Susceptibility of $Y_2Cu_2O_5H_x$

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Temperature dependence of the real and imaginary part of the ac susceptibility was measured for polycrystalline $Y_2Cu_2O_5H_x$ for $x=0$, 0.34, 0.72, 1.52, and 1.88. It was found that the effective magnetic moment of the copper ions decreases with increasing hydrogen content. Also, the height of the maximum at 13 K associated with the antiferromagnetic transition of Cu ions decreases while its position shifts slightly toward higher temperatures. Another maximum at about 5.8 K disappears almost completely for hydrogen content of $x=1.52$. A steady magnetic field also reduces the height of the lower temperature maximum, shifting it negligibly. For an external magnetic field above 200 Oe, this maximum disappears completely.

I. INTRODUCTION

The discovery of the magnetic ordering in $Y_2Cu_2O_5$[1] and in other member of the $R_2Cu_2O_5$ (R=rare earth) family[2] has stimulated considerable interest in the measurement of their other properties.[3,4] In our previous paper on AC-susceptibility measurements of $Y_2Cu_2O_5$ (Ref. 5), we confirmed the antiferromagnetic transition at about 13 K and reported the discovery of a zero-field magnetic transition in this compound at about 5.8 K. The appearance of the magnetic transition in this region was supported by muon-spin-relaxation experiments.[6] The height of the low-temperature susceptibility maximum is very field dependent and for the steady magnetic field of about 500 Oe, it disappears completely.

In this paper we present ac-susceptibility measurements on hydrogen-doped $Y_2Cu_2O_5$ material and discuss the magnetic interactions of the copper subsystem in an ordered state of that compound.

$Y_2Cu_2O_5$ crystallizes in the orthorhombic $Ho_2Cu_2O_5$-type structure (space group $Pna2_1$) with Cu coordination 4+1, typical for Cu^{2+}. The schematic representation of the structure is presented in Fig. 1, and has been analyzed in detail in Ref. 7. There are two nonequivalent Cu and Y positions. The copper-oxygen pyramids, CuO_5, are joined by the common edges into $Cu(1)Cu(2)O_8$ dimers, which form zigzagging chains along the a axis. These chains are linked, forming goffered ab planes. The distances between Cu ions in the neighboring planes are considerably larger than the ones along the chains.

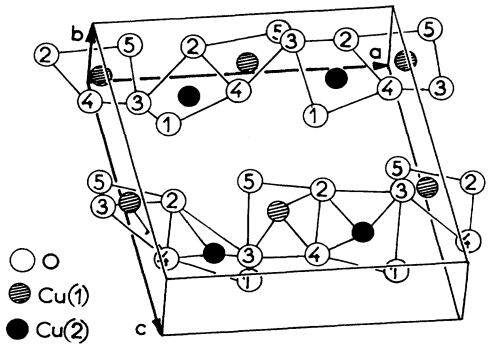

FIG. 1. Schematic representation of the $Ho_2Cu_2O_5$-type structure with marked positions of copper and oxygen only.

II. EXPERIMENT

Polycrystalline samples of $Y_2Cu_2O_5$ were prepared by mixing proper amounts of Y_2O_3 and CuO powders and firing them at 850 °C for 24 h, then at 950 °C for 24 h and finally at 1050 °C for 3 days with intermittent grinding and pressing. These single phased, orthorhombic samples were hydrogenated by standard techniques. Absorption reaction was performed at a constant temperature of 150 °C under hydrogen gas pressure of 500 mm Hg. Hydrogen concentrations were determined volumetrically by monitoring the pressure change in a calibrated, sealed volume. A series of samples with wide hydrogen concentrations from $x=0.34$ to 1.88 were synthesized. X-ray analysis proved all samples were single phased (except that of $x=1.88$).

ac magnetic-susceptibility measurements were performed on a Lake Shore model 7000 ac susceptometer. The magnetic susceptibility was measured in the temperature range of 4.2 to 320 K for a magnetic-field amplitude of 10 G and a frequency of 111.1 Hz.

III. RESULTS

Lattice-constant values together with the unit-cell volumes are presented in Table I for undoped and hydrogenated samples. Their dependence on the hydrogen content is depicted in Fig. 2. In most hydrogenated metals all lattice parameters increase with hydrogen content, which indicates that hydrogen atoms occupy essentially empty interstitial sites. In our case, for small hydrogen content (x below about 0.5) there is an increase of the a and b lattice constants while c is decreasing. It probably means that (a) the angles between dimers and between the tetraeders in dimers (angles between Cu-O-Cu and Cu-O_2-Cu) are changed; (b) the distances between the chains shortened while the ones between the planes lengthened.

TABLE I. Lattice constants, Curie-Weiss temperature, and effective magnetic-moment dependence on hydrogen index in $Y_2Cu_2O_5H_x$.

Hydrogen index	a (nm)	b (nm)	c (nm)	V (nm^3)	θ (K)	μ_{eff} (μ_B)
0	1.07740	0.34899	1.24590	0.46846	21	2.2
0.34	1.08006	0.34941	1.24405	0.46949	18	2.2
0.72	1.07845	0.34891	1.24360	0.46794	12	1.9
1.52	1.07848	0.34801	1.25005	0.46917	8.5	1.7

For higher hydrogen content (x above about 0.5) probably Cu-O chains become more separated and Cu-O planes come closer. The reason for such behavior (as suggested in Refs. 8 and 9 for 1-2-3-type compounds) may be connected with the fact that up to the content of about $x=0.5$, hydrogen atoms are incorporated into the lattice forming solid solution. For higher amounts of hydrogen, its atoms are positioned in interstitials, which in our opinion, are probably between the yttrium planes. In hydrogen-rich samples it may cause partial amorphization. For hydrogen content equal to $x=1.88$, no diffraction peaks are visible in the x-ray pattern.

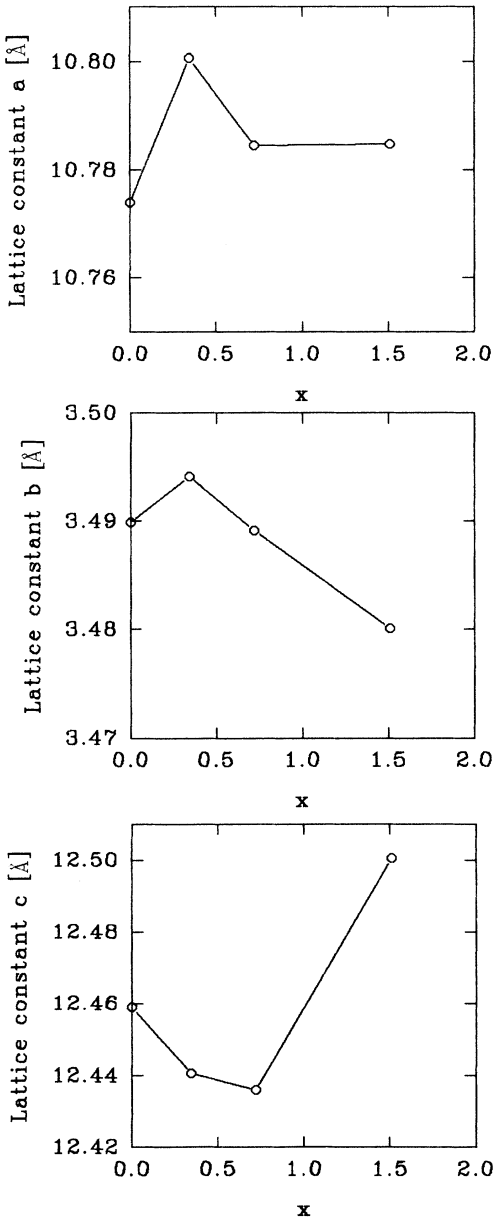

FIG. 2. Lattice-constant dependence on hydrogen content in $Y_2Cu_2O_5H_x$.

The results of the susceptibility measurements for zero steady magnetic field for samples with different amounts of hydrogen are presented in Fig. 3 for the real X' (in-phase) susceptibility component.

The temperature dependence of this component is similar to that obtained previously for undoped $Y_2Cu_2O_5$ with the exception of the curve for hydrogen content equal to $x=1.88$, for which it is almost zero and not temperature dependent. All other curves obey Curie-Weiss law (above about 100 K) with a paramagnetic Curie temperature of $\theta=21$ K for an undoped sample, $\theta=18$ K for the samples with $x=0.34$, $\theta=12$ K for the sample with $x=0.72$, and $\theta=8.5$ K for the sample with $x=1.52$. The resulting effective magnetic Cu moment is equal to $2.2\mu_B$ for undoped and lower hydrogenated samples, $1.9\mu_B$ for a sample with $x=0.72$, and $1.7\mu_B$ for the sample with $x=1.52$.

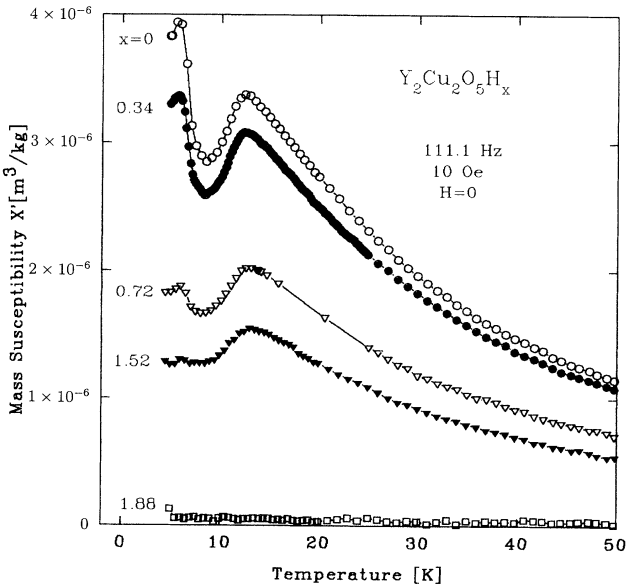

FIG. 3. Temperature dependence of the real part of ac susceptibility for $Y_2Cu_2O_5H_x$ for different hydrogen content in zero external magnetic field.

With increasing hydrogen content, susceptibility of the samples becomes smaller, but the temperature for which both maxima occur are the same within 1 K. The height of the maximum at about 13 K decreases with susceptibility decrease while low-temperature maximum decreases much more quickly, and for hydrogen content $x = 1.52$, is only slightly marked.

Field dependence of the susceptibility in the range of both maxima occurences is presented in Fig. 4 for the sample with hydrogen content $x = 0.34$. A strong effect of the magnetic field is seen only on the low-temperature maximum, while on a high-temperature maximum an effect is hardly visible. A steady magnetic field above about 100 Oe is enough for the low-temperature maximum to disappear. Similar results were obtained also for the sample with a hydrogen index equal to $x = 0.72$. Both increasing hydrogen content and magnetic field influence only the low-temperature maximum.

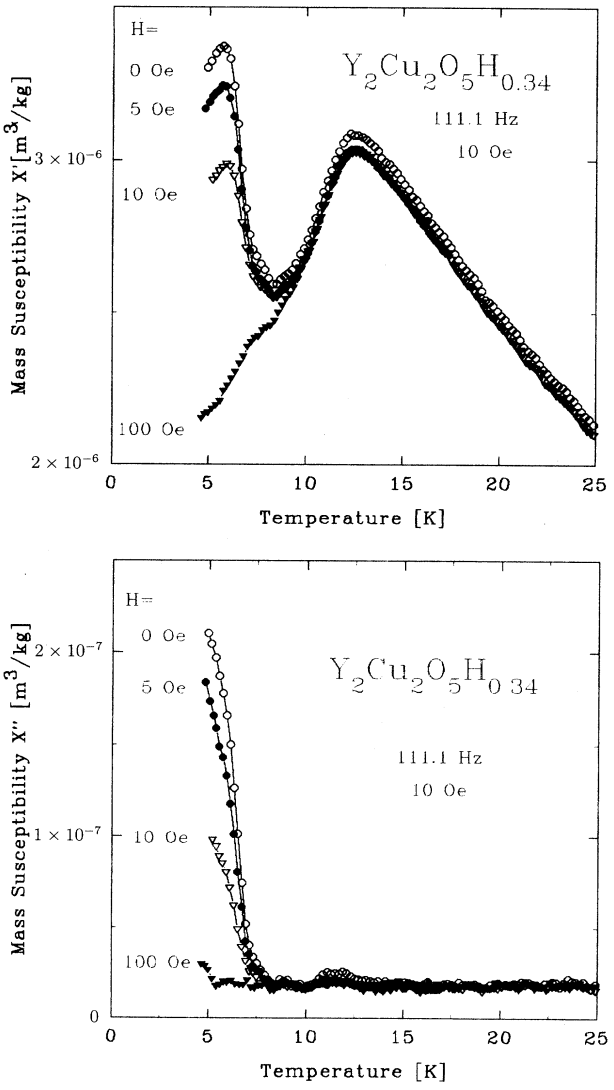

FIG. 4. Temperature dependence of real X' and imaginary X'' components of ac susceptibility for $Y_2Cu_2O_5H_{0.34}$ for different external magnetic fields in the anomaly region.

It should be added that for the temperature for which the minimum of the real component of susceptibility occurs, the imaginary susceptibility component starts to increase[5] (for all samples). Its magnitude is independent of the frequency used. It suggests some kind of hystertic behavior of the material and is connected with the energy-loss existence. It decreases with decreasing low-temperature maximum height and disappears together with it.

IV. DISCUSSION

There are few papers dealing with the magnetic structure of $Y_2Cu_2O_5$.[10–14] According to Sreedhar and Ganguly,[11] copper ions in dimers are coupled ferromagnetically, but at low temperatures these dimers are coupled antiferromagnetically. Different magnetic structures are proposed by Aride *et al.*,[12] Plakhti *et al.*,[13] and Golosovskii *et al.*[14] All of them claim, however, that copper ions are in-plane ferromagnetically ordered with antiferromagnetically ordered neighboring planes. From the paper of Ramakrishna, Ong, and Iqbal[10] it results that short-range ferromagnetic-type interactions along the chains may still survive in the region of higher temperatures, where susceptibility behaves according to Curie-Weiss law.

Our results for nonhydrogenated $Y_2Cu_2O_5$, concerning positive paramagnetic Curie temperatures and effective magnetic-moment values equal to $\mu_{\text{eff}} = 2.2\mu_B$, higher than the free-ion one, both confirm Ramakrishna's conclusions.

Gradual diminishing of the susceptibility and effective magnetic-moment values to the one expected for the free Cu^{2+} ion ($\mu = 1.73\mu_B$), indicate clearly that growing concentration of hydrogen suppresses short-range ferromagnetic-type interactions present at higher temperatures ($T > 35$ K) without visible changes of the long-range antiferromagnetic one. We think that the disappearance of the short-range ferromagnetic interactions between Cu ions in the region of higher temperatures is caused by the observed increase of the a lattice constant in hydrogen-doped samples. The increase of the a lattice constant induces an increase of the exchange Cu-O-Cu angle values along the chains. In such a way, the strength of ferromagnetic exchange constants between the two nonequivalent coppers within dimers are diminished and thereby no longer can determine the magnetic behavior of the compound at higher temperatures. The fact, as one can see from Fig. 3, also explains the behavior of the low-temperature maximum at 5.8 K. This maximum gradually vanishes and finally completely disappears for exactly the same hydrogen content ($x = 1.52$) for which magnetic Cu moments do not exhibit any evidence of short-range ferromagnetic interactions.

The nature of the low-temperature anomaly on susceptibility temperature dependence and its magnetic-field dependence is not yet clear. Our data proved that the mechanism determining the existence of this anomaly is probably connected with some peculiarities of ferromagnetic interactions within Cu-O-Cu chains. We believe that the so-called alternating intrachain ferromagnetic

model (see Ramakrishna[10]) can explain the origin and behavior of this anomaly. In this model the nonuniform intrachain ferromagnetic interaction is assumed. According to this, the magnetic coupling $J_F^{(1)}$ between two bridged copper ions Cu(1) and Cu(2) via O(2) and O(4) ions, while $J_F^{(2)}$ connects Cu(2) and $Cu(1)^i$ through the oxygen atoms $O(3)^i$ only. If the relation $J_F^{(1)} > J_F^{(2)}$ is fulfilled [which seems to be very probable, as Cu(1)-O(2)-Cu(2) and Cu(1)-O(4)-Cu(2) bands have dominantly covalent character, contrary to $Cu(1)^i$-$O(3)^i$ ones], we will expect two separate anomalies on the susceptibility temperature dependence. One of these two anomalies, in the form of the first-order transition should appear in the relatively low-temperature range (for $Y_2Cu_2O_5$ it will be at $T=5.8$ K). It should be also very sensitive to the external magnetic field. Magnetic field will make the interactions within the chains more uniform, inducing the transitions from an alternating ferromagnetic state to a uniform ferromagnetic one. When the magnetic-field strength exceeds some critical value, the low-temperature anomaly should no longer be observed.

V. CONCLUSION

We measured ac susceptibility of single-phased, polycrystalline samples of $Y_2Cu_2O_5H_x$, for $x=0, 0.34, 0.72, 1.52$. With increasing hydrogen content the effective magnetic moment of copper ions drives toward the free-ion value. The height of both temperature anomalies on the susceptiblity curve at 5.8 K and at about 13 K diminishes when hydrogen concentration in the samples increases. We believe that the behavior of the low-temperature maximum is strongly determined by the short-range ferromagnetic interactions between the copper ions along the chains, although the idea of some kind of reorientation of the copper magnetic moments cannot be rejected.

ACKNOWLEDGMENTS

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