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The magnetic hyperfine interaction in superconducting $\text{YBa}_2(\text{Cu}_{0.90}\text{Fe}_{0.10})_3\text{O}_{7-\delta}$

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Abstract. The temperature dependences of the magnetic hyperfine interactions of three iron species occurring in $\text{YBa}_2(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{7-\delta}$ have been studied by ^{57}Fe Mössbauer spectroscopy. The analysis was performed using the eigenvalues and eigenvectors of the Hamiltonian of the combined electric quadrupole interactions and the magnetic hyperfine interactions for determination of the line positions and intensities. This allows one to derive the electric field gradients with their signs and their directions versus the magnetic hyperfine fields. Evidence is given that the magnetic hyperfine splittings are not due to slow paramagnetic relaxation but are caused by magnetic order probably of a highly anisotropic antiferromagnetic type.

1. Introduction

Iron-doped superconducting $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ compounds have previously been studied using Mössbauer spectroscopy, giving valuable information firstly on the possible locations of the dopant and the symmetry of its surroundings, and secondly on the onset of magnetic order at low temperatures [1-4].

Several iron species mainly at the Cu(1) site could be identified depending on the concentration of iron and also depending on the oxygen content. The hyperfine parameters of these species found at room temperature are listed in table 1. For well oxidized samples in the superconducting state, magnetic hyperfine interactions at Fe have been observed at 4.2 K for Fe concentrations above $x = 0.03$ [3]. The analysis of the complex hyperfine spectra and their changes with temperature is not trivial and an interpretation in terms of magnetic structure and eventual dynamic effects is at present controversial.

In a previous study we have tried to obtain more information in this respect by applying strong external magnetic fields to samples with Fe concentrations ranging between $x = 0.005$ and 0.15 [3]. For low Fe concentrations ($x = 0.015$) the samples are orthorhombic with a high Meissner fraction and $T_C \approx 90$ K. Fe is present in mainly two different oxygen coordinations (A and B). Despite the fact that Fe reveals no magnetic hyperfine interaction in this case down to 2 K, the spectra in an applied field prove the presence of a paramagnetic moment at Fe for all species. For $x = 0.15$ (in the semiconducting tetragonal phase) four different species of Fe (B, C, D and F) were

Table 1. Isomer shifts with respect to iron metal and value of electric quadrupole splittings (Q_S) at 300 K.

Parameter (units)	Value for the following Fe species					
	A	B	C	D	E	F
S (mm s^{-1})	-0.18	0.03	0.19	0.04	0.13	0.30
Q_S (mm s^{-1})	1.56	1.20	0.30	1.98	0.70	0.55

found. The very defined magnetic hyperfine interaction at 4.2 K could not be influenced by the application of an external magnetic field of 5 T. This shows magnetic order with a high anisotropy probably of an antiferromagnetic or spin-glass type.

The ambiguity in the fitting procedure yielding highly correlated parameter sets and also the proposal by other groups [5, 6] that this type of spectra may also be interpreted by relaxation effects led us to perform a further study of the temperature-dependent magnetic hyperfine interaction for several samples with a Fe concentration x of 0.10.

2. Experimental results

Sintered samples with a Fe concentration x of 0.10 were prepared in two different batches in the usual way starting from high-purity oxides [1]. X-ray diffraction showed that the structure was tetragonal, as expected from the high degree of iron doping. The AC susceptibility gave $T_C \approx 30$ K (a decrease of 50%) as shown in [1]. The Meissner fraction was about 50%. This reduction in T_C and the low Meissner fraction reflect the influence of the iron doping.

^{57}Fe Mössbauer spectra were obtained between 1.6 and 300 K using a conventional spectrometer with a sinusoidal velocity sweep. The source was $^{57}\text{Co-Rh}$ kept at room temperature.

Figure 1 shows the ^{57}Fe absorption spectra at several temperatures. The 300 K spectra consist of three quadrupole doublets (B, C and D). Their relative intensities, isomer shifts and quadrupole splittings are given in table 2. The low-temperature spectra reveal magnetic hyperfine interactions for all three Fe species. The full curves in these spectra give the least-squares fits performed under the following assumptions: the isomer shifts, quadrupole splittings and relative intensities were kept fixed to the values found at temperatures above the onset of magnetic hyperfine interactions. The line positions and intensities were determined from the eigenvalues and eigenvectors of the combined Hamiltonian comprising both magnetic and quadrupolar hyperfine contributions allowing for variable angles θ between the magnetic field and electric field gradient and an eventual asymmetry parameter η . The commonly applied perturbational approach for combined magnetic and quadrupole interaction resulting in effective six-line patterns is inappropriate in the present case, in particular close to the magnetic transition since magnetic and quadrupole interaction become comparable in magnitude and also θ is non-zero. Neglecting this fact will inevitably lead to misinterpretations due to erroneously assumed line positions and intensities. A temperature-dependent field distribution (Lorentzian shape) was introduced to account for the line broadenings. The quality of fit of the magnetic spectra could be further improved for batch 1 by adding a paramagnetic

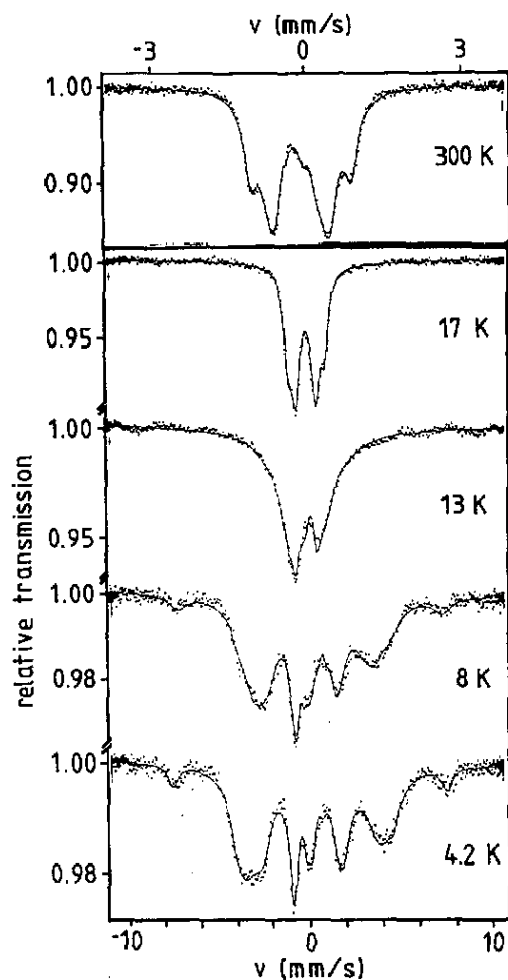


Figure 1. ^{57}Fe Mössbauer absorption spectra of $\text{YBa}(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{7-\delta}$ at various temperatures: —, least-squares fits as described in the text.

Table 2. Isomer shifts (with respect to iron metal at 300 K) and quadrupole splittings (QS) for $\text{YBa}(\text{Cu}_{0.9}\text{Fe}_{0.1})_3\text{O}_{7-\delta}$ at $T \leq 17$ K, θ is the angle between the electric field gradient main axis and the magnetic hyperfine field direction.

Parameter (units)	Values for the following Fe species		
	B	C	D
S (mm s^{-1})	0.09	0.31	0.14
QS (mm s^{-1})	-1.12	-0.28	-2.02
θ (deg)	Variable	0	90
Relative intensity (%)	61	10	29

fraction of species B (i.e. a doublet without magnetic splitting) with a relative weight of 5% of the total amount of species B. For batch 2 this doublet was not observed. Apart from this, all derived parameters are identical for both batches.

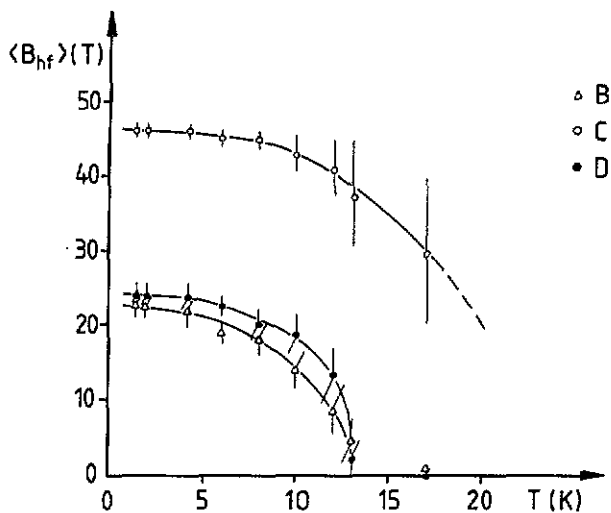


Figure 2. Temperature dependence of the average magnetic hyperfine fields for species B, C and D: the error bars give the widths of the field distributions; —, guides to the eye.

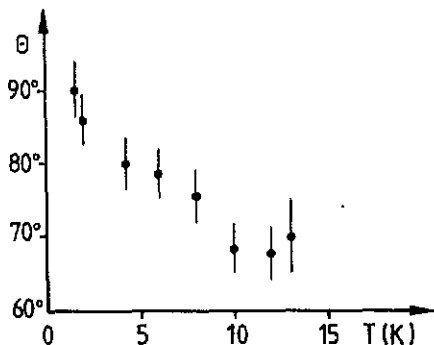


Figure 3. Temperature dependence of angle θ for species B.

The temperature dependences of the mean magnetic hyperfine fields are shown in figure 2. Two of the Fe species (B and D) reveal a magnetic hyperfine interaction below about 13 K. The temperature-dependent magnetic hyperfine interaction for species C extrapolates to an onset above 20 K. The field distribution for species B and D increases with increasing temperature (see figure 2); at 13 K the broadening is already of the same order as the mean field. For species C the broadening is much smaller and temperature independent up to 13 K. At 17 K the magnetic splitting is still finite; yet the spectrum is severely broadened and appears only as a wide background. Its area is fully accounted for by the relative areas determined from the paramagnetic spectra at high temperatures and is also in agreement with the area found at low temperatures.

We have tested the dependence of the fit on θ , the sign of quadrupole interaction and η . The best quality was obtained for the set of parameters given in table 2 together with small η (<0.1). For species B a slightly temperature-dependent angle θ was necessary (figure 3).

3. Discussion

One of the three Fe species (C) reveals a magnetic behaviour different from the other two species: the onset of the magnetic hyperfine interaction started about 10 K higher and at 4.2 K a well defined field is found. The isomer shift and low quadrupole interaction indicate a Fe species with probably sixfold oxygen coordination. Whether this corresponds to a phase different from $Y\text{-Ba-Cu-O:Fe}$ or a precipitate is unclear. The properties of this species will therefore not be discussed in detail in this context. Species B has previously been assigned to Fe in Cu(1) sites with fivefold oxygen coordination. This species is typical for high Fe concentrations in the strongly oxidized state. Species D is characteristic for more oxygen-deficient samples; it is due to Fe in Cu(1) with a lower oxygen coordination.

The almost temperature-independent linewidth in the paramagnetic state may indicate the distribution of hyperfine parameters due to distortions in the oxygen coordination. Species D (linewidth $W = 0.30 \text{ mm s}^{-1}$) corresponds to a fairly defined coordination, whereas $W = 0.67 \text{ mm s}^{-1}$ for species B indicates some distribution. This is a typical finding ascertained by previous experiments.

This less well defined coordination is also reflected in the stronger field distribution for species B found at low temperatures and the shape of the temperature dependence of the magnetic hyperfine field. This is relatively flat for species B whereas that for species D follows a curve close to the usual magnetization behaviour. Also the onset of magnetic hyperfine interaction for species B is less well defined than for species D. All this shows a distribution in exchange interaction or local anisotropy for species B. This is furthermore supported by the varying angle between magnetic field and the electric field gradient.

A recent [7] study on a similar sample with $x = 0.1$ published while this manuscript was under preparation reports on a very rapid drop in the hyperfine field at around 18 K for the subspectra B, F and another species (quadrupole splitting, 1.7 mm s^{-1}) which has been interpreted as due to quasi-one-dimensional ordering. The additional species was not observed at higher temperatures. Our data give no indication of its presence in our samples. Species D revealed [7] only a marginal field of less than 3 T. Our data point rather to a three-dimensional ordering for B and D (with a finite field) at about 13 K whereas C is already ordered at higher temperatures. This behaviour resembles that observed for iron-doped $Gd\text{-Ba-Cu-O}$ [7]. A finite hyperfine field for species D has also been observed earlier for various concentrations of iron and various oxygen deficiencies [1, 3, 4].

The differences in the spectra and also in the interpretation may in part be based on a different degree of ordering in the iron-holding clusters, but also on the different data analyses. Whereas the relative areas of the various subspectra were restricted in our present evaluation, the intensities given in [7] exhibit rather unsystematic variations with temperature. This in part may originate from known aging effects of the samples. Typically additional subspectra develop after thermal cycling even at relatively low temperatures (e.g. a doublet with about 0.6 mm s^{-1} splitting).

The evaluation of the angle θ from perturbational approach for $\eta = 0$ is possible via

$$e^2qQ(\text{ordered}) = \frac{1}{2}e^2qQ(\text{paramag})(3 \cos^2 \theta - 1).$$

There may be two solutions depending on θ and the sign of q which, however, may be distinguished by the complete diagonalization formalism if the magnetic hyperfine interaction is not much larger than the quadrupole interaction. Taking the quadrupole

splittings in [7] from above and below the ordering temperature, there are in fact ambivalent solutions possible for all species. The fits for our data favour the values shown in table 2, yielding appreciably better quality fits than the other choice of solutions.

Some controversial analyses with respect to the sign of the electric quadrupole interaction of species D exist [8]. Recent data on thin oriented films [9] agree with our result for species D, but disagree, however, for species B. A positive quadrupole interaction for species B is incompatible with our data. This discrepancy may occur if the electric field gradient main axis is not directed perpendicular to the crystallographic *c* axis as supposed in [9]. Recent data obtained on single-crystal material [10] support this.

Previously it has been proposed that the spectral shape of some iron-doped Y-Ba-Cu-O compounds may be interpreted by relaxation effects [5, 6]. In principle it is difficult to discern between inhomogeneous and dynamic broadenings in Mössbauer spectra. We believe, however, that relaxational broadening is not adequate for describing these spectra for the following reasons.

(i) Slow paramagnetic relaxation even in samples with iron doping in the percentage range where spin-spin relaxation may slow down is hardly to be expected in the temperature range studied here and elsewhere, where an onset of magnetic hyperfine splitting is observed (10 K range). The splitting of levels involved in spin-lattice relaxation then ought to be of the order of 10 K; the usual crystal-electric-field splittings for Fe^{3+} are, however, typically of the order of 1 K or less. Therefore fast paramagnetic relaxation is expected.

(ii) The line broadening ΔW is well reproduced by a distribution in field (i.e. $\Delta W \sim \Delta I_z$, with ΔI_z being the change in the nuclear spin *z* quantum number); relaxational broadenings for magnetic hyperfine splittings larger than the quadrupole interaction are typically $\Delta W \sim \Delta I_z^2$, which is not found here.

(iii) Despite the fact that the transition temperature is not very sharp for species B, the overall temperature dependence of B_{hf} follows a flat magnetization curve, and that of species D follows a common magnetization behaviour. The maximum in line broadening for species B and D occurs at around the temperature where the curvature of $B_{\text{hf}}(T)$ is strongest. This is for example typical for inhomogeneous broadening found in non-crystalline materials due to a distribution in exchange interaction.

(iv) If the broadening is not caused by paramagnetic relaxation of individual ions but by superparamagnetic relaxation of some clusters, then the ordering and the blocking temperatures have to be very similar and of the order of 10–15 K; otherwise the temperature-dependent hyperfine fields cannot be explained.

(v) In either case—paramagnetic or superparamagnetic relaxation—the spectra cannot be reproduced by a simplistic two-level kind of relaxation model. Either a distribution of relaxation frequencies and/or additional inhomogeneous broadenings are necessary. Thus an evaluation based on inhomogeneous effects only appears more appropriate.

Our way of interpreting the magnetic spectra is further supported by a fit to the spectra of a superconducting sample with an iron content *x* of 0.03. The fitted spectrum for 4.2 K is shown in figure 4. For this iron concentration, in addition to iron species B, C and D, species A is found with about 1% of total spectral weight. An upper limit for a possible hyperfine field is 1 T.

Species A is typical for samples with a low iron content and a high degree of oxidation and is assumed to be isolated iron at twin boundaries [2]. Its paramagnetic character has

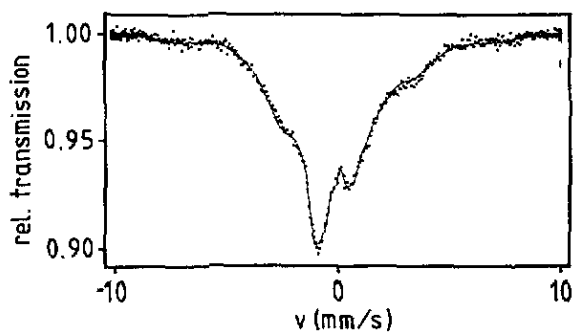


Figure 4. ^{57}Fe Mössbauer absorption spectrum of $\text{YBa}(\text{Cu}_{0.97}\text{Fe}_{0.03})_3\text{O}_{7-\delta}$ at 4.2 K.

been demonstrated from magnetic hyperfine spectra induced by an applied magnetic field. The relative intensities of the four subspectra were again derived from spectra taken at higher temperatures. The hyperfine parameters and angles θ found for species B, C and D are in excellent agreement with those found for the sample with $x = 0.10$.

4. Conclusion

Our Mössbauer data on Y-Ba-Cu-O doped with 10 at% Fe reveal three different species of iron. Two of them can be assigned to Fe in Cu(1) sites with different oxygen surroundings. The magnetic hyperfine interaction found below 15 K is interpreted as due to magnetic order probably of a highly anisotropic antiferromagnetic type. Slow paramagnetic relaxation of iron can be excluded. The method of analysing the combined magnetic and quadrupolar interactions used allows us to derive the signs of the quadrupole interactions and the angles θ between magnetic fields and electric field gradients.

An unambiguous assignment of the detailed coordination geometries of the various Fe species is, however, still missing. This necessitates careful model calculations for electric field gradients beyond simple point-charge considerations.

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