^{170}Yb Mössbauer study of magnetic ordering in $Yb_2Cu_2O_5$

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Abstract. ^{170}Yb Mössbauer shows that the Yb and Cu moments order at 15 K in $Yb_2Cu_2O_5$ and rule out models of the order that invoke distinct ordering temperatures.

Keywords: Ytterbium, Copper oxides, magnetic order

1. Introduction

$R_2Cu_2O_5$ compounds have recently been the subject of intense study, largely as a result of their relationship to the high-T_c $RBa_2Cu_3O_{7-\delta}$ materials. The blue-phase $R_2Cu_2O_5$ compounds crystallise in the orthorhombic $Pna2_1$ $Ho_2Cu_2O_5$-type structure [1] having two inequivalent rare-earth sites with equal occupancies. Susceptibility [2, 3] and neutron diffraction studies [4] show antiferromagnetic ordering of the Cu^{2+} moments accompanied by a more complex ordering of the rare-earth ion moments.

$Yb_2Cu_2O_5$ exhibits unusual magnetic behaviour. Susceptibility [2] shows two features, and heat capacity [5] yields a sharp peak well below the $\lambda-$type anomaly associated with the ordering of the Cu^{2+} ions. These results led to the suggestion of two independent orderings, with the copper ordering at 15 K and the ytterbium ordering independently at 8 K. In addition, two distinct models for the magnetic structure of $Yb_2Cu_2O_5$ have been proposed on the basis of neutron powder diffraction data. The first [4] attributes the upper transition to ordering of the copper moments, with the ytterbium moments ordering via a first-order process at the lower transition. By contrast, the other study [6] found no evidence for magnetic scattering until the lower transition was reached, and it was argued that the two magnetic species order together at the lower event.

Given the divergent views concerning magnetic order in $Yb_2Cu_2O_5$, it is clear that a direct study of the ytterbium moments in this system is needed. We present here a ^{170}Yb Mössbauer study of $Yb_2Cu_2O_5$ at temperatures from 2 K to 18 K.

2. Experimental methods

The sample was prepared by co-grinding stoichiometric amounts of Yb_2O_3 (99.9%) and CuO (99.9999%). The mixture was then pressed into a pellet and fired in air at 950°C for 24 hours. The pellet was then re-ground, pressed and re-fired for a further three days. Cu–K_α x-ray diffraction confirmed that the blue/green sample had the expected structure and no unreacted reagents were detected. ac susceptibility measurements showed the two features expected for this material [2] at 15 K and 8 K.

The 15 mCi ^{170}Yb Mössbauer source was prepared by neutron activation of a 10 wt.% Tm in Al alloy. Both source and absorber were cooled in a conventional helium-flow cryostat. Velocity calibration was achieved using a ^{57}Co source mounted on the back of the drive, with an $\alpha-$Fe foil as a standard. All of the spectra were fitted using a non-linear least-squares minimisation routine. Line positions and intensities were derived from an exact solution to the full Hamiltonian combining magnetic and electrostatic contributions.

3. Results and Discussion

While there are two inequivalent Yb sites in the $Yb_2Cu_2O_5$ structure, at 18 K (above both ordering temperatures) the ^{170}Yb Mössbauer spectrum consists of a single, quadrupole-split triplet (Fig. 1). Similar behaviour was observed in $Tm_2Cu_2O_5$, where only a single component was observed by ^{169}Tm Mössbauer spectroscopy [7]. The pattern is fully consistent with Yb^{3+} and could be fitted with eQV_{zz}=–11.2(1) mm/s and an asymmetry parameter (η) of 0.64(3). Point charge calculations yield η=0.97 and 0.62 for the two Yb sites, while perturbed angular correlation (PAC) measurements [8] found η ~0.82. We find no evidence for the presence of a divalent ytterbium contribution to the spectrum, contrary to the suggestion that non Curie-Weiss behaviour of the susceptibility may be due to Yb^{2+} in this material [2].

A substantial magnetic splitting develops immediately on cooling through the transition at 15 K, and the field grows steadily as T→0 K. At 13 K, the average hyperfine field is already 50 Tesla, and by 2 K it

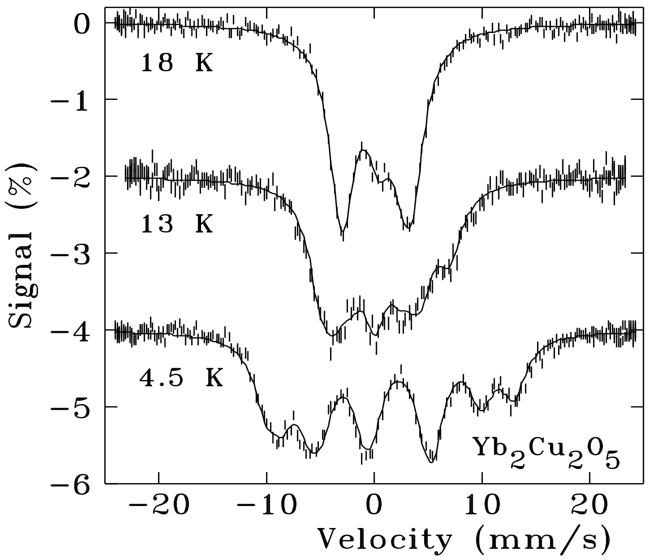

Figure 1. ^{170}Yb Mössbauer spectra of $Yb_2Cu_2O_5$. From top to bottom: 18 K, above the ordering temperature, showing a single paramagnetic triplet. 13 K, in the ordered state showing that the Yb is indeed magnetically ordered at this temperature. 4.5 K, showing two magnetically split quintets corresponding to the two crystallographically inequivalent Yb sites.

has reached 135 Tesla. While this field is below the 413 Tesla expected for a free-ion Yb^{3+} moment of 4 μ_B, it is far too large to simply be the result of transferred fields from the Cu^{2+} moments. Furthermore, the observed field is consistent with the reduced Yb-moments deduced from neutron scattering (1.4 μ_B [4] and 1.15 μ_B [6]) as simple scaling of the field suggests an average Yb moment of $\sim$1.3 μ_B. Our results thus show that the Yb moments order at the 15 K event and allow us to rule out any model of the magnetic structure that requires separate ordering of the Yb and Cu moments. Furthermore, it is clear that the onset of magnetic order occurs at the upper event, and is not delayed until the feature at 8 K.

Analysis of the data obtained at 4.5 K reveals further insight into the ordering. Unlike the ^{169}Tm spectrum of $Tm_2Cu_2O_5$ [7] where only a single component was observed both above and below the ordering temperature, we clearly see two magnetic quintets of equal area in the spectrum, consistent with the two crystallographically inequivalent Yb sites in the structure. The angle (θ) between the hyperfine field and the principal axis of the electric field gradient was observed to be close to 90° at both sites and at all temperatures, however the low point symmetry (1) at the Yb sites precludes identification of the principal axis of the electric field gradient with a particular crystal axis. The Yb sites exhibit distinct hyperfine fields (147(2) T and 119(2) T) and also different values for η (see below).

The spectral changes at 8 K are quite limited, and clearly do not reflect a major re-organisation of the magnetic order. The hyperfine field at the lower field site increases by $\sim$30 T while that at the higher field site shows at most a $\sim$10 T step. More significantly, η drops to zero at the higher field site on cooling through 8 K (the other site shows no change). As η is determined solely by electrostatic effects, it is not affected by the magnetic order. Since therefore, no magnetic structure change could cause the observed drop in η, we are led to the conclusion that the feature at 8 K is associated primarily with a distortion of the crystal structure, and that the magnetic effects may only be secondary.

4. Conclusions

^{170}Yb Mössbauer spectroscopy of $Yb_2Cu_2O_5$ shows that magnetic order is established at the Yb sites at 15 K and provides no evidence to support models invoking separate Cu and Yb ordering events. Changes observed at 8 K are more consistent with a distortion of the crystal structure than a major change in the magnetic order.

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References

1. H.-R. Freund and Hk. Müller-Buschbaum, *Z. Naturforsch.*, **32b** (1977), 609.
2. R. Tróc, J. Klamut, Z. Bukowski, R. Horyn and J. Stepién-Damm, *Physica B* , **228-231** (1997), 895.
3. Z.A. Kazei, N.P. Kolmakova, R.Z. Levitin, B.V. Mill, V.V. Moshchalkov, V.N. Orlov, V.V. Snegriev and Ja. Zoubkova, *J. Magn. Magn. Mater.*, **86** (1990), 124.
4. J.L. García-Muñoz, X. Obradors and J. Rodríguez-Carvajal, *Phys. Rev.*, **B51** (1995), 6594.
5. V.V. Moshchalkov, N.A. Samarin, I.O. Grishchenko, B.V. Mill and Y. Zoubkova, *J. Magn. Magn. Mater.*, **90 & 91** (1990), 533.
6. A. Murasik, P. Fischer, H. Rundlöf, R. Tellgren and R. Tróc, *Mater. Sci. Forum* , **228-231** (1996), 895.
7. G.A. Stewart and J.M. Cadogan, *J. Magn. Magn. Mater.*, **118** (1993), 322.
8. A. Bartos, M. Uhrmacher, L. Ziegler and K.P. Lieb, *J. Alloys and Comp.*, **179** (1992), 307.