^{57}Fe emission Mössbauer spectroscopy study of single-crystal La_2CuO_{4-y}

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Abstract. Emission Mössbauer studies using a ^{57}Co-doped single crystal of La_2CuO_{4-y} are reported. Measurements have been made at 78 K and at 295 K for different source orientations. Measurements made in the paramagnetic regime (295 K) show that the sign of the electric field gradient (EFG) is positive and that the magnitude of the quadrupole splitting is 1.76 mm s^{-1}. It is also found that the EFG forms an angle of 39° with respect to the crystalline c axis. Measurements made in the antiferromagnetic regime (78 K) show a Fe hyperfine field of 460 kOe which lies in the basal plane of the crystal structure. These measurements also show an EFG which is positive and in a direction which is consistent with that found in the room temperature measurements. In addition, the magnitude of the quadrupole splitting is consistent with that obtained from the 295 K spectra.

1. Introduction

Semiconducting L_2CuO_{4-y} is a layered orthorhombic perovskite with a slightly deformed K_2NiF_4 structure (space group *Cmca*) and lattice parameters $a = 5.365$ Å, $b = 5.411$ Å and $C = 13.028$ Å. This compound has been shown by neutron diffraction studies [1, 2] to order antiferromagnetically. In the ordered regime, copper moments of $0.43 \pm 0.13\ \mu_B$ are aligned along the [001] orthorhombic axis. The Néel temperature, T_N, is found to be highly sensitive to oxygen content ranging from $T_N \sim 0$ for $y = 0$ to about 220 K for $y = 0.03$. In some samples, values of T_N as high as 330 K have been reported [3].

The hyperfine magnetic properties of La_2CuO_{4-y} have been studied using a variety of techniques. NMR studies [4] have shown that ^{63}Cu and ^{65}Cu 'see' a hyperfine magnetic field of 78.78 kOe perpendicular to the electric field gradient (EFG) which is itself at an angle of about 11° with respect to the orthorhombic c axis.

^{57}Fe Mössbauer-effect studies by Nishihara *et al* [5] on $La_2Cu_{1-x}{}^{57}Fe_xO_{4-y}$ have shown magnetic order below 220 K. At 77 K they observed a hyperfine field at ^{57}Fe, which occupies the Cu sites of 395 kOe perpendicular to the c axis. At room temperature they observed a quadrupole-split doublet where the quadrupole splitting is $\Delta = 1.558$ mm s^{-1} and the isomer shift relative to αFe is $\delta = -0.305$ mm s^{-1}. Although these

authors did not explicitly measure the direction of the EFG they assumed it to be parallel to the c axis.

Jha *et al* [6] used ^{57}Fe emission Mössbauer spectroscopy on ^{57}Co-doped La_2CuO_{4-y} to show that $\Delta = 1.76$ mms^{-1} at room temperature. At 4.2 K these authors found an Fe hyperfine field of 494 kOe which was oriented at about 90° with respect to the EFG. They also assumed the EFG to lie parallel to the c axis and the hyperfine field to lie in the basal plane.

Further ^{57}Fe Mössbauer studies by Imbert *et al* [7] and Tang *et al* [8] gave values for the hyperfine field at 4.2 K of 475 kOe and 488 kOe, respectively. Once more they assumed that the EFG was parallel to the c axis. Since ^{57}Co- and ^{57}Fe-doped samples each yielded the same value of the hyperfine field, one may assume, as did Imbert *et al* [7], that both probes occupy the same site. As the Mössbauer line widths in such studies are not substantially greater than the natural line width, it is also reasonable to assume that the probes occupy only a single class of crystallographic site.

Thus, until about a year ago, the evidence accumulated on the basis of hyperfine interaction studies on La_2CuO_{4-y} suggested that below the Néel temperature, an Fe hyperfine field existed with a magnitude of about 490 kOe and that this field was more or less perpendicular to the c axis. There also seemed to be some evidence that the EFG was oriented at about 90° with respect to the hyperfine field and there was a general feeling that the EFG was parallel to the c axis. Recently however, work by Imbert and Jehanno [9] and de Reotier *et al* [10] on aligned crystallites of ^{57}Fe-doped $La_{2-x}Sr_xCuO_{4-y}$ ($0 < x < 0.35$) has shown that the EFG is tilted at 43° with respect to the c axis and that the Fe hyperfine field is inclined at 80° with respect to the c axis.

The purpose of the present paper is to resolve the outstanding questions concerning the orientation of the hyperfine field and the EFG in the antiferromagnetic state of La_2CuO_{4-y}. To this end we present the results of an emission Mössbauer effect study of a ^{57}Co-doped La_2CuO_{4-y} single crystal at 78 K and 295 K, which not only supports, but also adds to, these earlier results. The principal new feature of the present measurements is the very low concentration (ppm) of the dopant.

2. Experimental methods

A $3 \times 3 \times 1$ mm single crystal of La_2CuO_{4-y} with the c axis along the short crystal dimension was grown from PbO- and CuO-based fluxes. This crystal was characterized using x-ray-diffraction and magnetic-susceptibility measurements. Results of the latter have been presented by Cheong *et al* [3]. A drop of 0.05 M HCl solution of carrier-free ^{57}Co as cobalt chloride was deposited on one crystal face in the basal plane. The activity was diffused by prolonged cooking in the alumina crucible in a helium atmosphere at temperatures ranging from 500 °C to 850 °C. This sample was used as the Mössbauer source. Potassium ferrocyanide with 0.3 mg cm^{-2} enriched ^{57}Fe or ^{57}Fe-enriched stainless steel served as the Mössbauer absorber. Measurements were made with the source held at either room temperature (295 K) or at liquid nitrogen temperature (78 K). In all cases the absorber was held at room temperature. A conventional constant acceleration Mössbauer spectrometer was used to move the absorber.

The direction of the EFG was determined from Mössbauer measurements taken at room temperature (above the Néel temperature). In this temperature regime the Mössbauer spectrum consists of an asymmetric doublet. The orientation of the EFG is established on the basis of the relative intensity of the two spectral lines. The angular

dependence of the relative line intensities was confirmed by recording spectra for varying angles between the gamma-ray and the crystalline c axis.

The orientation of the hyperfine field was determined from spectra obtained at 78 K (below Néel temperature) both with the gamma-ray direction parallel to and perpendicular to the c axis.

3. Results and discussion

Room-temperature Mössbauer spectra obtained for La_2CuO_{4-y} for different angles between the gamma-ray direction and the c axis of the crystal are illustrated in figure 1. Spectra as shown in the figure display three resolvable lines. We believe that the two outer lines constitute a quadrupole-split doublet due to ^{57}Fe that resides at the Cu sites in the La_2CuO_{4-y} structure and that the central peak is due to undiffused ^{57}Co on the surface of the source. As evidence for this interpretation we have observed that the intensity of the central peak relative to the outer peaks decreases with larger cooking times but that the relative intensity of the two outer peaks themselves does not change. Detailed analysis of the spectra as described below is also consistent with this interpretation. We have therefore fitted these spectra to an asymmetric doublet with lines constrained to be of the same width and to a singlet with unconstrained width. If β is the angle between the gamma-rays and the EFG then the ratio of the line intensities, I, for the quadrupole doublet is given as [11]

$$I(\pm\tfrac{3}{2}\rightarrow\pm\tfrac{1}{2})/I(\pm\tfrac{1}{2}\rightarrow\pm\tfrac{1}{2}) = 3(1 + \cos^2\beta)/(2 + 3\sin^2\beta) \tag{1}$$

when the asymmetry defined in terms of the components of the EFG, V_{ii}, as

$$\eta = (V_{xx} - V_{yy})/V_{zz}. \tag{2}$$

Since the source used in this study was relatively weak (because of the difficulty in diffusing activity into the single crystal), it was not feasible to perform a detailed study of relative line intensities as a function of angle. For this reason, a precise value of η could not be extracted and, for simplicity, we have assumed that this asymmetry parameter is identically zero. In the spectrum shown in figure 1(b), the line intensity ratio of equation (1) is found to be 1.5 ± 0.2. This gives an angle of $\beta = 39° \pm 10°$ with the sign of the EFG being positive. This follows with the more intense and negative velocity component of the doublet corresponding to the $\pm\tfrac{3}{2}\rightarrow\pm\tfrac{1}{2}$ transition. Spectra shown in figure 1(a) and (c) demonstrate that the spectral asymmetry does in fact result from the angular relationship between the c axis and the gamma ray. The line widths observed for the quadrupole component of the spectrum are found to be consistent with the expected intrinsic line width of the system based on the effective thickness of the absorber. This shows that there is negligible source broadening and suggests that our interpretation of the spectrum as consisting of an asymmetric doublet and a singlet (rather than, e.g., two overlapping doublets) is correct. Other consistency is also observed: constraining the line width of the doublet to any reasonable value and/or letting the line width of the singlet be unconstrained does not measurably affect the resulting intensity rates for the doublet.

Mössbauer spectra were recorded with the ^{57}Co-doped single-crystal La_2CuO_{4-y} source immersed in a bath of liquid nitrogen. Figure 2(a) shows the spectrum recorded when the gamma rays travel parallel to the c axis, and figure 2(b) shows the spectrum recorded when the gamma rays travel in the basal plane, i.e., perpendicular to the c axis.
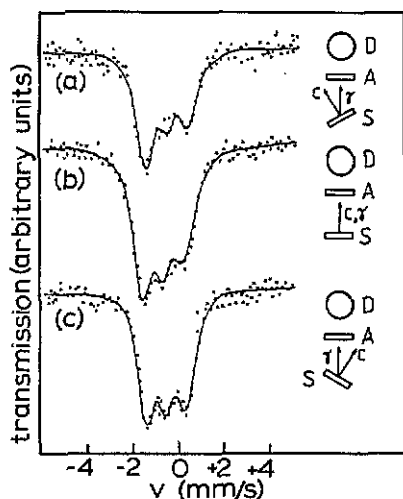
Figure 1. Room-temperature emission Mössbauer-effect spectra of ^{57}Co-doped La$_2$CuO$_{4-y}$, for different source orientations. The experimental geometry is illustrated for each spectrum.
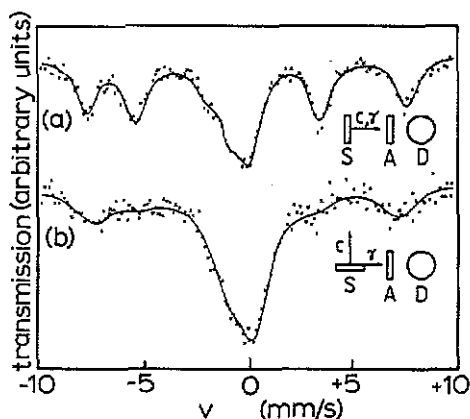
Figure 2. Mössbauer-effect spectra for ^{57}Co-doped La$_2$CuO$_{4-y}$, obtained at 78 K for different geometries as shown: (a) gamma ray parallel to the c axis, and (b) gamma ray perpendicular to the c axis.

The spectrum in figure 2(a) shows a sextet with an additional component near the centre. It is likely that the feature near the centre of the spectrum results from undiffused ^{57}Co activity on the surface of the source and that this spectral component is related to the additional singlet seen at room temperature. Although the relative intensity of the central component of the spectrum could be reduced by prolonged cooking of the sample, the latter also resulted in the general overall loss of activity. Thus the present sample is, we believe, the best compromise between the desire to eliminate the undissolved component and the need to retain sufficient radioactivity to perform the experiment. Since the magnetic splitting is seen to be much larger than the quadrupole splitting, it is appropriate to deal with the quadrupole interaction as a perturbation to the Zeeman Hamiltonian. We have, therefore, fit the spectrum of figure 2(a) to a sextet in which the line widths are all constrained to be equal and an additional singlet of unconstrained line width near the centre. Since the information of relevance to the present discussion is contained in lines 1, 2, 5 and 6 of the sextet, the details of the parameters extracted from the central portion of the spectrum or of the physical model used in describing this portion of the spectrum will not influence the following discussion.

From the spacing of the outer lines (lines 1 and 6), the Fe hyperfine field at 78 K can be determined to be 460 kOe. This is measurably larger than the value of 395 kOe at 77 K reported from the same geometry by Nishihara *et al* [5]. This discrepancy can readily be attributed to differences in Néel temperature. Nishihara *et al* [5] have reported $T_N = 220$ K, while our sample showed $T_N \simeq 290$ K. These effects are most likely due to differences in oxygen stoichiometry; in Nishihara's sample, this was presumably near 3.97, and for our sample it was near 3.95.

We see in figure 2(a) that the separation between spectral components 1 and 2 less than that between components 5 and 6, and this confirms that the sign of the EFG is positive. If θ is the angle between the EFG and the hyperfine magnetic field, then the

measured value of the difference between the separations of the components in velocity is [12]

$$(E_6 - E_5) - (E_2 - E_1) = (e^2qQ/2)(3\cos^2\theta - 1) = 1.85 \pm 0.2 \text{ mm s}^{-1} \tag{3}$$

where e is the electronic charge and Q is the quadrupole moment of ^{57}Fe and $q = V_{zz}$. The measured quadrupole splitting, $e^2qQ/2$, obtained from the room-temperature measurements is 1.76 ± 0.02 mm s^{-1} from which we calculate an angle $\theta = 34° \pm 3°$. Although there is no reason to expect *a priori* that the quadrupole splitting will be temperature independent, we do expect that any temperature dependence will be weak. Therefore, it is reasonable, as first an approximation, to use the measured room-tempeature quadrupole splitting.

From the spectrum of figure 2(a) we find that the ratio of the intensity of lines 1 and 6 to that of lines 2 and 5 is 0.81 ± 0.04. This ratio is given as [13]

$$I_{1,6}/I_{2,5} = 3(1 + \cos^2\phi)/(4\sin^2\phi) \tag{4}$$

where ϕ is the angle between the gamma-ray direction (in this case the c axis) and the hyperfine magnetic field. The present result yields a value of $\phi = 80° \pm 4°$. This result is corroborated by the spectrum taken with the gamma-ray direction perpendiclar to the c axis (figure 2(b)). Lines 2 and 5 have vanishing intensity indicating that θ is small. Furthermore, it is seen that if the EFG, the hyperfine field and the c axis are all coplanar, then $\beta + \theta = \phi$. The present numerical results $39° \pm 10° + 34° \pm 3° = 73° \pm 13°$ are consistent with the recent ^{57}Fe-doped La$_2$CuO$_{4-y}$ studies [9, 10] which found $\beta = 43°$ and $\phi = 80°$.

It is, perhaps, not surprising that the hyperfine field lies more or less in the basal plane as it is the nearest-neighbour exchange interaction between spins in this plane that is principally responsible for the existence of antiferromagnetic order. The reasons for the orientation of the EFG are not so clear. If the hyperfine field is oriented along (say) the (100) direction, then the angles measured in this work indicate that the EFG would lie along the (102) direction. This direction corresponds to the orientation of a plane containing ferromagnetically coupled Cu moments from adjacent Cu–O planes in the K$_2$NiF$_4$ structure. The reason for such an orientation is, at present, not clear.

In conclusion, we have shown that the Fe hyperfine field in La$_2$CuO$_{4-y}$ in the antiferromagnetic state lies approximately in the basal plane.Furthermore, we have shown that the EFG lies at an angle of about $39°$ with respect to the c axis of the crystal structure, and finally, that the c axis, the hyperfine field and the EFG are approximately coplanar.

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