Anisotropy of magnetic properties of $R_2Cu_2O_5$ cuprates (R=Y, Lu, Tm, Yb, Tb)

M. Baran and R. Szymczak

Institute of Physics of Polish Academy of Sciences, 102-668 Warszawa, Poland

R. Z. Levitin and B. V. Mill

Moscow State University, 119899 Moscow, Russia

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The magnetization and magnetic susceptibility of $R_2Cu_2O_5$ rare-earth cuprates classified as high-T_c superconductors have been measured using a SQUID magnetometer over the temperature range 2–100 K in a magnetic field of up to 50 kOe. The anisotropy of their magnetic properties and magnetic field induced phase transitions in these compounds have been studied.
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1. INTRODUCTION

$R_2Cu_2O_5$ (R=Tb, Lu, Y, Sc, In) rare-earth cuprates are classified as rare-earth high-T_c $RBa_2Cu_3O_y$ superconductors. They are often detected as a by-product (the so-called blue phase) of their synthesis.

These compounds arouse considerable interest because magnetic,[1–6] neutron diffraction,[7–14] and spectral measurements,[15–18] as well as measurements of the specific heat,[19] thermal expansion and elastic modulus[20] detected at low temperatures magnetically ordered states with complex, mostly low-dimensional magnetic structures, and both spontaneous and field induced phase transitions between magnetic states were observed.

Most of experiments listed above were performed with polycrystalline samples. The magnetization of two cuprates—$Y_2Cu_2O_5$[2,5,6] and $Er_2Cu_2O_5$[3]—was measured for single crystals only along their b-axis. Thus the anisotropy of their magnetic parameters has not been studied at all, although the low (orthorhombic) symmetry of their lattices and neutron diffraction measurements indicate that the anisotropy should be quite considerable. A knowledge of the magnetic anisotropy is essential to an understanding of the nature of the magnetic ordering and magnetic phase transitions in these compounds.

In this connection we concentrated our effort on measurements of magnetic parameters of some cuprates $R_2Cu_2O_5$ (R=Y, Lu, Tm, Yb, Tb) along various crystal axes with a view to studying their anisotropy.

2. CRYSTAL STRUCTURE

The compounds $R_2Cu_2O_5$ belong to the orthorhombic symmetry and are described by the polar space group $Pna2_1$.[21] All the atoms are located at general positions. The atoms R1 and R2 have a distorted octahedral coordination with oxygen atoms. Each octahedron has common edges with two neighboring octahedrons, and they form chains aligned with the b-axis. Six octahedrons form a channel aligned with the b-axis containing pairs of Cu1 and Cu2 atoms.

Cu^{2+} ions have the coordination 4+1, which is typical of these compounds. Four oxygen atoms are located at approximately equal distances (2.0Å), and the fifth atom is at a longer distance (2.8Å). Oxygen polyhedrons around copper atoms are usually described as distorted square pyramids, but they can be also treated as irregular trigonal bipyramids.

A typical feature of the structure is staggered copper–oxygen chains from Cu_2O_5 dimers aligned with the a-axis. The copper atoms Cu1 and Cu2 are connected via two asymmetrical oxygen bridges with Cu1–O–Cu2 angles approximately equal to 90°. Copper–oxygen chains are repeated along the b-axis with a period $b\approx3.5$Å and along the c-axis with a period $c/2\approx6.2$Å . Thus we can define warped Cu–O layers in the ab-plane with a separation of $c/2$ between them. The separation between copper atoms in the layers is considerably smaller than between copper atoms of neighboring layers.

3. SAMPLES AND EXPERIMENTAL TECHNIQUES

$R_2Cu_2O_5$ single crystals were grown from nonstoichiometric melts of R_2O_3–BaO–CuO oxides by the technique described in Ref. 3. Single crystals shaped as needles with a length of up to 5 mm and a thickness of 0.1–0.2 mm were fabricated by cooling the melt in an aluminum oxide crucible from a temperature of 1200–1250 °C to 1000 °C at a rate of two degrees per hour. X-ray measurements demonstrated that the crystalline b-axis was aligned with the long needle axis. In the simplest case, the cross section normal to the crystal axis is rhombic with the bisector of the obtuse angle aligned with the a-axis and that of the acute angle with the c-axis. However, side faces of crystals often have other orientations. For this reason and also because of the small cross section dimensions, it was difficult to determine the orientation of a and c-axes, so we measured the crystal magnetization perpendicular to the b-axis and aligned approximately with the a and c-axes. The chemical composition was monitored using electron spectroscopy with high spatial resolution (EDAX).

The magnetization was measured by a SQUID magnetometer in a field of up to 50 kOe over the temperature range 2–100 K. Note that in magnetization measurements in a magnetic field perpendicular to the crystal axis, allowance

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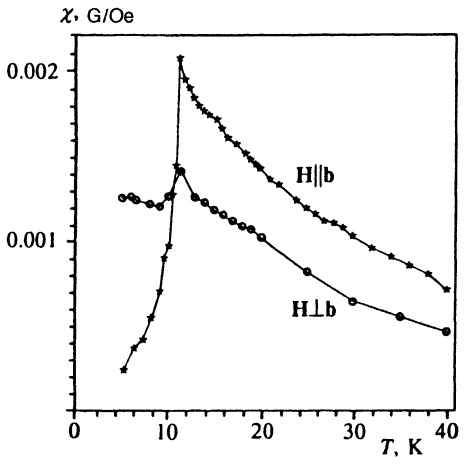

FIG. 1. Magnetic susceptibility of $Y_2Cu_2O_5$ single crystal versus temperature.

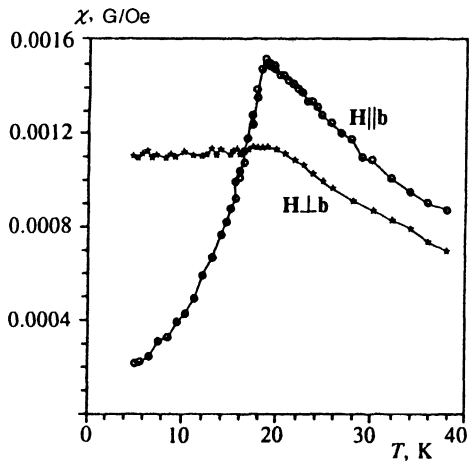

FIG. 2. Magnetic susceptibility of $Lu_2Cu_2O_5$ single crystal versus temperature.

for the demagnetization factor was essential. For simplicity we approximated the crystal cross section by a circle.

Although the accuracy of magnetic measurements in the SQUID magnetometer was high (an uncertainty of about 0.1%), the error in the absolute magnetization was much larger because of small dimensions and small masses of the samples. We estimate the uncertainty of absolute magnetization measurements at 5–10%. The magnetic susceptibility was derived from measurements of magnetization in low magnetic fields (below 1 kOe).

4. EXPERIMENTAL DATA AND DISCUSSION

4.1. $Y_2Cu_2O_5$ and $Lu_2Cu_2O_5$

Let us first discuss magnetic properties of $Y_2Cu_2O_5$ and $Lu_2Cu_2O_5$, in which the only magnetic ions are Cu^{2+}. Neutron diffraction measurements[7,10,12] indicate that these materials have identical antiferromagnetic structure. It is composed of magnetized ab-planes and has a wave vector $\mathbf{k}=(0,0,0)$. Copper magnetic moments in neighboring planes are antiparallel and collinear to the b-axis, but they may deviate from this axis by several degrees.[7,12]

Figures 1 and 2 demonstrate that the magnetic susceptibilities of these crystals versus temperature in a magnetic field aligned with the b-axis have sharp maxima at temperatures of 11.5 and 19 K, respectively, which indicate antiferromagnetic transitions. The susceptibility peaks with a magnetic field applied normally to the b-axis have much smaller amplitudes.

The Néel temperatures derived from these measurements are in agreement with results by other researchers. According to measurements of the magnetic susceptibility of single and polycrystals,[1–3,6] of specific heat,[19] optical spectra,[16] and thermal expansion factors and elastic moduli,[20] the Néel temperature of $Y_2Cu_2O_5$ ranges between 10.5 and 14 K, and that of $Lu_2Cu_2O_5$ between 17 and 21.5 K.

The magnetization curves of the yttrium and lutetium cuprates are given in Figs. 3 and 4. You can see that metamagnetic transitions take place in both materials in a magnetic field aligned with the b-axis. In the field range studied, two phase transitions were detected in $Y_2Cu_2O_5$ and one transition in $Lu_2Cu_2O_5$. Let us recall that earlier two metamagnetic transitions were detected in both single crystal[2,5] and polycrystalline samples[3,4] of $Y_2Cu_2O_5$. The $Lu_2Cu_2O_5$ magnetization was previously measured only for polycrystalline samples[3,4] in a field below 50 kOe, and the

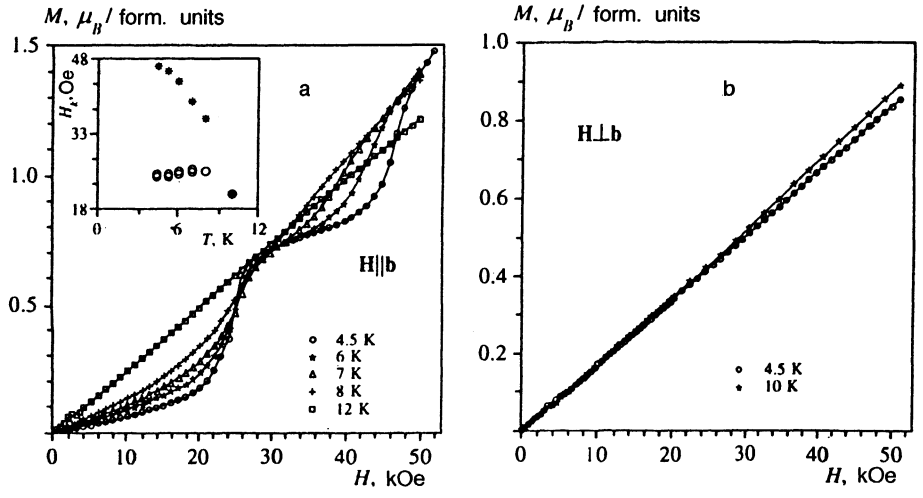

FIG. 3. Curves of $Y_2Cu_2O_5$ magnetization: a) along b-axis; the insert shows the metamagnetic transition field versus temperature; b) perpendicular to the b-axis.

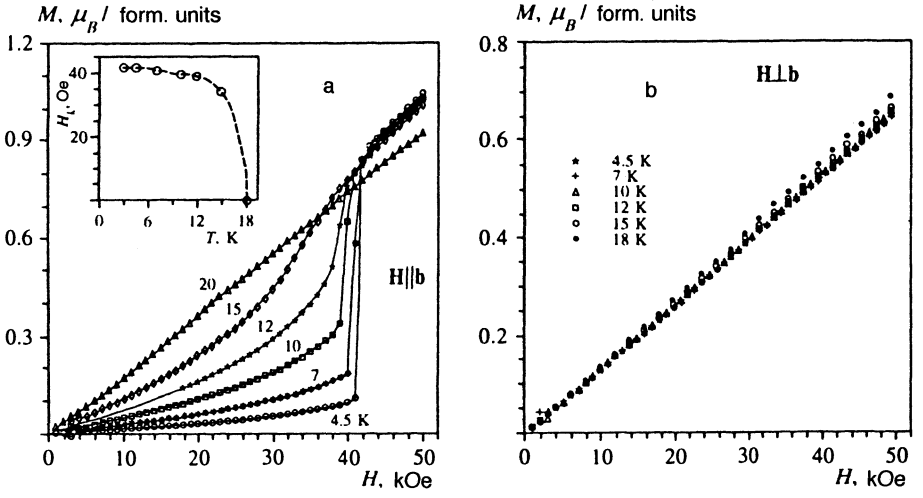

FIG. 4. Curves of $Lu_2Cu_2O_5$ magnetization: a) along b-axis; the insert shows the metamagnetic transition field versus temperature; b) perpendicular to the b-axis.

only metamagnetic transition detected was much wider than that recorded in single crystals of this material. Our data demonstrate that the field corresponding to the metamagnetic transition drops with the temperature and goes to zero at the Néel temperature (see inserts in Figs. 3 and 4). At higher temperatures the metamagnetic transitions are broadened.

The magnetization of yttrium and lutetium cuprates in a field perpendicular to the b-axis is linear with the field (Figs. 3 and 4). Assuming that the linear function can be extrapolated to the saturation (spin-flip) field and the Cu^{2+} magnetic moment $\mu_{Cu}=1\mu_B$, we derive from our data the low-temperature saturation field of 120 kOe for $Y_2Cu_2O_5$ and 156 kOe for $Lu_2Cu_2O_5$. These results agree with the saturation field derived from measurements of the polycrystal magnetization.[4]

In our treatment of magnetization of cuprates with non-magnetic R-ions (R=Y, Lu, Sc, In)[3–5] we take into account that copper ions in chains aligned with the c-axis may be coupled and considered as pairs with unit spin. This assumption allows us to interpret the observed copper anisotropy in these materials (the magnetic anisotropy of Cu^{2+} ions with a spin $s=1/2$ is zero in the first approximation).

The model adopted in Ref. 3 presumes that exchange integrals between neighboring ab-planes, J_1, and between planes separated by another plane, J_2, are negative. Then, if the magnetic anisotropy is much stronger than the exchange interaction (Ising approximation) and J_1 is comparable to J_2, two magnetic transitions are caused by the magnetic field aligned with the b-axis. A ferrimagnetic structure $++-++-$ with a magnetization of 1/3 of the saturation value is produced by the field H_{k1}, and the field H_{k2} transforms the material to the ferromagnetic state. This model, however, is not a faithful one, however, because according to experimental data, the magnetization of $Y_2Cu_2O_5$ is not saturated after the second transition (Fig. 3).

An improved model was proposed in Refs. 4 and 5. It presumes that the magnetic anisotropy is comparable to the exchange interaction. In this model the first transition is also a transition to the ferrimagnetic phase with a magnetization of 1/3 of the saturation value, but the second transition is a transition to a spin-flop phase in which magnetic moments are misaligned with the magnetic field. The spin-flop phase is magnetized as magnetic moments are gradually aligned with the external magnetic field. One advantage of this model is that it accounts for the small magnetization jump due to the second magnetic transition.

It seems, however, that this model is also not exact. Firstly, Fig. 3 indicates that the $Lu_2Cu_2O_5$ magnetization after the first magnetic transition is larger than 1/3 of the saturation ($2\mu_B$), and, secondly, the $Y_2Cu_2O_5$ magnetization is not described by a linear function beyond H_{k2},[5] as predicted by the model for the spin-flop phase. Further investigation is needed to clarify the nature of magnetic transitions in $Y_2Cu_2O_5$ and $Lu_2Cu_2O_5$.

4.2. $Tm_2Cu_2O_5$

According to the data reported by some researchers,[1,3,19,20] this material is magnetically ordered at a temperature below 15–17 K. The structure of the magnetically ordered state in thulium cuprate, however, remains unclear. The magnetization of $Tm_2Cu_2O_5$ in a low magnetic field (~1 kOe) rises rapidly[1,3] and is comparable to that of other rare-earth cuprates above the metamagnetic transition. In this connection, Troc *et al.*[1] assumed that the thulium cu-

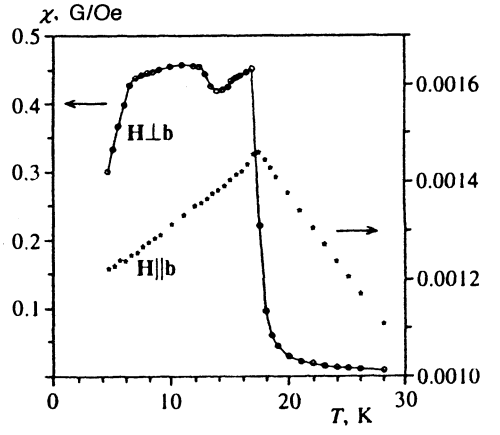

FIG. 5. Magnetic susceptibility of the $Tm_2Cu_2O_5$ single crystal.

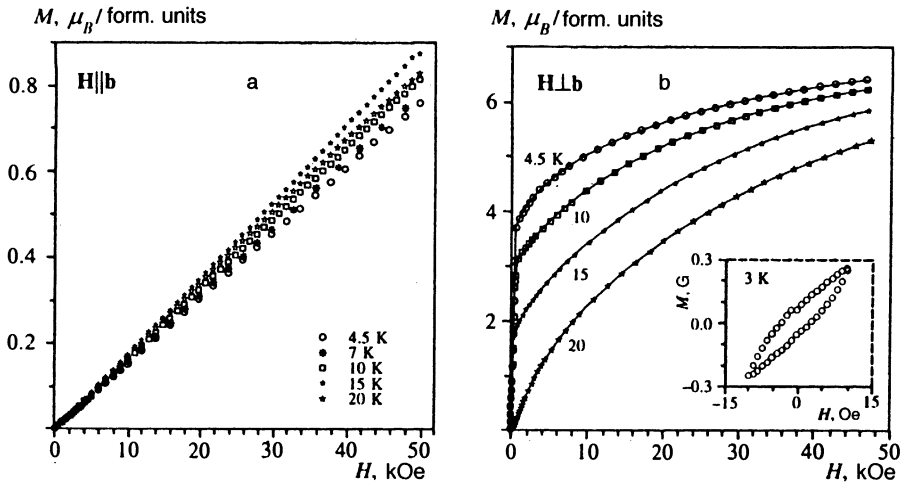

FIG. 6. Magnetization curves of the $Tm_2Cu_2O_5$ single crystal: a) along the b-axis; b) perpendicular to the b-axis; the insert shows the hysteresis loop at a low field.

prate is a ferro- or ferrimagnetic, and Kazeĭ *et al.*[3] concluded that the transition from the antiferromagnetic to ferro- or ferrimagnetic state takes place in a low magnetic field, although they did not detect the transition itself. The assumption that thulium cuprate is an antiferromagnetic was confirmed by neutron diffraction experiments,[11,12] which indicate that it has an antiferromagnetic structure at low temperatures with a wave vector $\mathbf{k}=(0,0,0)$ and a ferromagnetic component (canted ferromagnetism).

It follows from measurements of the magnetic susceptibility of single crystals (Fig. 5) that thulium cuprate transforms to a magnetically ordered state at 17 K. Note that its magnetic susceptibility is highly anisotropic, and in a field aligned with the b-axis it is about an order of magnitude lower than in a perpendicular field. Moreover, different components of the susceptibility have different temperature dependences. Under a field aligned with the b-axis the susceptibility has a maximum at the Néel temperature of 17 K, which is typical of the antiferromagnetic state, whereas under a perpendicular field the susceptibility rises rapidly as the temperature drops to the Néel point and it is nearly flat at lower temperatures. This behavior is typical of highly anisotropic materials with a ferromagnetic component in their magnetic ordering, which conforms with the neutron diffraction data.[11,12] Note that there is an additional broad minimum on the susceptibility curve in a perpendicular field below the ordering temperature at about 15 K. Earlier a similar feature was detected in the ac susceptibility of a polycrystal.[3] The nature of this minimum remains unclear since no features were detected on curves of other parameters of $Tm_2Cu_2O_5$ versus temperature, and neutron scattering measurements indicate that its magnetic structure is not changed in the temperature range between 2 K and the Néel point.[10] This feature may be due to a change in the state of the Tm^{3+} ion since spectral measurements indicate[16] that the gap between the ground and first excited states of Tm^{3+} is 14.7 cm^{-1} in one position and 16.3 cm^{-1} in the other position, and the high-energy level is emptied at a temperature of 14–15 K.[17]

Now let us discuss the $Tm_2Cu_2O_5$ magnetization (Fig. 6). The magnetization in a field parallel to the b-axis is linear, and in a perpendicular field it grows rapidly at a low field and saturates at a higher field, whereas hysteresis is observed at a very low field (the insert in Fig. 6). All this could be interpreted in terms of ferromagnetic ordering along this direction. But more detailed data about its magnetization

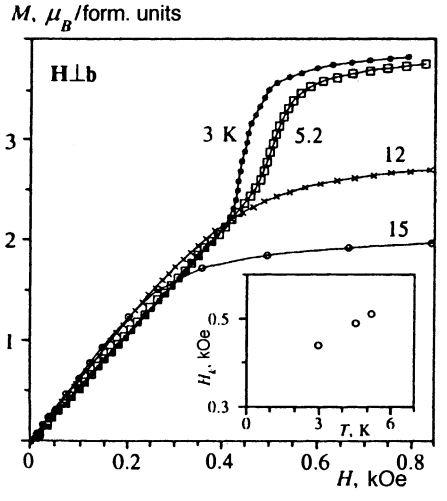

FIG. 7. Magnetization curves of $Tm_2Cu_2O_5$ single crystal under a low magnetic field perpendicular to the b-axis. The insert shows the metamagnetic transition field versus temperature.

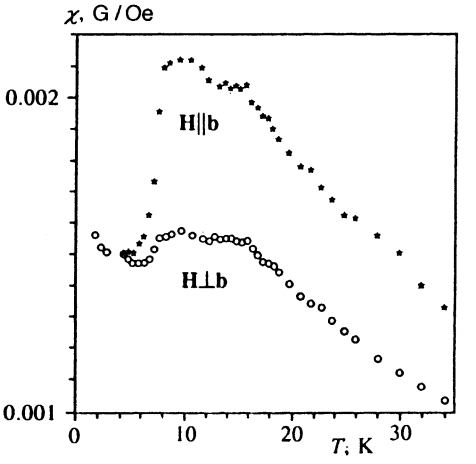

FIG. 8. Magnetic susceptibility of the $Yb_2Cu_2O_5$ single crystal.

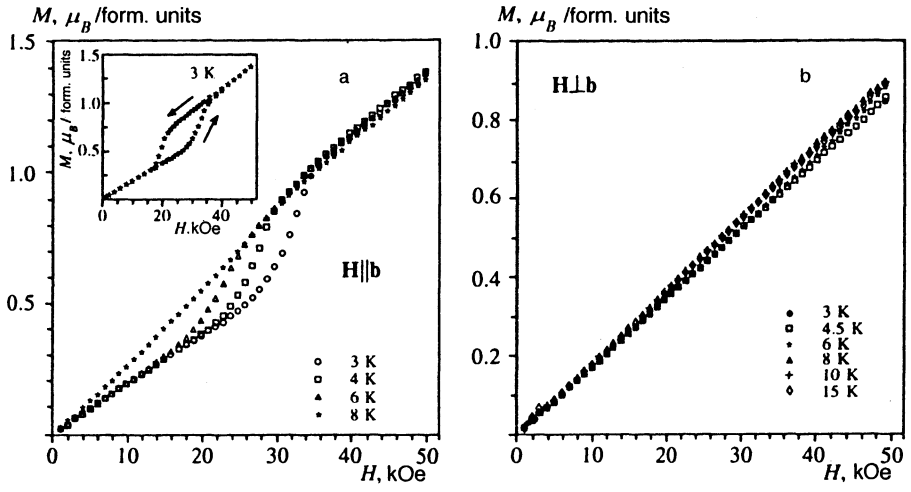

FIG. 9. Magnetization curves of the $Yb_2Cu_2O_5$ single crystal: a) along the b-axis (measurements under an increasing field are given); the insert shows the hysteresis loop at 3 K; b) perpendicular to the b-axis.

in a low magnetic field (Fig. 7) demonstrate that the situation is more complicated. At a low temperature a metamagnetic transition is detected on the magnetization curves under a field perpendicular to the b-axis, i.e., like most other cuprates, the thulium cuprate undergoes a metamagnetic transition, although at a lower magnetic field. Note that the transition takes place only at a temperature below 8–10 K (insert in Fig. 7). This may be caused by the change in the Tm^{3+} state discussed above.

To conclude this section, note that there is some anisotropy of magnetic parameters in the ac-plane of a thulium cuprate single crystal. The experimental data described above were obtained in a magnetic field approximately aligned with the c-axis (within 15–20°). If a crystal is turned through an angle of 90° (the field is approximately parallel to the a-axis), the magnetization is about 10% lower and the magnetic transition field is higher.

4.3. $Yb_2Cu_2O_5$

Measurements of various properties of polycrystals[1,3,15,19,20] indicate that ytterbium cuprate is an antiferromagnetic with a Néel temperature of 13–16 K. In contrast to other rare-earth cuprates, in which both the copper and rare-earth magnetic subsystems are ordered at one Néel temperature, neutron diffraction data[12,15] indicate that only the copper subsystem is ordered at the Néel temperature of 13–16 K, and the ytterbium subsystem is ordered at a lower temperature of 6–8 K. This conclusion is confirmed by notable features in temperature dependences of the susceptibility, spectral, thermodynamic, and magnetoelastic parameters in this temperature range.[1,3,15,19,20]

The antiferromagnetic structure of ytterbium cuprate has a wave vector $\mathbf{k}=(0,1/2,1/2)$, i.e., the lattice cell is doubled along the b and c-axes when it transforms to the antiferromagnetic state. Magnetic moments of copper and ytterbium belong to the ab-plane and are approximately aligned with the b-axis.

Figure 8 shows the magnetic susceptibility of a $Yb_2Cu_2O_5$ single crystal versus temperature at different orientations of the magnetic field. A notable anisotropy of the magnetic susceptibility is evident. A peculiarity that may be related to the ytterbium ordering is clearly seen at 8 K. A peculiarity in the susceptibility at 16 K, i.e., the copper Néel point, is less remarkable. Its amplitude is smaller, possibly, because it is masked by the drop in the ytterbium susceptibility with the temperature.

The magnetization of the single crystal versus magnetic field is plotted in Fig. 9. A metamagnetic transition in a field

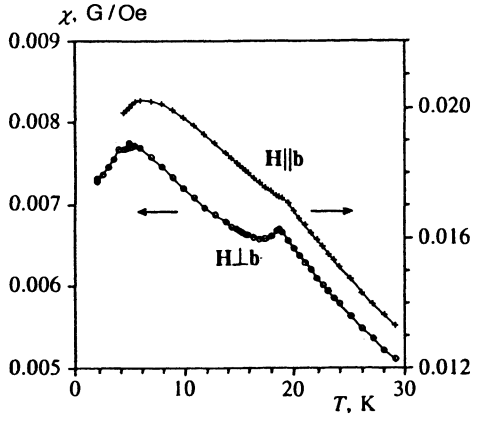

FIG. 10. Magnetic susceptibility of the $Tb_2Cu_2O_5$ single crystal.

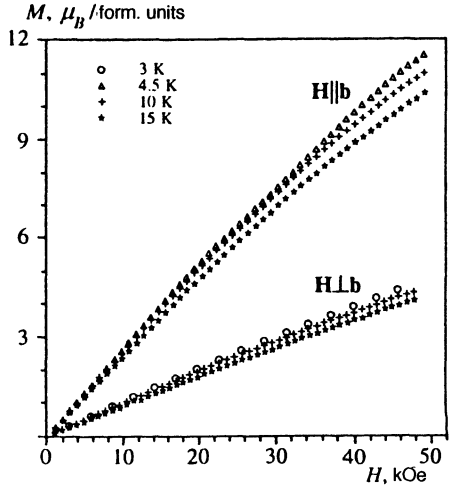

FIG. 11. Magnetization curves of the $Tb_2Cu_2O_5$ single crystal measured.

parallel to the b-axis can be seen. At a lower temperature the transition has a larger hysteresis. Both the hysteresis and field of the transition drop with the temperature. Note that the metamagnetic transition is not observed at a temperature higher than 8 K, i.e., when the ytterbium subsystem is disordered. Thus the metamagnetic transition is controlled by the magnetic ordering of ytterbium ions.

The absence of the metamagnetic transition when the ytterbium system is disordered demonstrates that the copper subsystem in $Yb_2Cu_2O_5$ is essentially different from those in $Y_2Cu_2O_5$ $Lu_2Cu_2O_5$.

4.5. $Tb_2Cu_2O_5$

The authors of the first publication on the magnetic properties of rare-earth cuprate polycrystals[1] concluded that $Tb_2Cu_2O_5$ remained paramagnetic at a temperature down to 4 K. Nonetheless, further experiments with polycrystalline samples using various techniques[3,16,19,20] demonstrated that terbium cuprate transformed to a antiferromagnetic state at a temperature of 17–21.5 K. An additional feature in the magnetic susceptibility was detected at 8 K.[3]

The magnetic susceptibility of a terbium cuprate single crystal at two magnetic field orientations versus temperature is plotted in Fig. 10. Small features are seen on the curves at 18.5 K and 5.5–6.5 K. The high-temperature feature corresponds to the transition to the antiferromagnetic state earlier detected in polycrystalline samples. The nature of the low-temperature feature is unclear. Neutron diffraction measurements[11] indicate that no restructuring of the magnetic system takes place at 5.5–6.5 K. No singularities were detected in this temperature range in spectral characteristics, specific heat, thermal expansion, and elastic moduli.[16,19,20] The low-temperature feature may be due to a change in the state of the Tb^{3+} ion since spectral measurements[17,18] indicate that the first excited level of this ion is 12 cm^{-1} above the ground state and should be emptied at a temperature of about 11 K.

Curves of the terbium cuprate single crystal magnetization versus field at two orientations at constant temperatures are plotted in Fig. 11. The magnetization is linear with the field at low and intermediate fields in both cases, and only at higher magnetic fields some saturation is observed. Note that the magnetic properties are highly anisotropic, and the magnetization aligned with the b-axis is a factor of two higher than in the perpendicular direction.

We should stress that, in contrast to other $R_2Cu_2O_5$ materials, no metamagnetic transitions were detected in $Tb_2Cu_2O_5$ single crystals under a field of up to 50 kOe and in polycrystals up to 250 kOe.[3] A possible explanation is that terbium cuprate has a more complicated antiferromagnetic structure. The terbium moment has nonzero projections on all the three crystal axis, whereas in other cuprates one crystal axis along which magnetic moments of rare-earth ions are aligned may be selected.

5. CONCLUSION

Our results demonstrate the versatility of magnetic properties of $R_2Cu_2O_5$ materials. Given their specific crystal structure, they are low-dimensional magnetics with a considerable magnetic anisotropy, and the presence of two magnetic subsystems, namely those of copper and rare-earth ions, gives rise to complicated magnetic structures and various field-induced magnetic phase transitions.

Further investigation, especially studies of single-crystal magnetic structures using neutron scattering, is needed for better understanding of the nature of these magnetic materials.

We are indebted to M. N. Popova for helpful discussions.

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