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Occurrence of weak ferromagnetism in T'-$(R_{1-x}Y_x)_2CuO_4$ (R = Sm and Eu)

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Results for the temperature dependence of the magnetic susceptibility for Gd_2CuO_4, $(Sm_{1-x}Y_x)_2CuO_4$, and $(Eu_{1-x}Y_x)_2CuO_4$ with various Y concentrations are reported. The magnetic anomalies that occurred at $T_N(Cu)\sim 285$ K and $T_m \sim 20$ K in Gd_2CuO_4, are not observed in Sm_2CuO_4 or Eu_2CuO_4, and are seen in $(Sm_{1-x}Y_x)_2CuO_4$ and $(Eu_{1-x}Y_x)_2CuO_4$ with $x \geq 0.3$ and $x \geq 0.05$, respectively. It is found that the transition temperatures $T_N(Cu)$ and T_m and the magnitudes of anomalies are very sensitive to Y substitution. Thus, the effect of small ionic radius for Gd plays a much more important role than its large moment on the anomalous magnetic properties of Gd_2CuO_4. This also provides clear evidence that the magnetic anomalies in Gd_2CuO_4 are due to weak ferromagnetism in the Cu-O plane resulting from the too small ionic radius of Gd, which induces a lattice distortion in the T' structure.

Rare-earth cuprates of composition R_2CuO_4 (R = Pr, Nd, Sm, and Eu) with the tetragonal T' structure play a unique role among cuprates, becoming so-called N-type superconductors when suitably doped.[1-4] The T' structure consists of only the square planar CuO_4 arrangement with no apical oxygen atoms.[5] Among the R_2CuO_4 family, Gd_2CuO_4 is the only member with the T' structure prepared in ambient pressure in which superconductivity cannot be induced either by doping with Ce or with Th. There have been several suggestions[6] for the absence of superconductivity in this compound, but no clear explanation has yet been given. Moreover, the Gd_2CuO_4 also exhibits a variety of interesting magnetic behaviors involving both the rare-earth and copper spin.[7-9] The Cu^{2+} moment forms an antiferromagnetically ordered structure with $T_N(Cu)\sim 260-280$ K.[7-10] At lower temperature, the magnetic susceptibility presents a strong peak at $T_m \sim 20$ K which is thought to be associated with a weak ferromagnetism in Cu-O planes.[6-10] Finally, the Gd^{3+} moments order antiferromagnetically with $T_N(Gd)\sim 6.5$ K.[7-10]

Recently, questions of relationship among the structural stability and magnetic properties of undoped and doped Gd_2CuO_4 have attracted much attention. For instance, copper antiferromagnetism persists in $(Gd_{1.85}Ce_{0.15})CuO_4$, which is probably related to the absence of superconductivity in this compound;[7] the strong peak at $T_m \sim 20$ K in Gd_2CuO_4 was found to be strongly suppressed by Ce^{4+} and Nd^{3+} doping;[11,12] the origin of the weak ferromagnetism in Gd_2CuO_4 may be due to a small distortion of the local copper environment.[13,14] In fact, the magnetic structures of the Cu and Gd sublattices in Gd_2CuO_4 have different symmetries, hence a specific-heat anomaly at the Gd ordering temperature $T\sim 6.5$ K is observed.[15,16] A similar situation also exists in Sm_2CuO_4,[17,18] while different cases are shown for Nd_2CuO_4 and Pr_2CuO_4.[15,16,19] Therefore, in spite of the overall similarity of T'-structure rare-earth cuprates, there are subtle differences between compounds with different rare earths, both in structural aspects and in magnetic properties. In this paper, we present the magnetic susceptibility data on $(Sm_{1-x}Y_x)_2CuO_4$ and $(Eu_{1-x}Y_x)_2CuO_4$ to study the ionic radius effect on the anomalous magnetic properties of Gd_2CuO_4.

All polycrystalline samples of Gd_2CuO_4, $(Sm_{1-x}Y_x)_2CuO_4$ and $(Eu_{1-x}Y_x)_2CuO_4$ ($0 \leq x \leq 0.5$) were prepared by the standard solid-state reaction method under identical conditions. High-purity Sm_2O_3, Eu_2O_3, Gd_2O_3, and CuO powders were mixed and fired in air at 900 °C for 24 h. The resultant powders were pressed into pellets and heated in air at 900 °C for 24 h. This process was repeated at least three times with intermediate grinding. These pellets were then heated in air at 1000 °C for 48 h and air quenched to room temperature. The structural analysis was carried out by the powder-x-ray diffraction. Lattice parameters were determined from least-squares fits of the diffraction lines indexed with the space groups $I4/mmm$. The dc magnetization for each sample was measured using a superconducting quantum interference device (SQUID) magnetometer (Quantum Design) over the temperature range 5–350 K.

Temperature dependence of the magnetic susceptibility for Gd_2CuO_4 in several applied magnetic fields $B_a = 10$, 100, 1000, and 10 000 Oe is shown in Fig. 1. The transition at $T_N(Cu) = 285$ K determined from the peak of the first temperature derivative of the magnetic susceptibility $d\chi/dT$ is undoubtedly associated with the antiferromagnetic ordering of the Cu sublattices[7-10] similar to the one observed in the La_2CuO_4 with a Néel temperature $T_N \sim 240$ K.[18] The apparent maximum that occurred at $T_m \sim 20$ K is thought to be related to a weak ferromagnetism in Cu-O planes.[6-10] This anomaly and T_m are strongly suppressed by the field and disappear at about 10 kOe. The other anomaly occurred at $T_N(Gd)\sim 7$ K, which is almost field independent and was also observed

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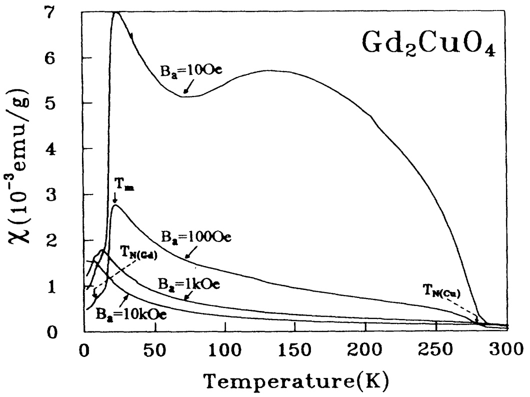

FIG. 1. Temperature dependence of the magnetic susceptibility for Gd_2CuO_4 in several applied magnetic fields $B_a = 10$, 100, 1000, and 10 000 Oe. See text for detail about the determination of T_N(Cu), T_m, and T_N(Gd).

as a λ-like peak in low-temperature specific heat,[8,13,15,16] indicates the antiferromagnetic order of Gd moments. These observations are in good agreement with those reported by other groups.[6-14] The magnetic anomaly at $T_m \sim 20$ K is accompanied by the appearance of a magnetic anomaly at $T_N(\mathrm{Cu}) \sim 285$ K in Gd_2CuO_4, which are not observed in the other R_2CuO_4 (R =Pr-Sm) cuprates. The weak ferromagnetism observed in a solution of $(R_{1-x}Gd_x)_2CuO_4$ (R =Nd and Sm) in the Gd-rich region,[11,13,14] has been attributed to the existence of local static distortion in the Cu-O plane.[13,14] In order to extensively study these magnetic anomalies in Gd_2CuO_4, two systems $(Sm_{1-x}Y_x)_2CuO_4$ and $(Eu_{1-x}Y_x)_2CuO_4$ have been synthesized in air at atmospheric pressure.

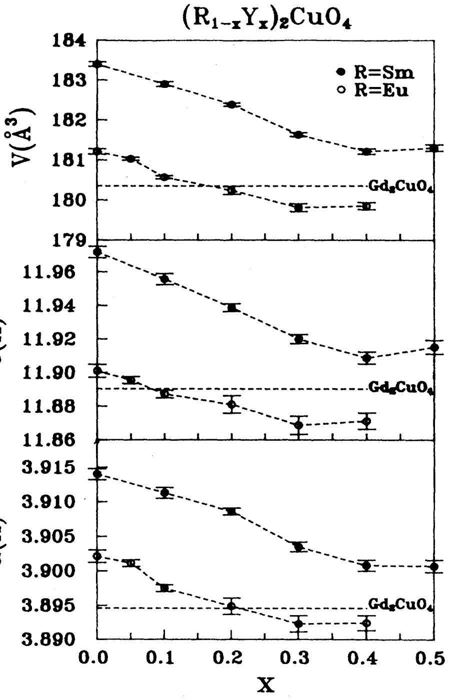

FIG. 2. Variation of lattice parameters a, c, and unit-cell volume V with Y concentration x in $(Sm_{1-x}Y_x)_2CuO_4$ and $(Eu_{1-x}Y_x)_2CuO_4$. For comparison, those of Gd_2CuO_4 are also included.

The variation of lattice parameters a and c, and unit-cell volume V with Y concentration x in $(R_{1-x}Y_x)_2CuO_4$ (R =Sm, Eu, and Gd) is shown in Fig. 2 and tabulated in Table I. The values for Eu_2CuO_4, Sm_2CuO_4, and Gd_2CuO_4 are in agreement with those reported in the literature.[6,11,14] Basically, lattice parameters decrease with increasing Y concentration x in both systems. However, given the error bars on data points in Fig. 2, it appears that Vegard's rule is not followed. If one looks carefully at the $(Eu_{1-x}Y_x)_2CuO_4$ case, there is a pronounced change of slope at $x \sim 0.1$ and the error bars on data points for $x > 0.1$ become larger as well. A similar situation is also observed in $(Sm_{1-x}Y_x)_2CuO_4$ at $x \sim 0.3$. This indicates a poorer fit to x-ray patterns indexed with space group $I4/mmm$ and may reveal a dissimilar crystal structure near and above those values of x. Similar results have been seen in $(Nd_{1-x}Gd_x)_2CuO_4$ for $x \sim 0.625$ (Ref. 13) and heavier R_2CuO_4 (Refs. 6, 20, and 21) sys-

TABLE I. Lattice parameters a and c, unit-cell volume V, and Néel temperatures T_N(Cu) and T_m for $(R_{1-x}Y_x)_2CuO_4$ (R =Sm, Eu, and Gd).

R	x	a (Å)	c (Å)	V (Å^3)	T_N(Cu) (K)	T_m (K)
Sm	0	3.914(1)	11.972(3)	183.40(6)		
	0.1	3.911(1)	11.956(3)	182.90(6)		
	0.2	3.909(1)	11.939(2)	182.39(4)		
	0.3	3.904(1)	11.920(3)	181.63(5)	~280	~9
	0.4	3.901(1)	11.909(4)	181.21(7)	~280	~9
	0.5	3.901(1)	11.915(4)	181.30(8)	~280	~9
Eu	0	3.902(1)	11.901(4)	181.21(7)		
	0.05	3.901(1)	11.895(2)	181.03(4)	~225	<5
	0.1	3.898(1)	11.887(2)	180.57(4)	~280	<5
	0.2	3.895(1)	11.881(5)	180.24(10)	~285	~7
	0.3	3.892(1)	11.869(5)	179.81(10)	~285	~7
	0.4	3.892(1)	11.871(5)	179.85(9)	~280	~8.5
Gd	0	3.895(1)	11.890(2)	180.35(5)	~285	~20

tems, which were subjected to the local structural distortion. It is noted that the T' (or T'-like) structure is only maintained at $x=0.4$ and 0.3 for $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ and $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, respectively. Those are also the solubility limit for these two systems prepared at ambient pressure. This can be confirmed from the x-ray-diffraction patterns (not shown) and the deviation of the decreasing trend in lattice parameters shown in Fig. 2. This result is consistent with that of the T'-type compounds prepared for $R=$Pr-Gd at ambient pressure; for $R=$Tb-Tm and Y (for which the ionic radius is smaller than Gd), these compounds can be synthesized only under high-pressure conditions.[20,21]

The temperature dependence of the magnetic susceptibility with various Y concentrations x for $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ is shown in Fig. 3. The inset shows the magnetic anomalies in the temperature range of 5–15 K and 260–300 K. No obvious change of signature is observed for $x \leq 0.2$; however, two clear features, one at ~280 K, the other at ~9 K, are exhibited for $x=0.3$, 0.4, and 0.5 (even though some impurity phases exist for $x=0.5$). This observation is similar to that seen in Fig. 1 for $\mathrm{Gd}_2\mathrm{CuO}_4$ at an applied field of 100 Oe, except that the $T_m \sim 20$ K shifts down to ~9 K. Figure 4 shows the temperature dependence of the magnetic susceptibility for $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$. An extremely sensitive feature with Y concentration is observed for $x \geq 0.05$. It is believed that this behavior is qualitatively the same as with $\mathrm{Gd}_2\mathrm{CuO}_4$. Therefore, these magnetic anomalies are also attributed to a weak ferromagnetic component in the Cu-O planes of the T' structure. Values of T_N(Cu) and T_m for $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, and $\mathrm{Gd}_2\mathrm{CuO}_4$ are also listed in Table I. The differences for T_N(Cu), T_m, and the magnitude of anomalies among these systems may be due to the background of susceptibility for different rare earths or to the atomic disorder effect in doped systems. Combining these magnetic results in Figs. 3 and 4 with the structural data in Fig. 2 and Table I discussed above, the boundary for the occurrence of weak ferromagnetism takes place at $x \sim 0.3$ and ~0.05 in $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ and $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, respectively. The corresponding lattice parameter $a \sim 3.901$ Å for this boundary is in qualitative agreement with that observed in $(\mathrm{Nd}_{1-x}\mathrm{Gd}_x)_2\mathrm{CuO}_4$ with $x \sim 0.625$ (Ref. 13), in $\mathrm{Sm}_{2-x}\mathrm{Gd}_x\mathrm{CuO}_4$ with $x \sim 1$ (Ref. 14), in $\mathrm{Eu}_{2-x}\mathrm{Gd}_x\mathrm{CuO}_4$ with $x \sim 0$ (Ref. 8), and in $\mathrm{Eu}_{2-x}\mathrm{Tb}_x\mathrm{CuO}_4$ with $x \sim 1$ (Ref. 8). For $\mathrm{Eu}_2\mathrm{CuO}_4$, an extremely weak interaction of weak ferromagnetism in the pure compound and difficulties to achieve superconductivity in the Ce-doped samples were reported,[3] indicating that it lies in the vicinity of the boundary. Since the tendency to structural instability is related to the decreasing ionic radius of the rare earths, the T' structure for the heavier $R_2\mathrm{CuO}_4$ compounds is maintained only in its distorted form, which also presents signatures of weak ferromagnetism.[6,20,21] For $\mathrm{Gd}_{1.85}\mathrm{Ce}_{0.15}\mathrm{CuO}_4$, the magnetic anomalies survive at T_N(Cu)~150–180 K and $T_m \sim 9$–14 K.[7,12] This can be explained by the fact that the doping of electrons with Ce^{4+}, indeed, depresses the T_N and T_m, while the doping of the smaller Ce^{4+} ion (compared to Gd^{3+}) pushes the system toward the distorted structure side. Thus, superconductivity and weak ferromagnetism seem to be mutually exclusive in these T'-structure materials. It is emphasized that the weak ferromagnetism in $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ should definitely not relate to rare-earth magnetism, since Eu and Y carry no moment. Therefore, the magnetic behavior of $\mathrm{Gd}_2\mathrm{CuO}_4$ is not unique to gadolinium but must be dominated by the copper magnetism that depends sensitively on the average Cu-Cu and/or Cu-R spacing.

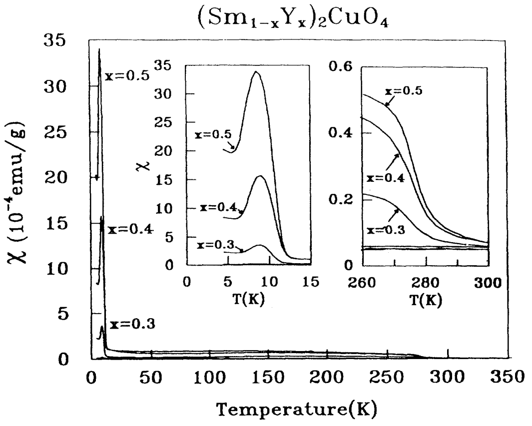

FIG. 3. Temperature dependence of the magnetic susceptibility for $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ with $x=0$, 0.1, 0.2, 0.3, 0.4, and 0.5. Magnetic field 100 Oe was applied to all samples. Insets show the magnetic anomalies in the temperature ranges of 5–15 K and 260–300 K.

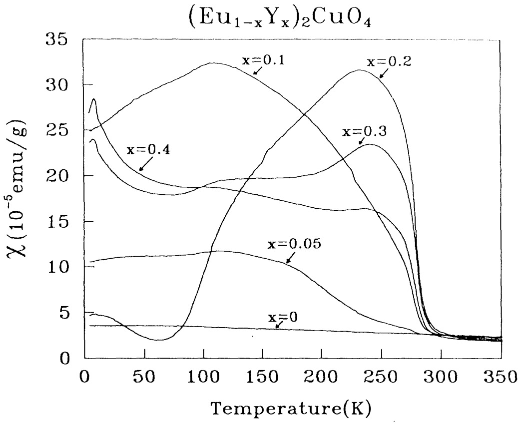

FIG. 4. Temperature dependence of magnetic susceptibility for $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ with $x=0$, 0.05, 0.1, 0.2, 0.3, and 0.4. Magnetic field 100 Oe was applied at all samples.

In summary, the structure and magnetic susceptibility of $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, and $\mathrm{Gd}_2\mathrm{CuO}_4$ are investigated. The solubility limits are $x \sim 0.4$ and ~0.3 for $(\mathrm{Sm}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$ and $(\mathrm{Eu}_{1-x}\mathrm{Y}_x)_2\mathrm{CuO}_4$, respectively. The magnetic anomalies occurred at T_N(Cu)~285 K and $T_m \sim 20$ K in $\mathrm{Gd}_2\mathrm{CuO}_4$, which are not observed in $\mathrm{Sm}_2\mathrm{CuO}_4$ and $\mathrm{Eu}_2\mathrm{CuO}_4$, can be clearly produced by substituting the nonmagnetic ion Y for either Sm or Eu. These magnetic anomalies are thought to be associated with a weak ferromagnetism, which is due to a local structural distortion in the Cu-O planes resulting from the too small rare-earth ions in the T' structure. The boundary for weak ferromagnetism in $(Sm_{1-x}Y_x)_2CuO_4$ and $(Eu_{1-x}Y_x)_2CuO_4$ lies at $x \sim 0.3$ and ~ 0.05, respectively. The corresponding lattice parameter $a = 3.901$ Å is consistent with that observed in the reported $(R_{1-x}Gd_x)_2CuO_4$ (R =Nd, Sm, and Eu) and $Eu_{2-x}Tb_xCuO_4$ systems. Thus, the effect of the small ionic radius for Gd plays a much more important role than its large moment on the anomalous magnetic properties of Gd_2CuO_4. Furthermore, it may be speculated that the absence of superconductivity in $Gd_{1.85}Ce_{0.15}CuO_4$ is due to the mutual exclusion between superconductivity and weak ferromagnetism in this material.

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