

Dynamical information for Fe-doped $\text{YBa}_2\text{Cu}_3\text{O}_7$ superconducting oxides obtained from high-temperature Mössbauer studies

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In situ high-temperature ^{57}Fe Mössbauer measurements were performed on samples of $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$, in pure oxygen or in air, both at a pressure of about 1 atm. Three samples were studied with $x = 0.005$ and 0.010 , respectively, in the temperature range from 295 to 640 K. As in previously published papers, the fitted quadrupole doublets were associated to different oxygen configurations around the Fe ions on the Cu(1) chain site, whose temperature-dependent behavior can be summarized by (i) the f factor for the different configurations are very similar; (ii) the effective Debye temperature (≈ 350 K) is rather insensitive to the Fe content and oxygen coordination; (iii) the electronic configuration of Fe is very stable up to 320°C ; and (iv) the quadrupole splitting $q(T)$ can be well described within the picture used for noncubic metals. Finally a partial change from doublet A to B induced by temperatures is observed. This change is completely or partially reversible, depending on the sample.

I. INTRODUCTION

The intense effort to understand the high- T_c values observed in the superconducting oxides from experimental and theoretical points of view has produced considerable results although there are still many open questions. The substitution of impurity ions in various lattice sites with quite different effects on T_c has been extensively performed in an attempt to increase the experimental ensemble of information. Since it is generally assumed that the fundamental units responsible for the high- T_c values are the Cu-O planes and chains, it is of particular interest to study impurity ions which are stabilized at the Cu sites in order to propose mechanisms for the decrease in T_c , for example observed in oxides where the Cu ions are replaced by transition metal ions like Fe, Cu, and Ni. For that reason, many ^{57}Fe Mössbauer effect (ME) spectroscopy experiments of Fe-substituted $\text{YBa}_2\text{Cu}_3\text{O}_7$ (Y-Ba-Cu-O) in the orthorhombic phase have been reported.¹⁻⁵ The interpretation in the observed ^{57}Fe ME was quite contradictory in the beginning,^{4,5} but essentially converged in the meantime to the two following facts: (i) Fe preferentially occupies the Cu(1) sites, and (ii) the different ^{57}Fe ME subspectra (quadrupole doublets) are due to different oxygen configurations at the Cu(1) sites.

Based on comparison of the ME spectra for O_7 and O_6 Y-Ba-Cu-O phases and taking into account results from electron and neutron diffraction,^{6,7} as well as existing extended x-ray absorption fine structure data,⁸ we have proposed⁹ the following oxygen configurations for Fe in Cu(1) sites: (a) (tetrahedral); (b) (pyramidal); and (c) (octahedral) oxygen coordinations (Fig. 1), in the orthorhombic phase. These oxygen configurations, which occur at low Fe concentration ($x < 0.01$), result in the three quadrupole doublets A , B , and C whose Mössbauer parameters are shown in Table I. Doublets A and B ,

which are the main doublets at low Fe concentration, are typical for Fe located in twin boundaries.^{7,10} At higher Fe concentration and low oxygen content three new doublets (D , E , and F) appear with the hyperfine (hf) parameters reported in Table I. While doublet D probably is due to the square planar coordinated Fe [two O(1) and both O(4)—Fig. 1(f)], which is the regular oxygen configuration at the Cu(1) site in the O_7 phase, the assignment of both E and F is still not yet clear, but they are very likely to be influenced by Fe clustering occurring at these Fe concentrations.⁷

In order to get a wider understanding of the possible oxygen configurations occurring at the Cu(1) site at room temperature (RT) and their thermal stability, we have studied ^{57}Fe : Y-Ba-Cu-O at high temperature (up to 320°C) by heating the sample either in pure oxygen or in

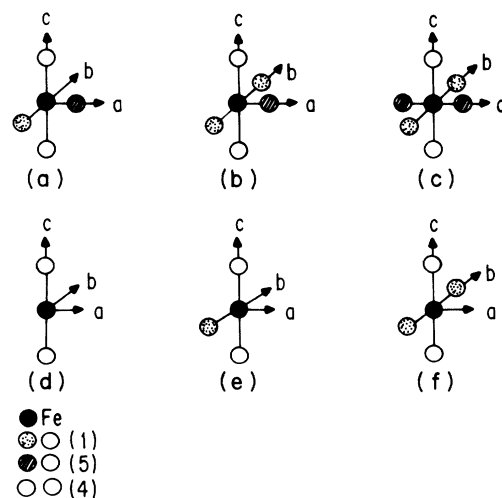


FIG. 1. Possible local environment of Fe at the Cu(1) site.

TABLE I. Mössbauer hyperfine parameters of the quadrupole doublets associated to Fe species *A*, *B*, *C*, *D*, *E*, and *F* present in $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-\delta}$ for different oxygen contents: IS (isomer shift) relative to iron metal; QS (quadrupole splitting).

	Iron species					
	<i>A</i>	<i>B</i>	<i>C</i>	<i>D</i>	<i>E</i>	<i>F</i>
IS (mm s^{-1})	-0.18	0.03	0.19	0.04	0.13	0.30
QS (mm s^{-1})	1.56	1.20	0.30	1.98	0.70	0.55

air, both at a pressure of about 1 atm and measuring *in situ*. Preliminary results have been reported before.¹¹ To our knowledge, these are the first *in situ* high-temperature ME experiments performed so far in these compounds. It should be mentioned that high-temperature annealing in vacuum or air and successive ⁵⁷Fe ME experiments at RT have been reported by other groups.¹²⁻¹⁴ In these experiments, however, the change of the oxygen content and its influence on the ME spectrum is studied, whereas in our experiments the oxygen content is kept constant (at least for the experiments done in 1 atom of pure oxygen). Thus, from our experiments one will learn about the thermal stability of oxygen configurations present at RT and about possible other configurations stabilized at high temperatures. Furthermore, from such experiments the temperature dependence of the hf parameters [isomer shift (IS) and quadrupole splitting (QS)], as well as of the recoilless fraction *f*, is obtained. Such data are important from the theoretical point of view, since they give information about possible low-lying excited electronic states as well as on lattice dynamics (effective Debye temperature) of the Fe ions in this superconducting oxide.

II. EXPERIMENTAL

Three different Fe-substituted $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_7$ samples prepared by the standard procedure⁵ with different ME spectra at RT were chosen for high-temperature ME studies: samples I and II with $x=0.005$ from different batches, sample III with $x=0.01$, quenched from 800 °C during preparation and reloaded with oxygen at about 400 °C for 15 h. The ME spectra of samples I and II, taken at RT, show the main quadrupole doublets *A* and *B* characteristic for low Fe concentration, however with different relative intensities of these two doublets. In addition all the samples show a third doublet, named *C* for samples I and II and *C'* for sample III with slightly different hyperfine parameters.

The samples were kept in a temperature controlled oven with a boron nitride sample holder and mylar windows which allowed us to perform *in situ* high-temperature studies in oxygen (sample III) or air (samples I and II) at about 1 atm pressure at temperatures between 22 and 320 °C. The Co:Rh source was kept at RT. Typically measuring time at a fixed temperature was about 12 h.

III. RESULTS AND DISCUSSION

A. Behavior of Fe species in Y-Ba-Cu-O at high temperature

Figure 2 shows the Mössbauer spectra obtained for sample I with 0.5% Fe heated in air at the indicated tem-

peratures. Similar spectra are shown in Fig. 3 for sample III with 1% Fe heated in O₂ atmosphere. The main information obtained from the visual and computer analysis of these spectra is concerned with the relative intensity of the doublets associated to Fe species *A* and *B*, which are plotted in Fig. 4 (the lines are only a guide to the eyes). The relative intensities of species *C* and *C'* are not shown because they remain constant with temperature within the experimental error.

In Fig. 4(a) two heating cycles for sample I are shown: The solid line is related to the data points obtained for the intensities of doublets *A* and *B* in the first heating from 295 to 533 K, while the dashed line is associated with the second cycle of measurements from 22 to 320 °C. It is important to notice that the relative intensities for doublets *A* and *B* are recovered when the sample is

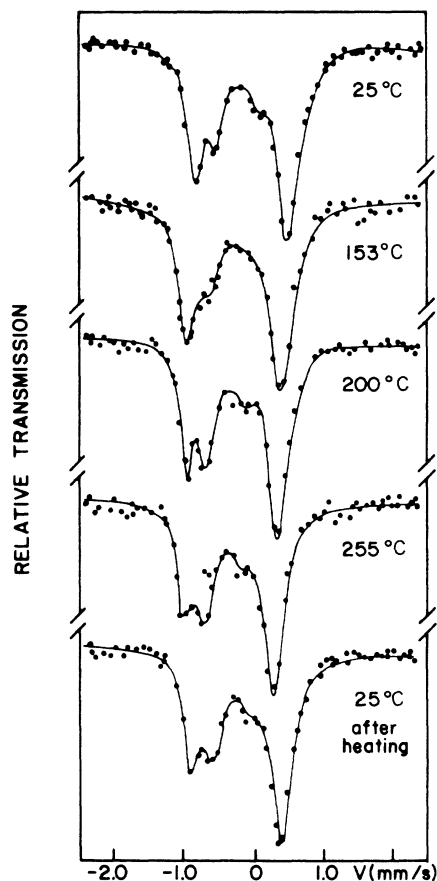


FIG. 2. Mössbauer spectra of sample I with 0.5% Fe heated in air at the indicated temperature.

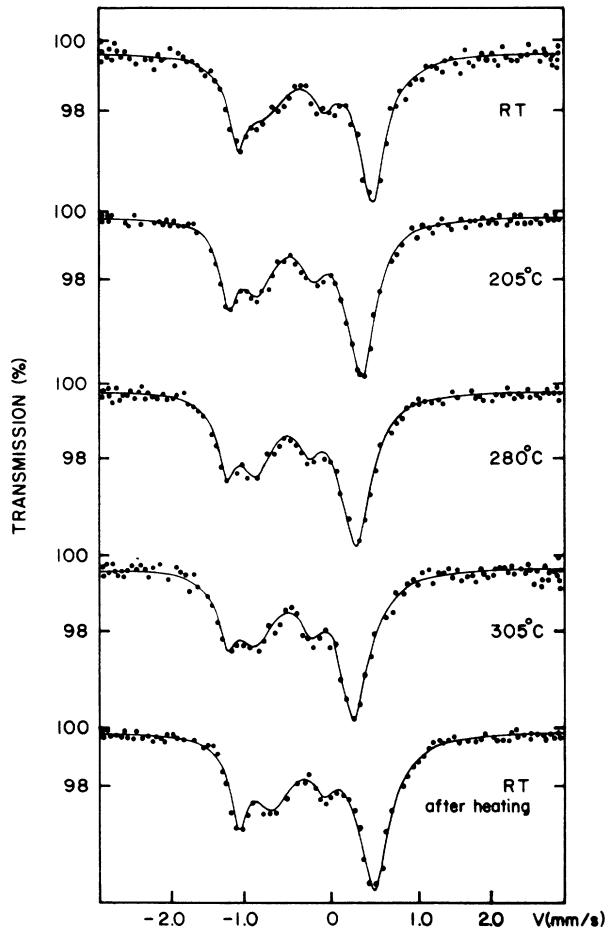


FIG. 3. Mössbauer spectra of sample III with 1% Fe heated in O_2 atmosphere at the indicated temperatures.

cooled down to RT. Sample II exhibits similar behavior as can be seen in Fig. 4(b), except for the nonreversibility of the initial values of the relative intensities for *A* and *B*. Despite the fact that sample III was heated in O_2 atmosphere [Fig. 4(c)], the same results related to the intensities of doublets *A* and *B* have been observed.

The main effect to be seen in Fig. 4 is an increase of the intensity associated to species *B* at the expense of species *A*, in spite of the differences displayed by the detailed behavior. For example the reversibility at RT for intensities *A* and *B* may depend partially on the initial concentration of both Fe species. The results shown in Fig. 4(a) and 4(c) (samples with initial intensity 30% for *A* and 60% for *B*) reveal a total reversibility, whereas sample II, with initial intensity of 45% for *A* and *B*, exhibits only a partial reversibility [see Fig. 4(b)]. The relative intensities after cooling this sample to RT become 30% for *A* and 60% for *B*. This may be an accidental result or an indication that 30% and 60% are some kind of equilibrium concentration for both species *A* and *B*.

The present result is an additional confirmation of the correlation already observed between the two iron species *A* and *B*. The behavior of the species corresponding to *A* is similar to that reported by transmission electron mi-

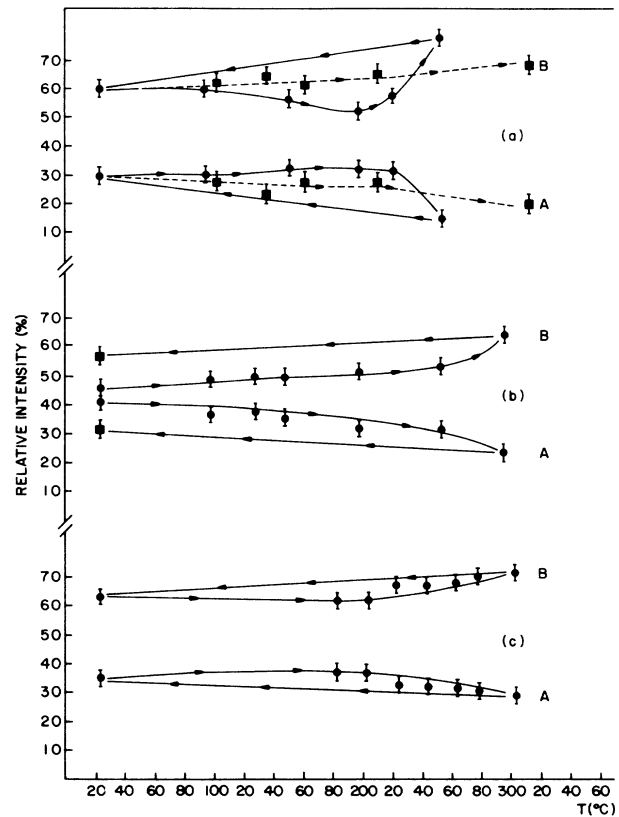


FIG. 4. Relative intensities of the doublets associated to Fe species *A* and *B* as a function of temperature with different heating cycles. Solid line is related to the data points in the first cycle (22 to 320°C) and dashed line is associated to the second cycle (22 to 320°C). (a) sample I with 0.5% Fe heated in air; (b) sample II with 0.5% Fe heated in air; (c) sample III with 1% Fe heated in O_2 atmosphere.

croscopy (TEM) measurements for twin boundaries in pure Y-Ba-Cu-O as a function of temperature¹⁰ and to the results from high resolution electron microscopy on iron concentration in doped samples.⁷ Based on such information and present results an assignment for the oxygen configuration corresponding to *A* and *B* has been proposed.⁹ The species *A* is attributed to tetrahedral coordination [Fig. 1(d)] typical for twin boundaries, while species *B*, which dominates the Mössbauer spectra at high Fe concentration, would be attributed to a pyramidal coordination of oxygens [Fig. 1(b)]. Indeed the configuration attributed to *A* can transform to *B* if an oxygen atom from a neighboring ion jumps to the O(1) site and completes the fifth coordination. This process needs a certain activation energy and can be reversible. The probability of such a mechanism may depend very much on sample preparation.

B. Temperature dependence of recoilless fraction

The recoilless fraction f measured in an ME experiment at different absorber temperatures T gives information about the mean square displacement $\langle x^2(T) \rangle$ of Mössbauer isotopes in the absorber. Within the Debye

model and at high temperatures ($T \sim \Theta_D/2$) (Θ_D = effective Debye temperature of ME nucleus) f can be approximated by¹⁵

$$\ln f = \langle x^2(T) \rangle \cong \frac{6E_R}{k\Theta_D} \left[\frac{T}{\Theta_D} \right],$$

where E_R is the recoil energy ($E_R = 22.6$ K for the 14.4 keV γ transition in ^{57}Fe). Figure 5 shows a plot of the total ME absorption area as a function of T for the two different samples studied. All data are consistent with $\langle \Theta_D \rangle = 350 \pm 5$ K, independent of sample. This indicates that $\langle \Theta_D \rangle$ is rather insensitive to the Fe content in Fe:Y-Ba-Cu-O compounds in this range of concentration.

A similar plot for the absorption areas of the individual quadrupole doublets is not possible, since there occurs a temperature-induced change in the oxygen configuration of the Fe ions, resulting in different relative line intensities of these doublets with temperature (see Sec. III A). The observation that all data points in Fig. 5 are on a straight line, i.e., that no change of the slope occurs with temperature, on the other hand, indicates that the f factor for the different quadrupole doublets (different oxygen configurations) are very similar.

The absolute value of $\langle \Theta_D \rangle$ is relatively high for a metal but typical for Fe oxides like, e.g., Fe_3O_4 .¹⁶ This means that the phonon spectrum determining $\langle x^2(T) \rangle$ of Fe in Y-Ba-Cu-O compounds does not show any abnormal behavior as one may speculate as one of the possibilities to explain the high T_c of these oxides. However, since $\langle \Theta_D \rangle$ gives only rather integral information on the phonon spectrum, this conclusion has to be treated with some care.

C. Temperature dependence of hyperfine parameters

1. Isomer shift

The center shifts (S) (relative to the Co:Rh at RT) of the individual quadrupole doublets A , B , and C , as obtained from least-squares fits to the ME spectra, are given

in Fig. 6 as a function of temperature T . While the center shift of doublet A does not depend on the Fe content, a small difference in S is observed for doublets B and C between the 0.05 and 1% Fe samples. This fact, together with the observation of a rather large linewidth of these doublets, may indicate that they are not due to Fe with a unique nearest-neighbor configuration.

Different subspectra (quadrupole doublets), whose relative intensities will vary with the Fe or O content, probably are adding up to the doublets B and C . Independent of this finding, a linear change of S with T is observed for all quadrupole doublets which is given by $(\partial S/\partial T)_p = (6.5 \pm 0.5) \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ and $(8.0 \pm 1.0) \times 10^{-4} \text{ mm s}^{-1} \text{ K}^{-1}$ for doublets A , B , and C , respectively. In order to extrapolate from these data the temperature dependence of the isomer shifts $S_{IS}(T)_v$ at constant volume one has to correct S for the second-order Doppler shift $S_{\text{SOD}}(T)$ and for thermal expansion¹⁷

$$\left(\frac{\partial S}{\partial T} \right)_p = \left(\frac{\partial S_{\text{SOD}}}{\partial T} \right)_p + \left(\frac{\partial S_{IS}}{\partial \ln V} \right)_T \left(\frac{\partial \ln V}{\partial T} \right)_p + \left(\frac{\partial S_{IS}}{\partial T} \right)_v.$$

The second term, which corrects for the thermal expansion, usually is more than one order of magnitude smaller than the observed value of $(\partial S/\partial T)_p$ and will be neglected [typical values are $(\partial S_{IS}/\partial \ln V)_T \cong 1 \text{ mm s}^{-1}$ and $(\partial \ln V/\partial T)_p = \beta_p \lesssim 10^{-4} \text{ K}^{-1}$].¹⁸ The second-order Doppler shift is given by¹⁹

$$S_{\text{SOD}}(T) = -\frac{1}{2c} \langle v^2(T) \rangle,$$

where $\langle v^2(T) \rangle$ is the mean square velocity of the ME nucleus. Using the Debye model with $\langle \Theta_D \rangle = 350$ K, as obtained from the temperature dependence of the recoilless fraction (Sec. III B), the temperature dependence of $S_{\text{SOD}}(T)$ in the temperature region $300 < T < 640$ K can be approximated by $(\partial S_{\text{SOD}}/\partial T)_p = 6.8 \times 10^{-4}$

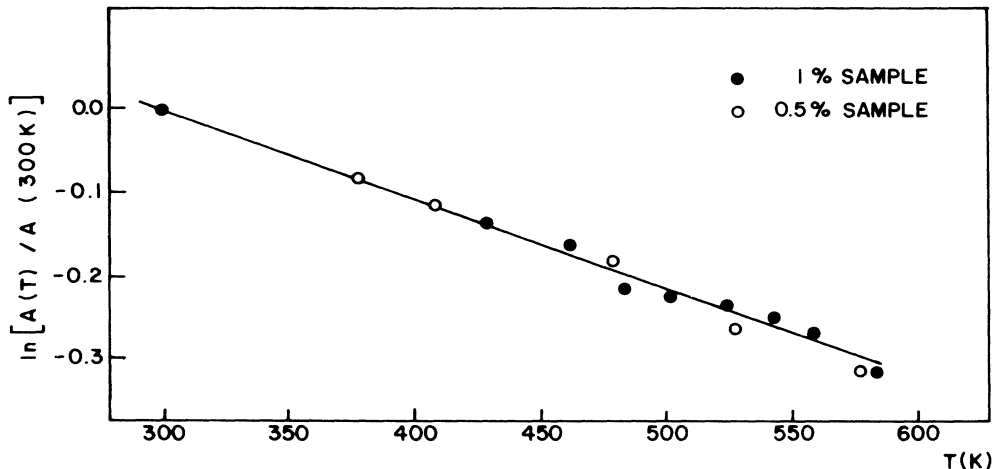


FIG. 5. Temperature dependence of the total area of Fe:YBa₂Cu₃O₇, normalized to the room temperature data.

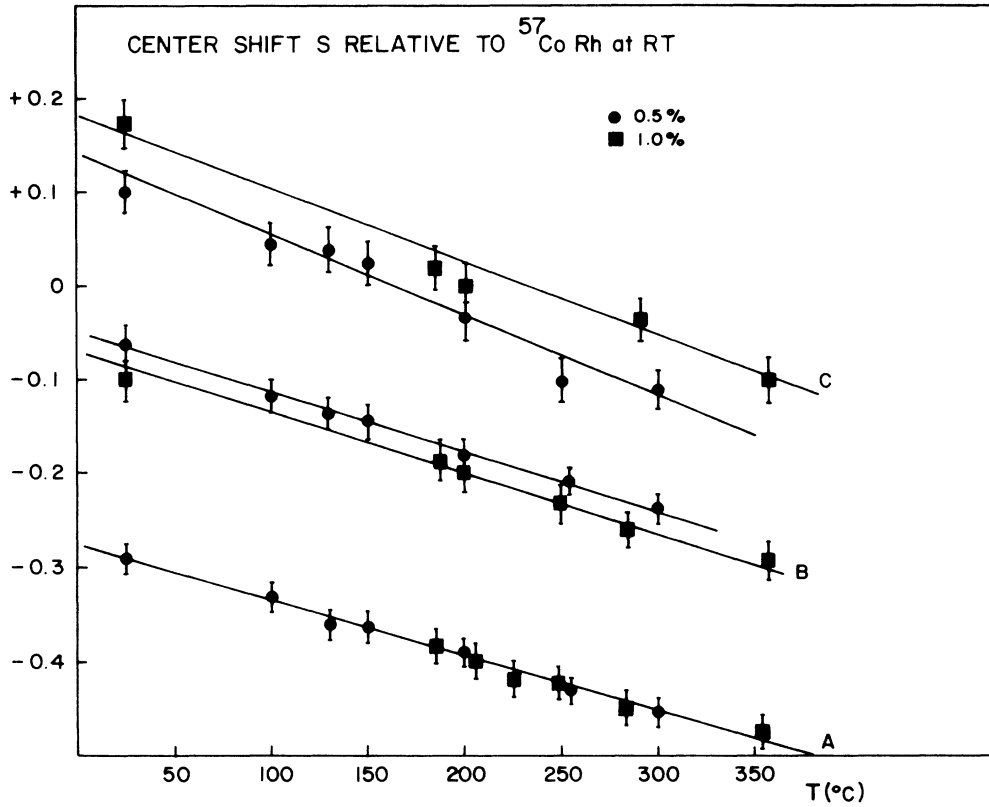


FIG. 6. Center shift (S) of the individual doublets A , B , and C as a function of temperature.

$\text{mm s}^{-1} \text{K}^{-1}$. Thus, the observed temperature dependence of the center shift S is completely due to the second-order Doppler shift, i.e.,

$$\left(\frac{\partial S}{\partial T} \right)_p \cong \left(\frac{\partial S_{\text{SOD}}}{\partial T} \right)_p$$

or

$$\left(\frac{\partial S_{\text{IS}}}{\partial T} \right)_v \approx 5 \times 10^{-5} \text{ mm s}^{-1} \text{K}^{-1}.$$

This means that the change of the isomer shift of ^{57}Fe in the Y-Ba-Cu-O compounds, in the temperature region $300 < T < 640 \text{ K}$, is smaller than 0.02 mm s^{-1} . Therefore, we can conclude that the electronic configuration of the Fe ions in this compound is very stable up to 640 K .

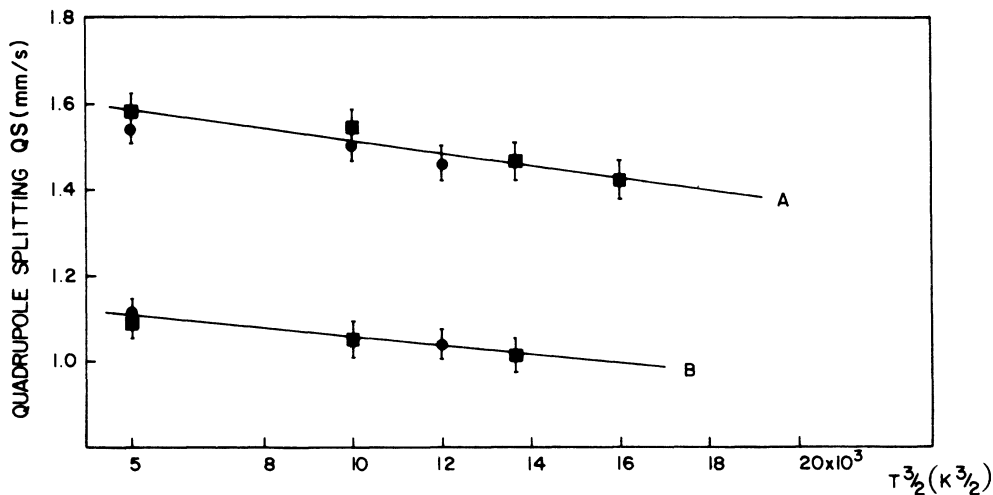


FIG. 7. Quadrupole splitting of the two main doublets A and B as a function of $T^{3/2}$.

2. Quadrupole splitting

The temperature dependence of the electric field gradient (EFG) $q(T)$ in noncubic metals which leads to a temperature-dependent quadrupole splitting $\Delta E_Q(T) = \frac{1}{2}e^2Qq(T)$ of the ($I = \frac{3}{2}$) excited nuclear state of ^{57}Fe with the nuclear quadrupole moment Q usually is written as²⁰

$$q(T) = q_0[1 - \beta T^{3/2}].$$

This empirically found relation can be interpreted in the following way: The averaging of the EFG due to thermal motions of the lattice ions leads to a reduction of q with increasing T . The proportionality constant β , therefore, is a measure of the "force constant" which determines θ_D , i.e., in the Debye model $\beta \propto (M\theta_D^2)^{-1}$ where M is the mass of the vibrating ion.

We have plotted in Fig. 7 the quadrupole splitting $q(T)$ of the two main doublets A and B as a function of $T^{3/2}$. The data are consistent with a linear decrease of q versus $T^{3/2}$ with a slope of $\beta \cong 8 \times 10^{-5} \text{ K}^{-3/2}$. This rather small value of β is in agreement with the large value of $\langle \theta_D \rangle$ or small value of $(M\langle \theta_D \rangle^2)^{-1} = 1.4 \times 10^{-7} \text{ K}^{-2}$, if one compares with the values found in other noncubic metals.²¹ Thus the temperature dependence of $q(T)$ in the Y-Ba-Cu-O compounds can be well described within the picture used for $q(T)$ in noncubic metals. Furthermore, we can exclude the existence of low-lying excited electronic states of the Fe ions, which may be populated at these high temperature, since this should lead to a significant additional

change in $q(T)$. This conclusion agrees with that drawn from the temperature dependence of the isomer shift (Sec. III C).

IV. CONCLUSIONS

Our *in situ* high-temperature Mössbauer studies of ^{57}Fe doped Y-Ba-Cu-O show a reversible (or partially reversible) change in the relative intensities of the two main doublets A and B corresponding to Fe species, which differ in the number of oxygen nearest-neighbor atoms (4 and 5, respectively). This is an extra confirmation that both species correspond to Fe occupation of the same Cu site, namely the Cu(1) site. This change can be explained by a thermal activated oxygen hopping.

Moreover, these high-temperature ^{57}Fe Mössbauer studies indicate a quite normal behavior of both the recoilless fraction and of the hyperfine parameters of the Fe ions: The effective Debye temperature is typical for Fe in oxides and is insensitive to Fe content, at least in the low concentration limit, and oxygen coordination; the quadrupole splitting behaves like that found in noncubic metals and the temperature dependence of the center shift is completely due to second-order Doppler shift. Thus, there is no indication of any low-lying electronic excited states of the Fe ions. From the ^{57}Fe Mössbauer spectroscopy point of view this compound shows the expected "double face"; it behaves on one side like an ordinary Fe oxide (high effective Debye temperature) and on the other side like a normal, noncubic metal ($T^{3/2}$ dependence of the quadrupole interaction).

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