{2-x}Ce_xCuO_4$) and the interactions of the rare-earth sublattice with the superconducting $CuO_2$ planes. While initial experiments showed that the rare-earth sublattice is electronically isolated from the superconducting planes (see for instance Ref. 1), the interplay between the magnetism of $R$ and superconductivity in these materials is not well understood yet. For instance, in the system $RBa_2Cu_3O_7$ the rare-earth planes are far away from each other and $R$ layers are bracketed by $CuO_2$ planes; nevertheless, three-dimensional (3D) magnetic ordering has been discovered in the compounds with $R$ = Er, Gd, Dy, and Nd.[2]

In this context, other rare-earth copper oxides have been considered. In the ternary $R$-Cu-O phase diagram, the series with the stoichiometry $R_2Cu_2O_5$ arises when the rare earth is smaller than Gd: $R$ = Tb → Lu,Y,Sc. This family of insulating cuprates is the object of extensive studies in connection with the problem of magnetic interactions between rare earth and Cu atoms in superconducting cuprates.

In the present work, we report some results of several neutron-powder-diffraction experiments carried out on the $R_2Cu_2O_5$ "blue phases" with the rare earths Y, Ho, Er, Yb, and Tm. In this Rapid Communication we describe the magnetic structures at 1.5 K and give a brief overview about some implications on the metamagneticlike transitions previously seen in these compounds.

Though extensive details of the orthorhombic crystal structure can be found in Refs. 3 and 4, it is worth remembering that there are two nonequivalent positions with a very similar oxygen polyhedra around. Rare-earth ions are octahedrally coordinated and also located in two different sites.

Magnetic susceptibility measurements show antiferromagnetic transitions in most of the compounds at temperatures ranging from 11 K (Dy) to 30 K (In).[4-6] For those compounds with diamagnetic rare earths, the paramagnetic Curie temperatures indicate the presence of dominant ferromagnetic interactions, in contrast with the negative values obtained in all of the systems with magnetic trivalent rare-earth ions. Also, the shape of the maximum in the susceptibility measurements reveals a wide variety of situations achieving magnetic ordering[5] which are not explained yet.

One of the most interesting effects found in this family of cuprates is their metamagnetism. The behavior of $R_2Cu_2O_5$ under magnetic field presents striking anomalies indicating complex metamagnetic transitions: one for In, Lu, Er, Ho, and Dy, two for Y and Sc, and four for Yb.[7] The nature of these field-induced changes in the magnetic ordering remained unknown, as well as the magnetic ordering itself.

The method of sample preparation is described elsewhere.[5] All the samples were studied on the D2B high-resolution powder diffractometer of the Institut Laue-Langevin in Grenoble, France, in its high-flux mode of operation at low (1.5 K) and room temperatures. In addition, neutron-diffraction studies of the magnetically ordered phase as a function of temperature (in 1-K steps) were carried out on the high-flux D1B diffractometer. The wavelengths $\lambda=1.595$ and 2.52 Å were used in the refinements of the data from D2B and D1B, respectively.

The studies of $Y_2Cu_2O_5$ and $Er_2Cu_2O_5$ were completed with diffraction patterns recorded on the also high-flux D20 diffractometer ($\lambda=2.42$ Å) at 1.5 K, ac susceptibility and magnetization measurements in a vibrating sample

 

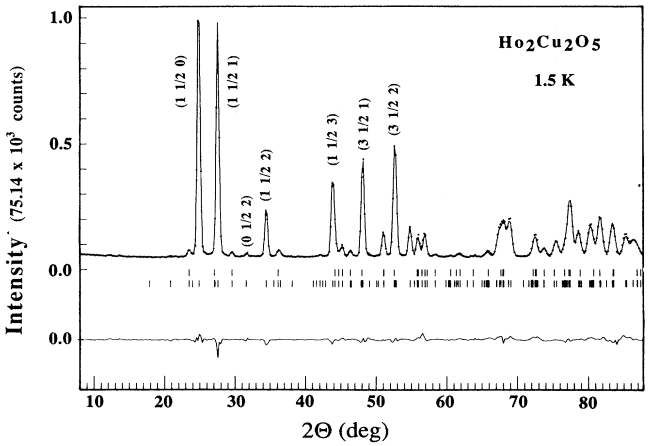


FIG. 1. Observed (+) and calculated (—) neutron-diffraction patterns of $Ho_2Cu_2O_5$ at 1.5 K. The curve at the bottom is the difference (observed-calculated) pattern; the two rows of small bars indicate the angular positions of the allowed nuclear and magnetic Bragg reflections, respectively.

magnetometer, and intense magnetic field measurements (up to 20 T) at the SNCI (Service National des Champs Intenses) in Grenoble, France.

The analysis of the diffraction data was performed using the Rietveld method by means of the program FULLPROF.[8] In relation to the crystal structure, the five $R_2Cu_2O_5$ compounds studied were isostructural and the final $R_{nuclear}$ factors at 1.5 K range from 3.1% to 8.07%.

We found all the magnetic structures to be commensurate at 1.5 K with the propagation vectors: $\mathbf{k}=(0,0,0)$ for $R$=Y,Er,Tm, $\mathbf{k}=(0,\frac{1}{2},0)$ for $R$=Ho, and $\mathbf{k}=(0,\frac{1}{2},\frac{1}{2})$ for $R$=Yb. As an example of the nuclear and magnetic refinements, Fig. 1 shows the observed and calculated neutron-diffraction pattern of $Ho_2Cu_2O_5$ obtained from the data taken with D1B at 1.5 K.

In order to perform the symmetry analysis of the magnetic structure, we have numbered the four equivalent sublattices of a site in $Pna2_1$ as follows: $1\rightarrow(x,y,z)$, $2\rightarrow(-x,-y,z+1/2)^*$, $3\rightarrow(-x+1/2,y+1/2,z+1/2)^*$, and $4\rightarrow(x+1/2,-y+1/2,z)^*$, where $x,y,z$ correspond to the crystallographic coordinates of the reference atoms in the asymmetric unit:[3,4] Cu(1), Cu(2), $R$(1), or $R$(2). The asterisk means that (if necessary) a lattice translation has been applied to keep the atoms inside the original unit cell. The resulting labeling is indicated in Fig. 2(a). To describe the magnetic structures we have used the so-called magnetic modes[9] which are the following linear combinations of magnetic moments: $\mathbf{F}=\mathbf{m}_1+\mathbf{m}_2+\mathbf{m}_3+\mathbf{m}_4$, $\mathbf{G}=\mathbf{m}_1-\mathbf{m}_2+\mathbf{m}_3-\mathbf{m}_4$, $\mathbf{C}=\mathbf{m}_1+\mathbf{m}_2-\mathbf{m}_3-\mathbf{m}_4$, and $\mathbf{A}=\mathbf{m}_1-\mathbf{m}_2-\mathbf{m}_3+\mathbf{m}_4$, where 1, 2, 3, and 4 refer to the numbering of the four equivalent sublattices.

Carrying out group-theoretical calculations we found the combination of magnetic modes compatible with symmetry for each propagation vector $\mathbf{k}$. After different trials

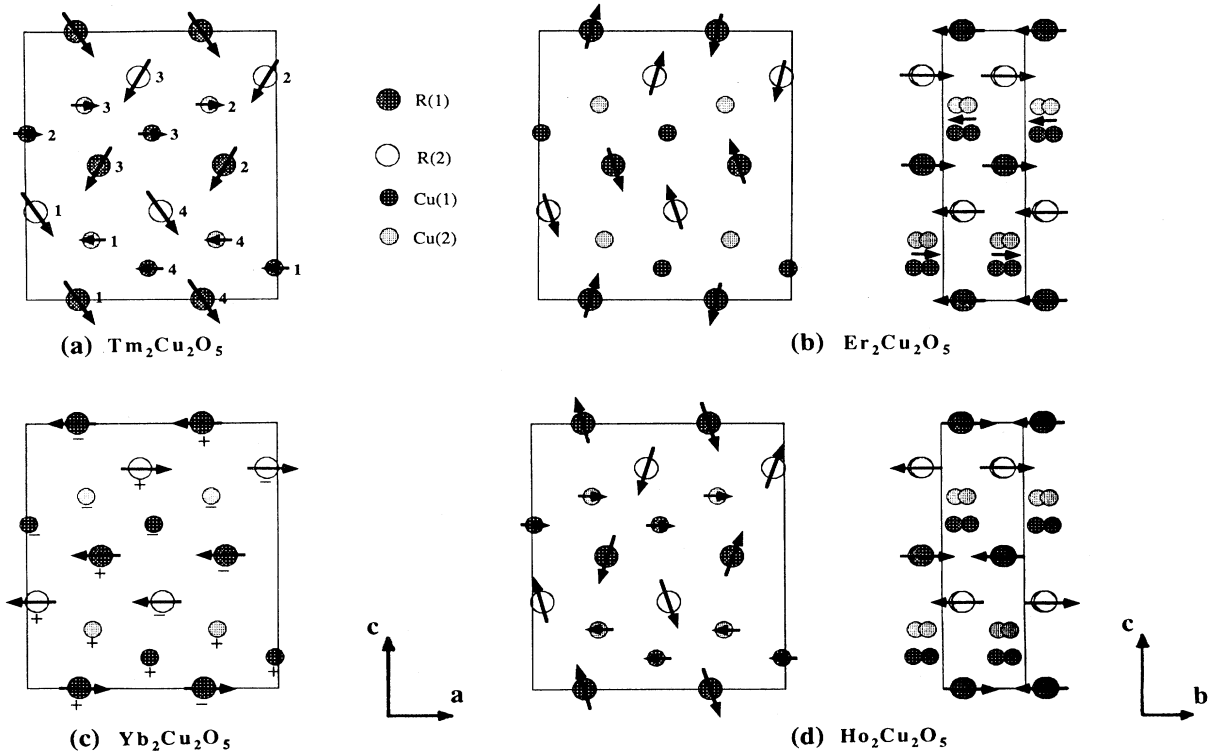


FIG. 2. Projection of the magnetic structures onto *ac* and *bc* planes as were found at 1.5 K in (a) $Tm_2Cu_2O_5$, (b) $Er_2Cu_2O_5$, (c) $Yb_2Cu_2O_5$, and (d) $Ho_2Cu_2O_5$. In the *ac* projection it is represented the magnetic moment direction, whereas in the *bc* projection only the *y* components are shown. In the case of Fig. 2(c) the orientation of magnetic moments along **b** are represented by "+" and "−" signs. Absolute values of magnetic moment components are in Table I.

TABLE I. Magnetic structure data for $R_2Cu_2O_5$ compounds at 1.5 K. Magnetic moments are given in $\mu_B$. Superscripts (1) and (2) refer to the two different sites for Cu and $R$. The three components of the magnetic moments $(m_x,m_y,m_z)$ correspond to the reference atom as explained in the text.

| | | | Magnetic modes of $R(1)$ and $R(2)$ sublattices | | Magnetic modes of Cu(1) and Cu(2) sublattices | |
|---|---|---|---|---|---|---|
| | $T_N$ (K) | k | $R$-$(m_x,m_y,m_z)$ | $R$-$m_T(m_{\text{free ion}})$ | Cu-$(m_x,m_y,m_z)$ | Cu-$m_T(m_{\text{free ion}})$ |
| Y | 13 | (0,0,0) | | | $\{0,A^{(1)}+A^{(2)},0\}$ | |
| | | | | | [0,1.1(1),0] | 1.1(1)[1] |
| Yb | 8.5/13.5 | $(0,\frac{1}{2},\frac{1}{2})$ | $\{A^{(1)}-A^{(2)},G^{(1)}+G^{(2)},0\}$ | | $\{0,A^{(1)}+A^{(2)},0\}$ | |
| | | | [0.6(1),1.2(1),0] | 1.4(1)[4] | [0,1.1(1),0] | 1.1(1)[1] |
| Tm | 17 | (0,0,0) | $\{A^{(1)}+A^{(2)},0,F^{(1)}+F^{(2)}\}$ | | $\{A^{(1)}+A^{(2)},0,0\}$ | |
| | | | [2.6(1),0,−3.0(1)] | 4.0(1)[7] | [−0.9(1),0,0] | 0.9(1)[1] |
| Er | 28 | (0,0,0) | $\{G^{(1)}+G^{(2)},A^{(1)}+A^{(2)},C^{(1)}-C^{(2)}\}$ | | $\{0,A^{(1)}+A^{(2)},0\}$ | |
| | | | [0.7(1),−5.5(1),2.9(1)] | 6.2(1)[9] | [0,1.2(1),0] | 1.2(1)[1] |
| Ho | 13 | $(0,\frac{1}{2},0)$ | $\{G^{(1)}+G^{(2)},A^{(1)}-A^{(2)},C^{(1)}+C^{(2)}\}$ | | $\{A^{(1)}+A^{(2)},0,0\}$ | |
| | | | [−4.4(1),1.0(2),7.8(1)] | 9.0(1)[10] | [−0.8(2),0,0] | 0.8(2)[1] |

for the orientation of the reference magnetic moments ($\mathbf{m}_1$) for each possible spin arrangement, we started the refinements. The preliminary ones led to **m** components on the two sites of Cu [Cu(1) and Cu(2)] and $R$ [$R(1)$ and $R(2)$], separately, with very similar absolute values within the error. Thus, and considering the fact that the two different sites of Cu and $R$ atoms have very similar coordination and orientation, final refinements were undertaken with the only restriction of making the absolute values of the three components at the (1) and (2) sites respectively identical. Refinements of magnetic structures converged in all the cases and the agreement factors $R_{\text{mag}}$ were the following: Y, 16.3%; Yb, 15.6%; Tm, 6.2%; Er, 9.4%; and Ho, 4.9%.

The magnetic structures of the five compounds (determined at 1.5 K) are described in Table I. The relative arrangement of **m**'s is indicated between brackets {}, e.g., a symbol of the form $\{A^{(1)}-A^{(2)},G^{(1)}+G^{(2)},0\}$, corresponding to the Yb sites 1 and 2, means that the sequence of **m** components in the chemical unit cell (according to the sublattice numbering above mentioned) is $(+--+)^{(1)}-(+--+)^{(2)}$ along $x$, $(+-+-)^{(1)}+(+-+-)^{(2)}$ along $y$, and there is no component along the $z$ direction.

In $R_2Cu_2O_5$, Cu(1), and Cu(2) sites are strongly coupled constituting dimers organized in zigzag chains along [100], which should be considered as forming *ab* "pseudolayers" (see Fig. 3). The magnetic structure of $Y_2Cu_2O_5$ consists of a ferromagnetic arrangement of $Cu^{2+}$ moments within the *ab* pseudolayers, pointing along [010], while the neighboring ones are stacked antiparallel, leading to 3D antiferromagnetic long-range order. As in the other rare-earth systems, the amplitude of the magnetic moment of $Cu^{2+}$ [$m(Cu^{2+})=1.06(5)\mu_B$], is very close to the free ion value. The two metamagnetic transitions take place at $H=3$ and 5.5 T at 1.5 K. Taking into account the jump of 0.3 $\mu_B$/Cu ion in the first transition,[6] we propose a mechanism for the metamagnetism involving a tripling of the magnetic cell along **b** or **c** after the first magnetization step.

Clearly, from the data it is not possible to infer unequivocally the pathway of the weaker effective superexchange interaction, therefore we illustrate, in Fig. 3(a), the proposed process considering that the magnetic unit cell changes along **b**. In the first magnetization step, only one chain flips their **m**'s in the tripled cell [(*F*) in the figure]. In the second step, the two remaining chains with inverted **m** in the upper pseudolayer of Fig. 3(a) would become ferromagnetically aligned to the others.

The magnetic structure of $Er_2Cu_2O_5$ is represented in Fig. 2(b). The onset of long-range order occurs at the same time on Cu and Er sublattices. The first order as in $Y_2Cu_2O_5$, with neighboring pseudolayers coupled antiferromagnetically. These Cu pseudolayers are bracketed by two Er layers having their main moment component (along [010]) antiparallel to $\mathbf{m}(Cu^{+3})$. This result indicates that the superexchange interaction $Er^{3+}-Cu^{2+}$ is antiferromagnetic.

A field-induced transition[7] takes place in $Er_2Cu_2O_5$ at low temperature. Figure 3(b) shows the proposed new magnetic ordering (only $y$ components are shown in the projection) which results from the flip of the $m_y$ components of Er atoms indicated by (*F*). Using values from Table I, this new configuration implies an increment of 14.5$\mu_B$ per unit cell in very good agreement with the ex-

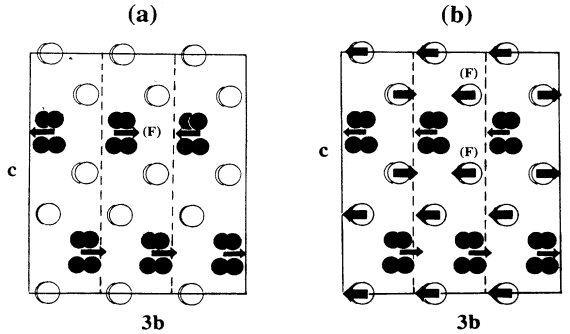


FIG. 3. Proposed magnetic order (only $y$ components) of (a) $Y_2Cu_2O_5$, (b) $Er_2Cu_2O_5$ after the first field-induced transition. (*F*) marks the flipped **m**'s (see explanation in the text). In this figure, rare earths are represented by open circles and copper atoms by solid circles.

perimental value (14.4 $\mu_B$/unit cell) obtained from magnetization measurements. We have observed, for the first time, a second field-induced transition at $\approx 14$ T. This second transition may be explained by an alignment along **b** of the $m_x$ components of the same Er atoms with inverted **m**'s in Fig. 3(b) (the measured jump is 0.96 $\mu_B$/unit cell, while from Table I this model implies a change of 0.93 $\mu_B$/unit cell).

In $Ho_2Cu_2O_5$, there exists short-range magnetic ordering up to $\approx 25$ K above $T_N$, indicating strong $\mathbf{m}(Ho^{3+})$-$\mathbf{m}(Ho^{3+})$ correlations. Because of the large moment of $Ho^{3+}$, it was not easy to discern the behavior of Cu atoms. However, we found out that $Cu^{2+}$ ions were magnetically ordered. It was confirmed by the presence of a weak reflection, $(0, \frac{1}{2}, 2)$, clearly associated to the existence of Cu moments. Finally, we obtained unambiguously the best agreement ($R_{mag}=4.9\%$) by considering the $A$ mode along **a**. That is, $\mathbf{m}(Cu^{2+})$ has rotated 90° in the *ab* plane with respect to the Y or Er case, but, because of the propagation vector, the pseudolayers are no longer ferromagnetic. The main component of $\mathbf{m}(Ho^{3+})$ is $m_z$.

The other compound with a nonzero propagation vector is for $R=$Yb. In this system, at 1.5 K, the magnetic cell is doubled along **b** and **c** directions and the magnetic structure inverts from cell to cell according to $\mathbf{k}=(0, \frac{1}{2}, \frac{1}{2})$. Inside the original cell, Cu sublattices keep the same **m** arrangement as in previous systems ($R$ =Y,Er), while Yb ones have $x$ and $y$ components. The magnetic ordering found, together with the existence of at least four magnetic transitions induced by externally applied fields suggest a high degree of frustration of $Yb^{3+}$-$Cu^{2+}$ and/or $Yb^{3+}$-$Yb^{3+}$ interactions. The order of Cu and Yb sublattices occurs at 13.5 and 8.5 K, respectively.

In the case of $Tm_2Cu_2O_5$, there is only one ordered magnetic state at low temperatures, in which the coupling between copper ions remains identical but, as in the case of Ho, the antiferromagnetic interaction $Cu^{2+}$-$Tm^{3+}$ forces the $Cu^{2+}$ ions to rotate their moments until they are parallel to **a**. This is the only case in the series where the rare earths have a net canted ferromagnetic ground state, which explains the absence of induced transitions on powder samples of this cuprate and the magnetization measurements from Troc *et al.*[5]

In conclusion, we have shown the magnetic ordering at 1.5 K of five $R_2Cu_2O_5$-type compounds, ruling out definitively several magnetic structures previously proposed.[5,7,10] This is a basic step to explain the observed field-induced transitions. Simple models account for them in the compounds with Y and Er. We are able to confirm that copper and rare-earth sublattices order in most of the cases at the same temperature (ytterbium is clearly an exception). This fact suggests quite strong interactions between these sublattices, and the magnetic structures seem to indicate that crystal-field energies are comparable to exchange interactions. In forthcoming publications we will give more detailed information concerning the magnetization measurements and the behavior of the different sublattices as they achieve the magnetic structure at 1.5 K described in this paper.

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