

HIGH-TEMPERATURE SUPERCONDUCTORS AND RELATED COMPOUNDS STUDIED BY MÖSSBAUER SPECTROSCOPY

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⁵⁷Fe, ¹¹⁹Sn, and ¹⁵¹Eu Mössbauer spectroscopy was used to study the chemical structure, phonon mode changes, and low-temperature phase transformation around the T_c as well as suppression of superconductivity in high-temperature superconductors and related compounds. Anomalous temperature-dependent changes in the total ⁵⁷Fe spectral area fraction and in the Mössbauer line shift were simultaneously found around the T_c in a $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor. These anomalous changes were attributed to phonon softening and low-temperature phase transformation occurring around the superconducting transition. Significant differences were observed between the ⁵⁷Fe Mössbauer spectra of superconducting $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$ and the isostructural non-superconducting $\text{PrBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$. The differences were interpreted in connection with the suppression of superconductivity (by hole filling or hybridization of Pr, Cu and O states) in the Pr-containing compound. The unusually high isomer shift value observed in the Pr-containing material can give evidence for the charge transfer mechanism between the Cu(1) chains and the Cu(2) planes and for its role in the suppression of superconductivity.

INTRODUCTION

Mössbauer spectroscopy can be advantageously applied to study the following topics of high temperature superconductors:

- Determination of valence state of cations
- Localization and site preference of Mössbauer-nuclides (¹⁵¹Eu, ¹¹⁹Sn, ⁵⁷Fe, ⁵⁷Co, etc.) incorporated into high T_c superconductors
- Changes in oxygen content
- Location of hydrogen
- Study of crystal structure
- Effect of preparation parameters
- Anomalous temperature dependences
 - low temperature phase transformation
 - phonon softening
- Anomalous time dependences
 - metastability
 - relaxation
- Magnetic interactions

This wide range of applications becomes possible because Mössbauer spectroscopy can detect the energy changes between the levels of Mössbauer nuclei due to different hyperfine interactions between the nucleus and the electrons, with high sensitivity.

For the Mössbauer investigations, the high temperature superconductor samples must contain Mössbauer nuclides. They can either be constituents (e.g., Eu, Sn) or impurities (e.g., Fe, Co). The latter ones must be introduced as probes for the Mössbauer measurement in a small amount (usually enriched ^{57}Fe , ^{119}Sn or ^{57}Co) to minimize the disturbance of superconducting properties of the material.

The high interest in this field is demonstrated by a large number of publications referenced in [1]. The authors have been investigating a large number of superconducting oxides [2–25] since 1986, and they have been studying all of the topics listed above.

Instead of giving a summary of our previous works, we would like to call attention to one of them that is closely related to the mechanism of high T_c superconductivity. Temperature-dependent anomalous changes were found around the T_c in ^{57}Fe Mössbauer spectra of a Tl-containing superconductor [13]. These changes were interpreted by us as a relaxation process due to Cooper pairing with energy predicted by the BCS theory [26]. Namely, an evidence for the possibility of BCS type superconductivity in high temperature superconductors was obtained by Mössbauer spectroscopy.

In the present paper we show a few results obtained recently by Mössbauer investigation of high- T_c superconductors and related compounds.

EXPERIMENTAL

High-temperature superconductor $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ was synthesized from Eu_2O_3 , CuO , BaCO_3 , and $^{57}\text{Fe}_2\text{O}_3$ at 930°C for 120 min and heat treated at 430°C for 960 min in an oxygen atmosphere.

We succeeded in preparing a single-phase material of a $\text{PrBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ compound that was synthesized from $\text{Ba}(\text{NO}_3)_2$, CuO , Pr_6O_{11} , and Fe_2O_3 materials at 930°C for 12 hours in oxygen atmosphere.

The synthesized material was given subsequent heat treatments ($400^\circ\text{C}/120$ min, $600^\circ\text{C}/40$ min, $600^\circ\text{C}/180$ min, $450^\circ\text{C}/480$ min, $450^\circ\text{C}/120$ min) and finally was heat treated at 600°C for 180 min and 450°C for 600 min either in a nitrogen (sample A) or in an oxygen (sample B) atmosphere.

The $\text{SnSr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+d}$ material was prepared from a 1:1 mixture of SnO and $\text{Sr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{7-d}$ by subsequent heat treatments ($300^\circ\text{C}/2\text{h}$, $400^\circ\text{C}/2\text{h}$, $820^\circ\text{C}/3\text{h}$, $400^\circ\text{C}/5\text{h}$) in a nitrogen atmosphere. After grinding and homogenization, a pellet was formed and heat treated at 800°C for 3 hours and then at 200°C for 4 hours. Precursors $\text{SrCa}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{7-d}$ were prepared from a well-homogenized stoichiometric mixture of SrCO_3 , CaCO_3 , Y_2O_3 , and CuO . The mixture was calcined between 950 – 1000°C for 4 hours and then kept at 750°C for 4 hours. After cooling, it was powdered and heat treated at 1000°C for 8 hours. The SnO precursor was prepared from $\text{SnCl}_2 \cdot \text{H}_2\text{O}$ dissolved in HCl, neutralized with a Na_2CO_3 solution, washed with H_2O , and dried at 110°C .

^{57}Fe , ^{151}Eu and ^{119}Sn Mössbauer spectra of the powdered samples were recorded at transmission geometry. A temperature-controlled cryostat was used for the low-temperature measurements. Isomer shift values are given relative to alpha-iron, EuF_3 , and CaSnO_3 . Providing the gamma rays $3.10^9\text{Bq } ^{57}\text{Co}$, $10^9\text{ Bq } ^{151}\text{EuF}_3$ and $3.10^8\text{ Bq Ca}^{119}\text{SnO}_3$ sources were used. The evaluation of the spectra was performed by conventional least-square fitting of lines using MOSFUN and SIRIUS programs.

RESULTS AND DISCUSSION

1. Chemical Structure

1.1 Location of Mössbauer Nuclides

Fig. 1 shows the structure of 1-2-3 type (e.g., $\text{EuBa}_2\text{Cu}_3\text{O}_{7-d}$) and 1-2-4 type (e.g., $\text{EuBa}_2\text{Cu}_4\text{O}_8$) superconductors. By introducing ^{151}Eu , ^{119}Sn , or ^{57}Fe into the lattice of these orthorhombic perovskites, the location and distribution of these probing nuclides can be determined by Mössbauer spectroscopy [10, 11, 30].

The Mössbauer spectra (Figs. 2–4) of superconductor samples are considered as superpositions of subspectra belonging to Mössbauer nuclides occupying different sites with various surroundings in the lattice.

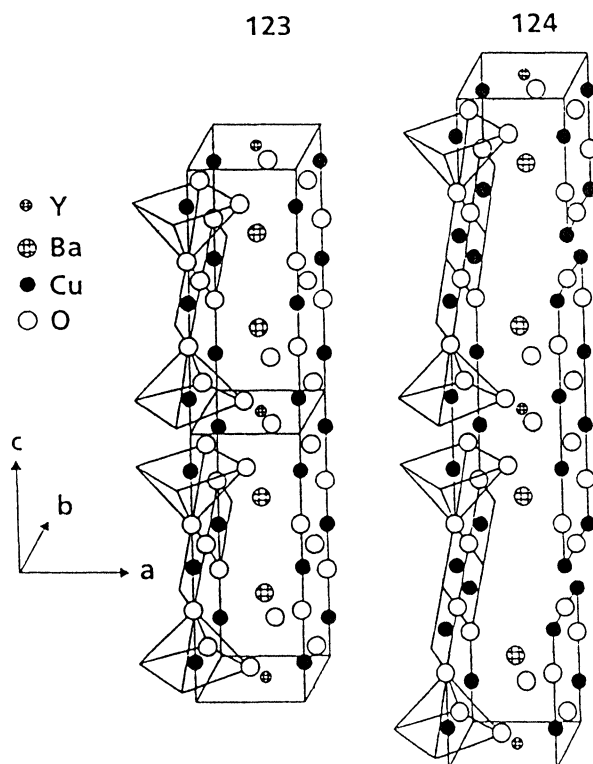


FIGURE 1 Structure of the 1-2-3 and 1-2-4 type superconductors.

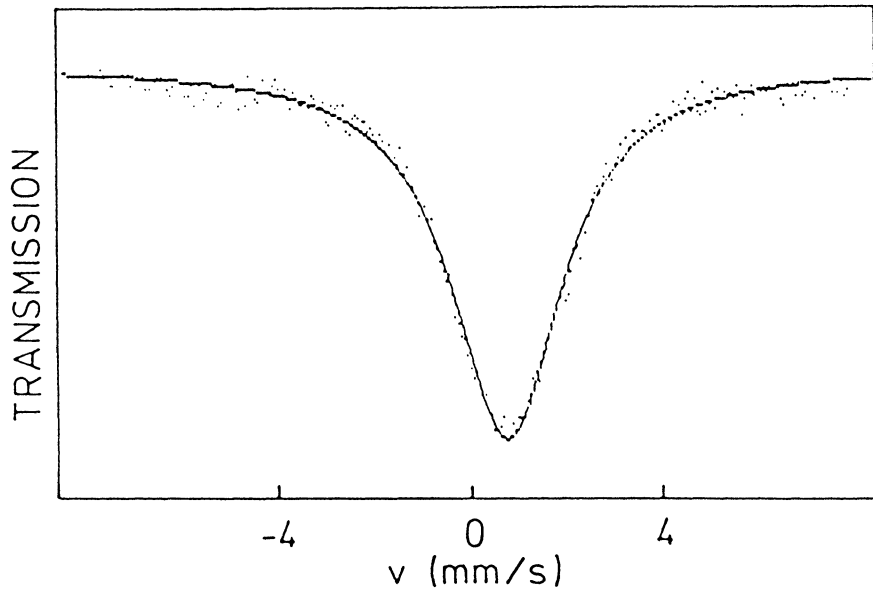


FIGURE 2 Room temperature ^{151}Eu Mössbauer spectrum of $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor.

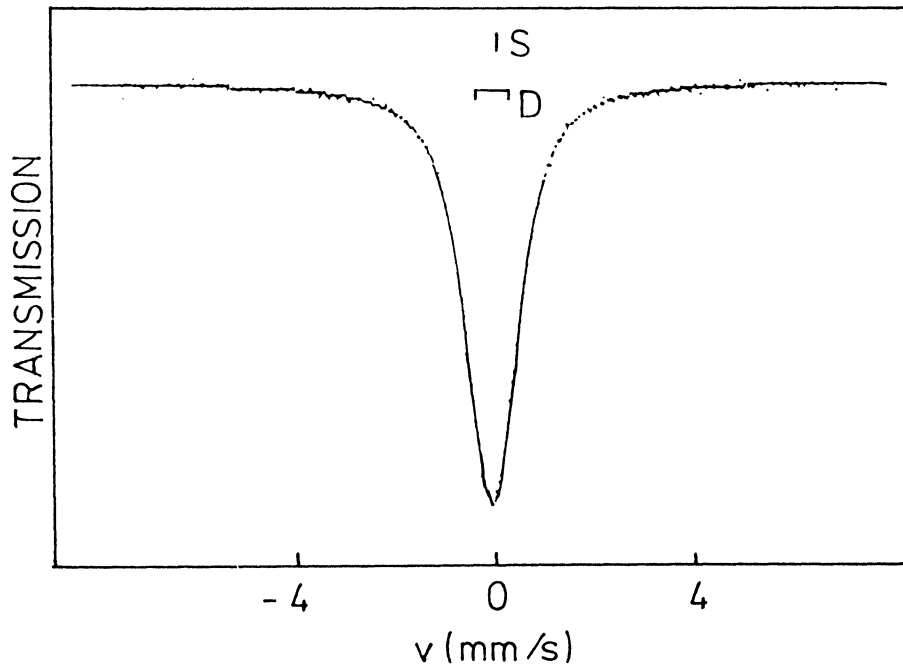


FIGURE 3 Room temperature ^{119}Sn Mössbauer spectrum of $\text{EuBa}_2(\text{Cu}_{0.99}^{119}\text{Sn}_{0.01})_3\text{O}_{7-d}$ superconductor. Singlet S and doublet D correspond to Sn at the Cu(2) and the Cu(1) site, respectively.

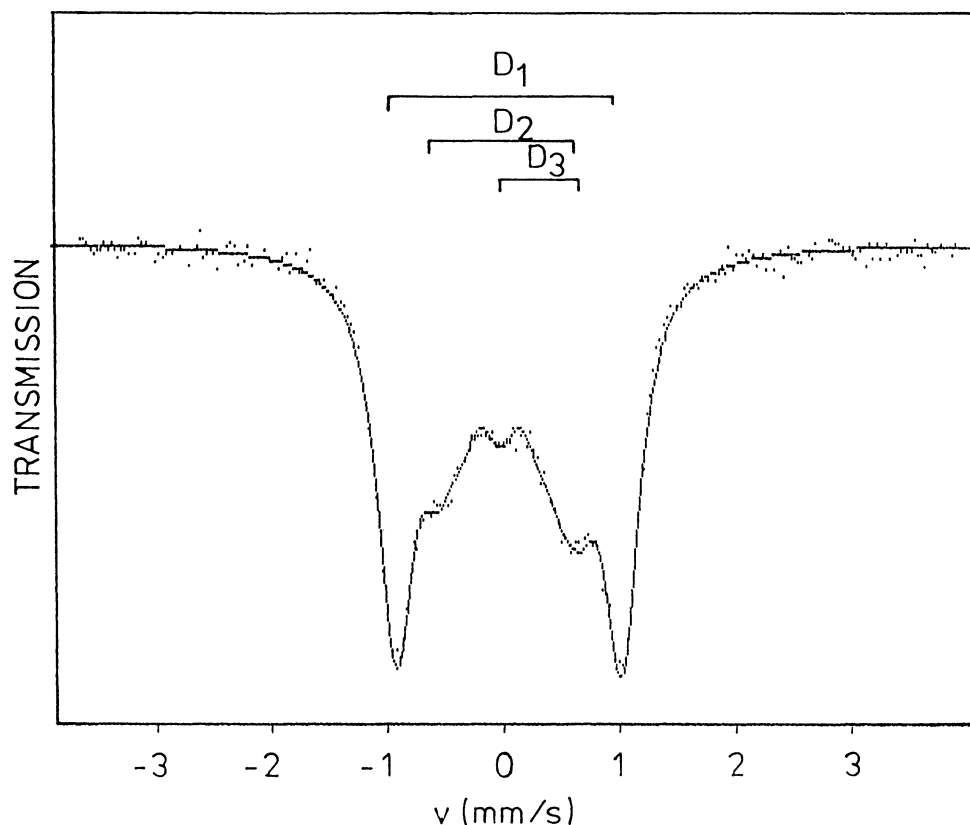


FIGURE 4 Room temperature ^{57}Fe Mössbauer spectrum of $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor. Doublet D1 and D2 are associated with Fe at four or five-coordinated Cu(1) site, while D3 belongs to Fe at the Cu(2) site.

The ^{151}Eu spectrum of the $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor (Fig. 2) can be evaluated as a singlet corresponding to Eu situated at the normal rare earth site.

The ^{119}Sn spectrum of the $\text{EuBa}_2(\text{Cu}_{0.99}^{119}\text{Sn}_{0.01})_3\text{O}_{7-d}$ superconductor (Fig. 3) is decomposed into a singlet and a doublet, which is associated with Sn atoms at the Cu(2) and Cu(1) sites.

The ^{57}Fe (and the ^{57}Co) spectra could be fitted with three (or four) doublets (D1, D2 and D3 in Fig. 4) representing Fe atoms at the Cu(1) and the Cu(2) sites.

Comparing the relative area fractions of Mössbauer lines corresponding to different Cu sites, it was suggested [6, 10] that iron and cobalt prefer the Cu(1) site while tin prefers the Cu(2) site in these superconductors.

1.2. Valence State of Cations

The valence state of ^{57}Fe , ^{57}Co , ^{119}Sn , or ^{151}Eu substituted into the high- T_c superconductors can be established by the determination of isomer shift from the Mössbauer spectra.

The isomer shift depends on the electron density at the nucleus and can be expressed under certain conditions [27] by the formula:

$$\delta = C \Delta R/R \{|\Psi_s(0)|^2 - |\Psi_a(0)|^2\}$$

where $|\Psi_s(0)|^2$ and $|\Psi_a(0)|^2$ are the s electron densities at the nucleus and $\Delta R/R$ is the relative change in the radius of nucleus. From the known interrelation [27] between the isomer shift and the valence state the latter can be obtained.

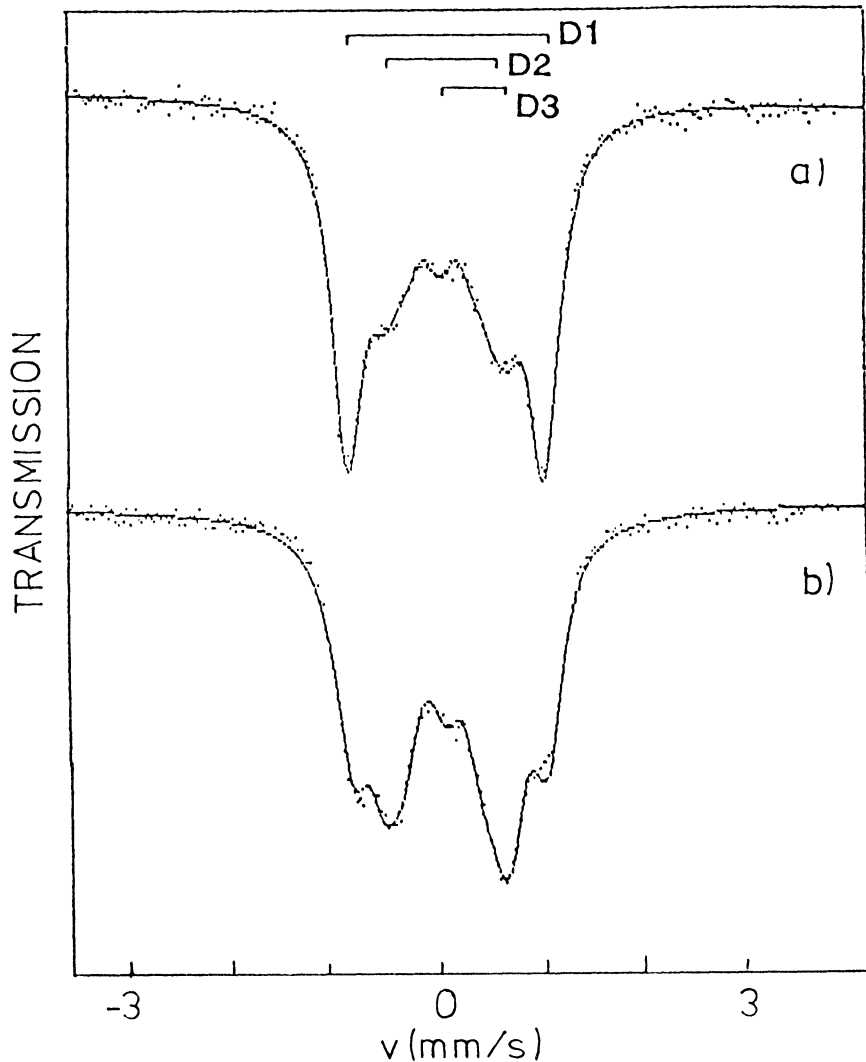


FIGURE 5 ^{57}Fe Mössbauer spectra of $\text{BaCu}_{0.99}^{57}\text{Fe}_{0.01}\text{O}_2$ precursor (a) and $\text{EuBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor (b).

In each superconductor, Eu and Sn was found in the valence state Eu(III) and Sn(IV). However, the valence state of Fe and Co could be either three or four [2-5].

1.3. Checking the Solid State Reaction Used for Preparation

Mössbauer spectroscopy can be utilized as a fingerprint method [33] to check the product of the solid-state reaction used for the preparation of high- T_c superconductors.

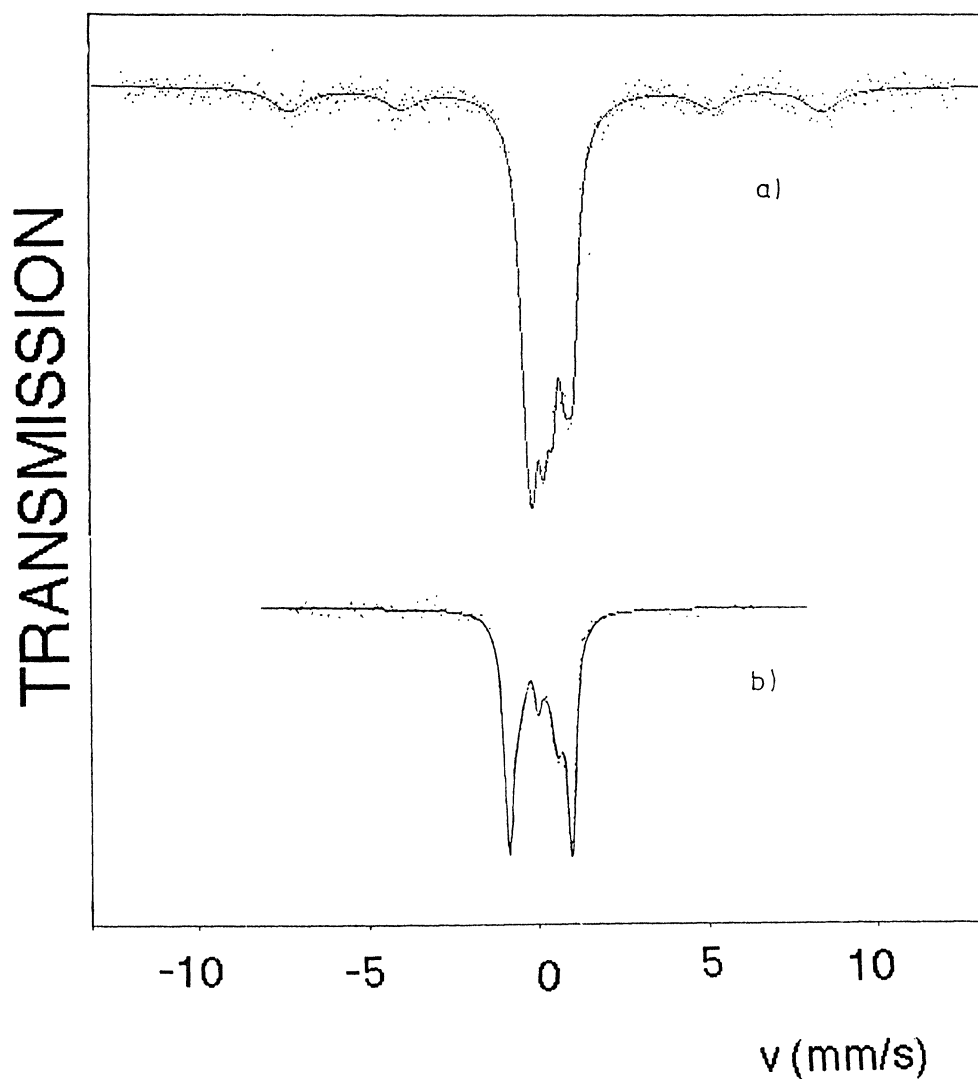


FIGURE 6 ^{119}Sn Mössbauer spectrum of SnO_2 precursor of $\text{SnSr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+d}$.

Fig. 5 shows the difference between the ^{57}Fe Mössbauer spectra of an intermediate (or precursor) $\text{BaCu}_{0.99}\text{Fe}_{0.01}\text{O}_2$ and the superconductor $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$. We can conclude from the spectra that the superconductor sample does not contain the precursor.

In the case of Sn, which has several possibilities to form perovskite compounds other than the desired superconductor, one of the first questions is whether or not one has succeeded in preparing the right compound. Since the valence state of the regular Sn environment (an Sn-O layer) in the 1-2-4 compound $\text{SnSr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+d}$ is supposed to be similar to that in SnO (i.e., (II)), we used Mössbauer spectroscopy to determine whether or not this is really the case.

Fig. 6 shows the Mössbauer spectrum of an SnO precursor. As expected, the main part of the spectrum is a doublet characteristic of Sn(II). The parameters of this component correspond to those observed with SnO. Fig. 7 shows a typical ^{119}Sn spectrum of $\text{SnSr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+d}$. It is obvious from the spectrum that there is no Sn(II) present here. All Sn atoms have valence state IV. A closer look reveals at least two components belonging to Sn atoms with different surroundings.

1.4. Variations with Oxygen Content

Fig. 8 shows ^{57}Fe Mössbauer spectra of $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{6.8}$ and $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{6.95}$ superconductors. It can be well seen that the Mössbauer spectra reflect sensitively the changes in the oxygen content of the superconductor by the change in the relative intensity of doublet D2 associated with Fe atoms at five-coordinated Cu(1) site. Similar changes have already been found in other cases [31].

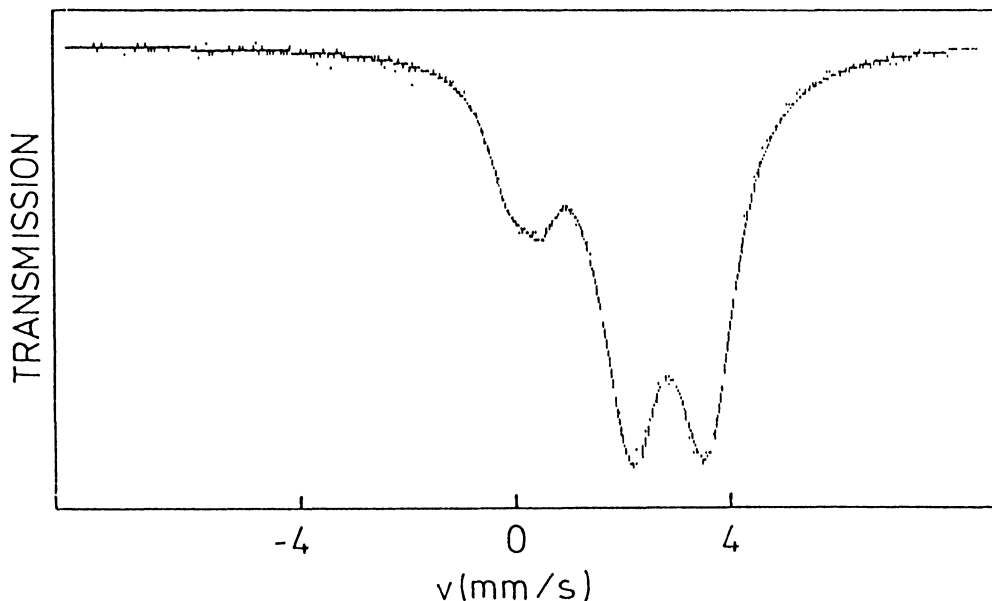


FIGURE 7 ^{119}Sn Mössbauer spectrum of $\text{SnSr}_2\text{Ca}_{0.5}\text{Y}_{0.5}\text{Cu}_3\text{O}_{8+d}$.

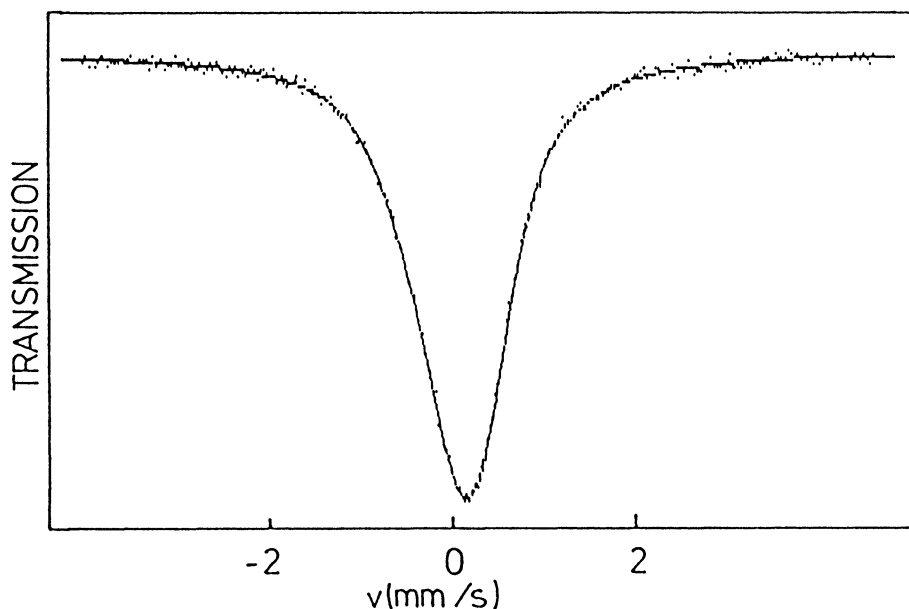


FIGURE 8 ^{57}Fe Mössbauer spectra of $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{6.8}$ (a) and $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{6.95}$ (b) superconductors.

Another interesting variation of Mössbauer parameters with the oxygen content was also found in a previous work [21]. The magnitude of the isomer shift of the Mössbauer probe at the Cu(1) site in $\text{YBa}_2\text{Cu}_3\text{O}_{6+x}$ was found to increase continuously with decreasing oxygen content (Fig. 9) and to undergo a sharp leveling off just below $\text{O}_{6.4}$, in which the oxygen content corresponds to a superconductor (metal)-to-insulator transition [28]. This can be interpreted in terms of electronic charge transfer between the chain and plane sites.

2. Phonon Softening and Low Temperature Phase Transition

We have found an anomalous temperature dependence of the total area fraction of ^{57}Fe Mössbauer spectra of a $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor at the T_c . This is illustrated in Fig. 9. The change in the area fraction reflects a corresponding change in the Mössbauer-Lamb factor f (probability of the Mössbauer effect). Theoretically in the case of $T < \Theta_D$ the f factor can be given [29] as:

$$f = e^{-\langle x^2 \rangle / \lambda^2} \\ = e^{-3h^2/4Mk\theta_D} \left(1 + \frac{4T^2}{\theta_D^2} \int_0^{\theta_D/T} \frac{udu}{e^u - 1} \right)$$

where Θ_D is the Debye temperature defined by $h\omega_D = k\Theta_D$, where ω_D is the characteristic Debye frequency, M is the mass of the nucleus, λ is the wavelength of the Mössbauer gamma radiation, and $\langle x^2 \rangle$ is the mean square amplitude of the lattice vibration.

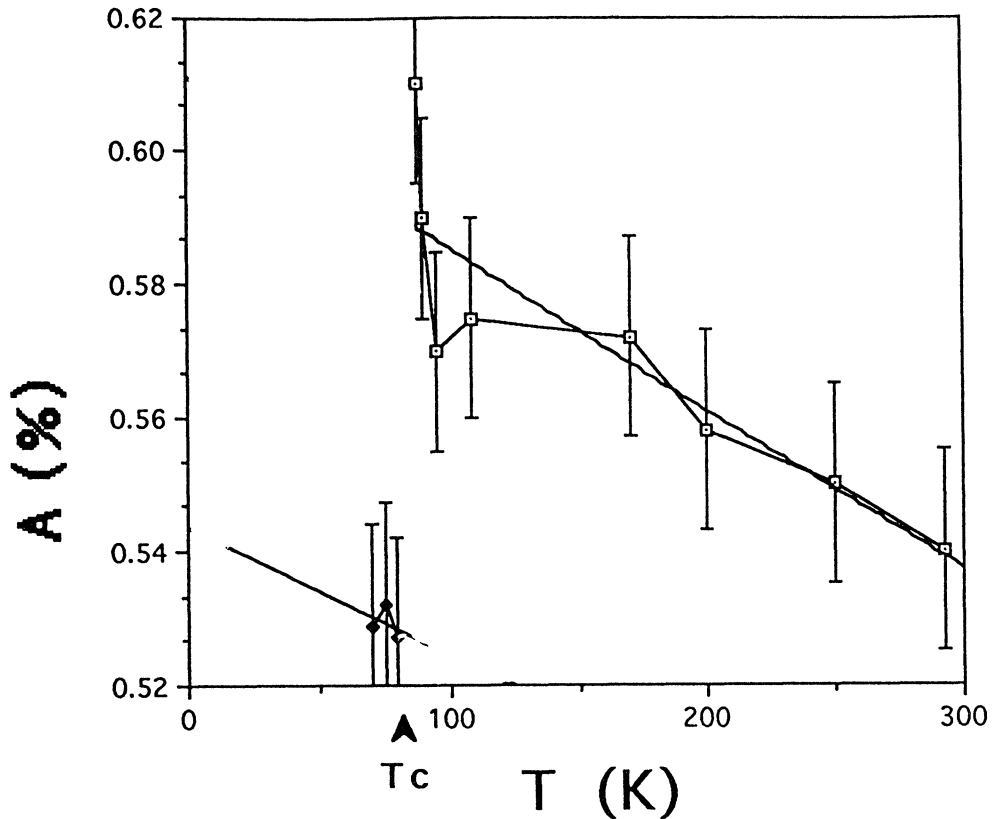


FIGURE 9 Temperature dependence of the total area fraction of ^{57}Fe spectrum of $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor.

In the normal case, the temperature dependence of the f factor is characterized by a single Debye temperature. However, the parts of the plot demonstrated in Fig. 9 belong to different values of Θ_D . The lower value of Θ_D found at temperatures lower than T_c can be attributed to a lower ω_D . This can be interpreted as phonon softening. Our result suggests that phonons must have a role in the mechanism of high-temperature superconductivity.

At the same time, we have also found anomalous temperature dependence of line shifts with the same $\text{EuBa}_2(\text{Cu}_{0.99}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor between T_{onset} and T_c (Fig. 10). The temporary decrease in the line shift with decreasing temperature around the T_c is in contradiction with the expectation for normal state based on the temperature dependence of second-order Doppler shift [27]. This anomaly can be explained by a change in the local environment of Fe atoms. We suppose that the dimension of the environment concerned is shorter than the interatomic distances in the lattice. This means that the temperature dependent line shift anomalies reflect low temperature phase transformation.

Assuming correlation between the low temperature phase transformation and phonon softening, the phonon mode changes could be partly attributed to the low temperature phase transformation.

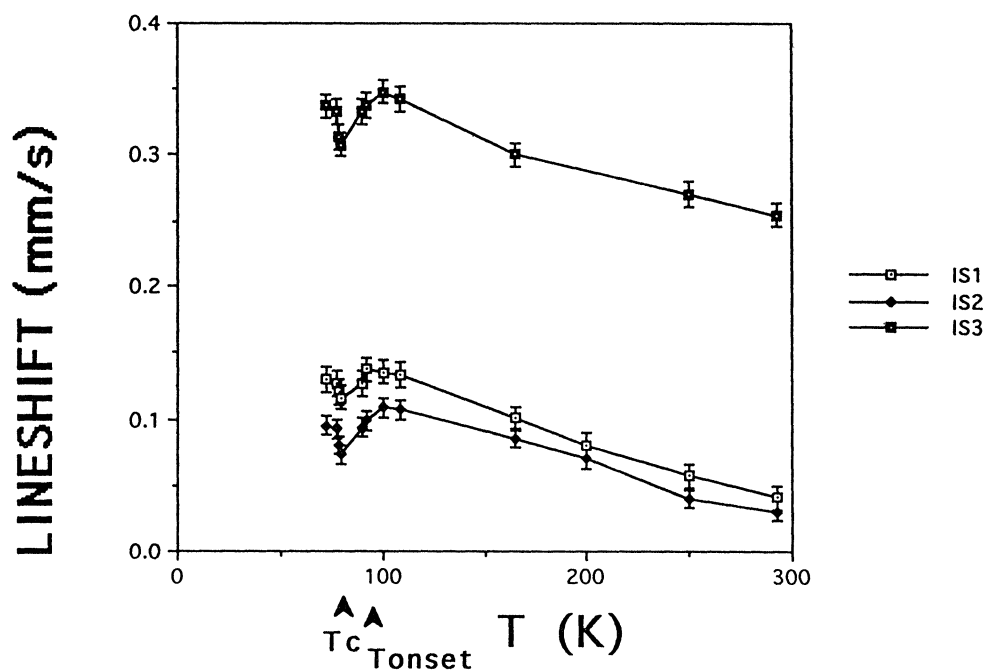


FIGURE 10 Temperature dependence of line shift of doublets in ^{57}Fe spectrum of $\text{EuBa}_2(\text{Cu}_{0.9957}\text{Fe}_{0.01})_3\text{O}_{7-d}$ superconductor.

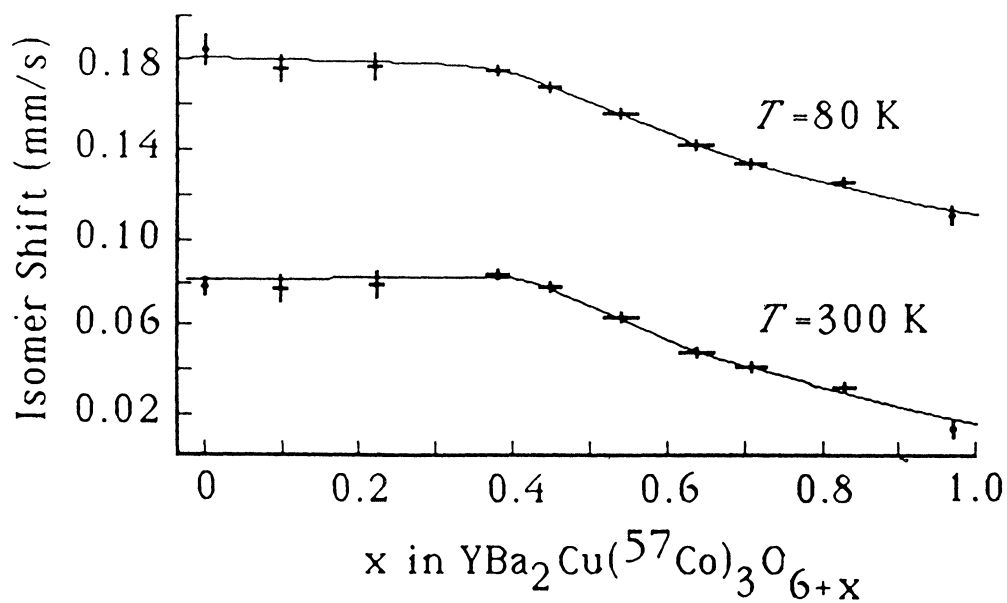


FIGURE 11 Dependence of ^{57}Co isomer shift on oxygen content of $\text{YBa}_2(\text{Cu}(\text{Co}))_3\text{O}_{7-d}$ superconductor [21].

3. Suppression of Superconductivity

Superconductivity is lost in $\text{EuBa}_2\text{Cu}_3\text{O}_{7-d}$ when Eu is replaced by Pr, although the $\text{PrBa}_2\text{Cu}_3\text{O}_{7-d}$ is isostructural with the Eu-containing compound. Fig. 11 shows ^{57}Fe Mössbauer spectra of a $\text{PrBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7-d}$ compound with different oxygen contents. The spectra of non-superconducting Pr-containing materials are significantly different from those of superconducting perovskites (compare Fig. 6 and Fig. 11). The characteristic isomer shifts of the doublets D1, D2, and D3 are 0.11 mm/s, 0.13 mm/s, and 0.07 mm/s, respectively. These data are unusual for 1-2-3 type superconductors that have isomer shifts 0.03 mm/s, 0.01 mm/s, and 0.15 mm/s for doublets D1, D2, and D3. The differences among the isomer shifts of Pr- and Eu-containing materials reflect changes in the electronic densities at both

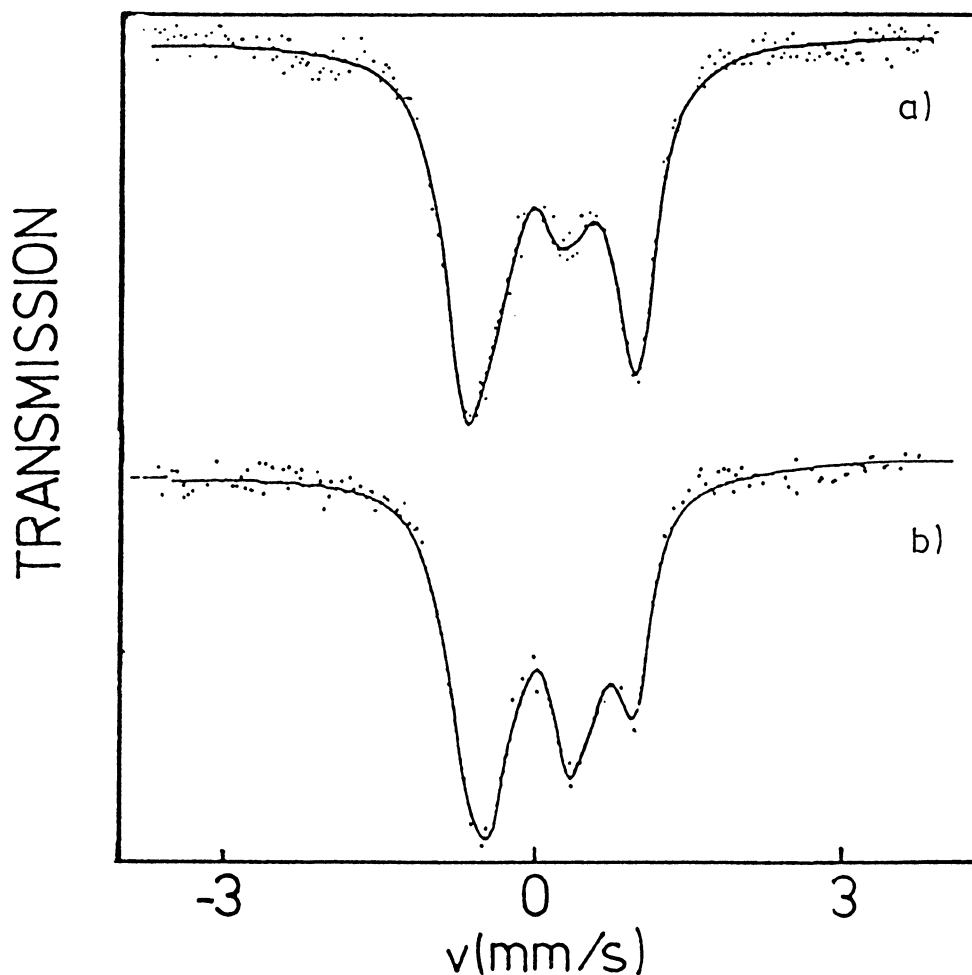


FIGURE 12 ^{57}Fe Mössbauer spectra of $\text{PrBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{6.8}$ (a) and $\text{PrBa}_2(\text{Cu}_{0.99}^{57}\text{Fe}_{0.01})_3\text{O}_{7.1}$ (b) compounds.

the Cu(1) and the Cu(2) sites. This can be considered as the consequence of the suppression of superconductivity in the Pr-containing compound. The effect of Pr can be explained by hole filling, which means that the Pr ion having a valence state greater than three gives an extra electron to neutralize a hole in the CuO network, rendering the system non-superconducting. On the other hand, suppression of superconductivity can also be achieved by the hybridization of Pr 4f states with O 2p-Cu 3d states. Both mechanisms result in a change in the electronic density at the Cu(2) site, which is indicated by the change of the isomer shift of doublet D3. A very similar change as we observed for the Cu(2) site was predicted [32] for the suppression of superconductivity by oxygen loss involving the charge transfer mechanism between the chains and planes [28]. The chains can be pictured as charge reservoirs, and the charge transfer can control the T_c of the superconducting state. The changes in the isomer shift of doublet D1 and D2 belonging to Fe at Cu(1) site can be considered as evidence for the existence of a charge transfer mechanism between the Cu(1) chains and the Cu(2) planes, because otherwise it would be hard to explain these as an effect of the Pr. On the other hand, the observed differences in the isomer shift of doublet D1 are close to those found by ⁵⁷Co experiments [21] with decreasing the oxygen content (Fig. 9).

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