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Interpretation of Mössbauer spectra of $YBa_2Cu_{3-x}Fe_xO_{7-d}$

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Abstract. We have studied the Mössbauer spectra of $YBa_2Cu_{3-x}Fe_xO_{7-d}$ (11 compositions) and present here the results obtained from quantitative analyses of the paramagnetic and magnetic spectra.

Keywords. Mössbauer spectra; paramagnetic spectra.

1. Introduction

The magnetic splitting of the spectrum of Fe in 123 superconductor at low temperatures has been the subject of intense research for a long time, mainly because its implications to our understanding of superconductivity are important. We have studied these aspects extensively by varying the associated parameters and observing the effects. We present the conclusions arrived at from our measurements done so far.

2. Experimental

We have prepared 11 compositions of $YBa_2Cu_{3-x}Fe_xO_7$ with different x. In addition, we have studied the non-superconducting phase of $YBa_2Cu_{2.94}Fe_{0.06}O_6$ extensively, in the absence of an external field (H_{ext}) as well as in the presence of fields up to 5·5 tesla. We show a few spectra (figures 1–2) which are relevant to the present discussion. The sample preparation has been described elsewhere (Bhargava *et al* 1988; Dormann *et al* 1989).

3. Discussion

The magnetic splitting of a Mössbauer spectrum results when one or both of the following conditions are satisfied: (i) thermal populations of ionic levels are unequal; (ii) spin relaxation rates are comparable to the nuclear precession frequencies.

It has been shown in earlier studies (Bhargava and Zeman 1980) on magnetic oxides which are insulators that spin relaxation frequencies are low whenever Fe is surrounded by dissimilar ions. Thus, in $YBa_2Cu_3O_6$ spin relaxation frequencies (Ω) of Fe ions are expected to be low. In metallic $YBa_2Cu_3O_7$, on the other hand, large Ω of Fe are expected if Fe is free to exchange energy with the carriers of

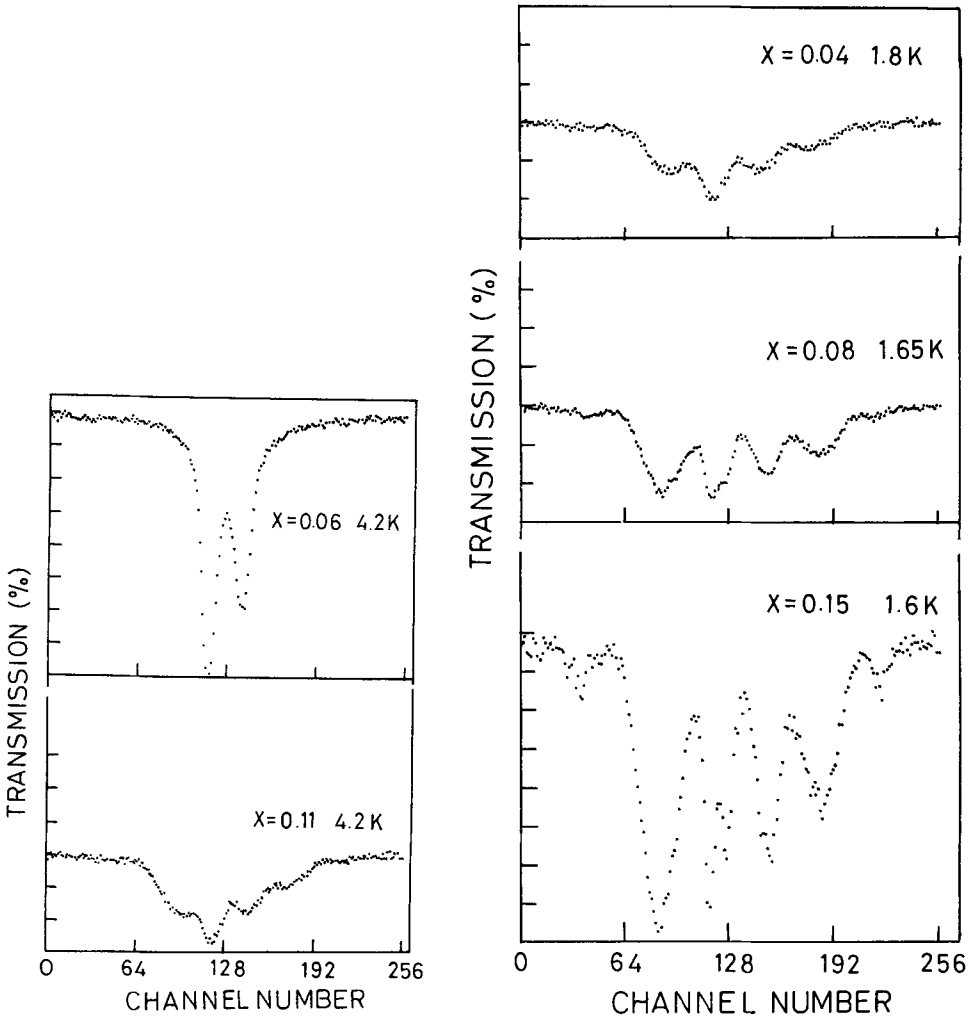

Figure 1. Mössbauer spectra of $YBa_2Cu_{3-x}Fe_xO_7$ showing the characteristics of spin relaxation effects as described in the text.

superconductivity. Experimental spectra provide ample proof of the low spin relaxation frequencies in both, superconducting as well as nonsuperconducting phases:

(i) The change from paramagnetic to magnetically split spectrum occurs through the appearance of an asymmetric doublet.*

(ii) The values of $(P_2-P_5)/(P_3-P_4)$ in the magnetic spectra are different from 3·6773. Here, P_i denotes the position of the ith line. The values are very large when the magnetic splitting just appears and decrease when either the temperature is lowered or the concentration of the magnetic ions is increased.

This happens due to the gradual decrease of the spin relaxation frequencies when either the temperature is lowered or the concentration of the dopant is increased. The spin relaxation is mainly due to Korringa relaxation and spin-spin relaxation

*The asymmetry provide the sign of V_{zz} of the EFG tensor. This is found positive for most of the components.

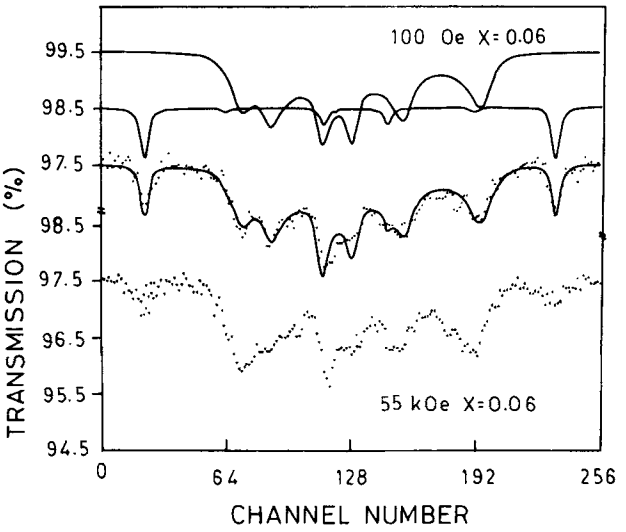

Figure 2. Mössbauer spectra of $YBa_2Cu_{2.94}Fe_{0.06}O_6$ at 4·2 K in the presence of longitudinal fields of 0·01 and 5·5 tesla. The solid lines show the theoretical spectra which fit the experimental spectrum.

processes. In superconductors, the frequency due to the Korringa process can be written as

$$\Omega_K = \Omega_0 \exp(-\delta E/kT),$$

where δE is the superconductivity band gap. Thus, when the temperature alone changes, the factor inside the exponential changes, whereas when the concentration of the magnetic ions at any temperature increases, Ω_0 decreases due to the decrease in the metallic nature of the oxide. This decrease is more than the increase which occurs due to spin-spin relaxation as well as the decrease in the superconductivity band gap, as a result of the increase in the concentration of the magnetic ion. Thus, Ω decreases either by decreasing the temperature or increasing the concentration of the magnetic ions, and we should observe similar changes in the spectral shapes in both cases. This is indeed experimentally found. The spectral shapes are similar when either the temperature is lowered sufficiently, the concentration of the magnetic ions is increased or the metallic nature of the oxide is decreased by lowering the oxygen content. They are characterized by the low values of Ω. The small differences in shapes result from the differences in the relative intensities of the component spectra, which are characterized by differing quadrupole shifts.

In the nonsuperconducting phase, Cu_2 ions are antiferromagnetically ordered in the *ab* plane. The Fe-substituting Cu_2 ions are thus expected to be magnetically coupled to the lattice. On the other hand, Cu_1 ions are in Cu^{1+} state in $YBa_2Cu_3O_6$. Thus, they are not magnetically ordered. Fe at these sites carry magnetic moment but are not expected to be exchanged coupled to the Cu_2 ions also due to the large Cu_2–O distance (2.23 Å) along the *c* axis. Thus, they experience magnetic dipolar fields only which is also expected to be small due to the antiferromagnetic nature of the coupling of the Cu_2 ions. These features are borne out by the experimental spectra. The spectrum of ions exchange coupled to neighbours should necessarily show narrow lines at low temperatures ($T/T_N < 0{\cdot}1$), as is observed for the outermost component spectrum corresponding to the Cu_2 sites. This is because as the relative thermal

population of the lowest non-degenerate level increases to 100%, the relaxation effects are not observable whatever be the value of Ω. On the other hand, the lines in the component spectra of Fe at Cu_1 sites are broad even at 1·5 K. This component is paramagnetic, coexisting with magnetic spectrum of Fe at Cu_2 sites, for a large range of temperature below T_N. Only at low temperatures, magnetic splitting appears, due to lowering of the Korringa relaxation frequency which in the normal state is proportional to the temperature. At lower temperatures, thermal population of ionic levels also become unequal. Both of them favour magnetic splitting at lower temperatures. Only if, $\pm 1/2>$ Kramers doublet is the lowest energy level, the effects of relaxation are not suppressed even at low temperatures. To see this, we obtained spectra of the non-superconducting phase in the presence of external fields of 0·01, 3 and 5·5 tesla. There is no important difference in the zero field spectrum and the spectrum in the field of 0·01 tesla, showing that the ground state in the absence of H_{ext} is not the degenerate $\pm 1/2>$ doublet.

We simulated the shape of the spectrum in field of 0·01 tesla (figure 2). At Cu_2 site the EFG is axial, V_{zz} is positive and along the *c* axis. The spin moments are in the *ab* plane. Thus, the expected quadrupole shift in the magnetic spectrum

$$2\varepsilon = -1/2 \times \delta E_q \times (\text{sign } V_{zz})$$

is very small. Here, δE_q is the splitting of the paramagnetic lines. The observed value of ε is −0·127 which is larger than expected. On the other hand, 80% of the Fe ions occupy the site with axially symmetric EFG, V_{zz} positive and in the *ab* plane. As the dipolar magnetic field experienced by the ion is small in comparison to the crystal field, we expect the *z* axis of EFG tensor to provide the quantization direction for the spin also. Thus,

$$2\varepsilon = \delta E_q.$$

The splitting in the paramagnetic state is equal to 1·9 mm/s. However, the experimental value observed in the magnetic spectra for 2ε is half this value. The reason for this disagreement is not clear. The other relevant parameters of the simulated spectra are summarized below.

Hyperfine fields = 514·6 and 313 kG
Relative intensities of the two component spectra = 12·3:87·7
Relaxation times = 1×10^{-5} and $0{\cdot}46 \times 10^{-7}$ s
$\langle S_z \rangle / \langle S_z \rangle_{sat} = 0{\cdot}95$ and 0·59

As the external field is increased, we see broadening of the lines but no shift in their positions in the outer component spectrum. This indicates an antiferromagnetic lattice or spin glass type of ordering of the Fe ions which is not affected by the external field. Further work is required to understand the complicated magnetic spectra and the implication of the analyses.

References

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