AN ^{57}Fe MÖSSBAUER EFFECT STUDY OF THE HIGH T_c SUPERCONDUCTOR $GdBa_2Cu_3O_{7-y}$

S. JHA, D. SUYANTO and C. MITROS

Department of Physics, University of Cincinnati, Cincinnati, OH 45221, U.S.A.

G. STROINK, Z.M. STADNIK and R.A. DUNLAP

Department of Physics, Dalhousie University, Halifax, N.S., Canada B3H 3J5

and

G.M. JULIAN

Department of Physics, Miami University, Oxford, OH 45056, U.S.A.

Split source ^{57}Fe Mössbauer effect spectroscopy has been performed between 4 K and 295 K on the superconducting perovskite $GdBa_2Cu_3O_{7-y}$. No evidence is seen for magnetic splitting at low temperatures as reported in some split absorber ^{57}Fe Mössbauer experiments on this material. There is evidence for phonon mode softening, as observed for ^{119}Sn Mössbauer spectra of some other high T_c superconductors.

1. Introduction

There has been considerable interest in superconducting perovskites and related metallic oxides since the first report of high T_c superconductivity in 1986 by Bednorz and Müller [1]. Among the most interesting aspects of these materials are their unusual magnetic properties [2]. One of the most versatile techniques for the investigation of magnetic behaviour, as well as microstructure, is Mössbauer spectroscopy. One difficulty in performing Mössbauer measurements on superconducting perovskites is the choice of a suitable probe. In some cases, e.g. for Eu and Gd containing systems in particular, studies can be made using the rare earth atoms present in the material [3–7]. Information concerning the transition metal site is more difficult to obtain. It has been common to introduce Fe or Sn (either natural or enriched in ^{57}Fe or ^{119}Sn) into the structure for the purpose of Mössbauer studies (e.g. [3,8–13]. In many cases, however, the inclusion of a sufficient quantity of Fe or Sn nuclei for the purpose of performing Mössbauer measurements has severe and undesirable effects on the structural and electrical properties of these materials. We have found [14,15] that split source Mössbauer experiments performed using sources prepared by diffusing ^{57}Co into the super-

conductor provide more consistent and reliable results. In the present work, we report on an investigation of the temperature dependence of the ^{57}Fe Mössbauer effect spectrum of $GdBa_2Cu_3O_{7-y}$ doped with ^{57}Co.

2. Experimental results

A sample of $GdBa_2Cu_3O_{7-y}$, with a value of $y \sim 0.3$, was prepared by dissolving stoichiometric quantities of the component oxides in HNO_3. The precipitate, formed by the addition of oxalic acid, was calcined at 600 °C for a few hours, followed by the annealing procedure given previously in ref. [15]. Carrier free ^{57}Co in the form of a $CoCl_2$ solution was deposited on the sample, followed by a final annealing in O_2 at 950 °C for about 12 hours. Sample structure was confirmed by X-ray diffraction measurements and the superconducting transition was determined on the basis of the observation of the Meisner effect to be about $T_c \approx 90$ K.

Mössbauer measurements were made with the split source in a temperature controlled He cryostat and a room temperature ^{57}Fe enriched potassium ferrocyanide absorber with a density of 0.5 mg ^{57}Fe/cm^2. The absorber was oscillated sinusoidally using a Wissel System II Mössbauer spectrometer and the resulting data was transformed to a linear velocity scale.

3. Results and discussion

Mössbauer spectra obtained at various temperatures are shown in fig. 1. Fits to asymmetric doublets were used to extract average quadrupole splittings and isomer shifts. The results of these fits are illustrated in fig. 2. Relative recoil-free fractions derived from the area of the absorption lines in the spectra are also shown in the figure. From figs. 1 and 2 we observe the following:

(i) There is a fairly linear decrease in the isomer shift as function of temperature. The slope of this is -8.0×10^{-4} mm/s/K, in good agreement with the second order Doppler shift for ^{57}Fe.

(ii) There is relatively weak dependence of the mean quadrupole splitting on temperature.

(iii) There is no evidence of anomalous structure in the spectra at 4 K, as has been seen in some previous studies of Fe-doped $GdBa_2Cu_3O_{7-y}$. As this material is not known to order magnetically above 2.2 K [6], the magnetic splitting observed by Tang et al. [12] presumably results from the excessive Fe content of the compound (6 at%).

(iv) In fig. 1 the solid line represents the calculated temperature dependence of the relative recoil-free fraction for a Debye-like density of states and a Debye temperature of 300 K [9]. The down turn in f at low temperatures and the

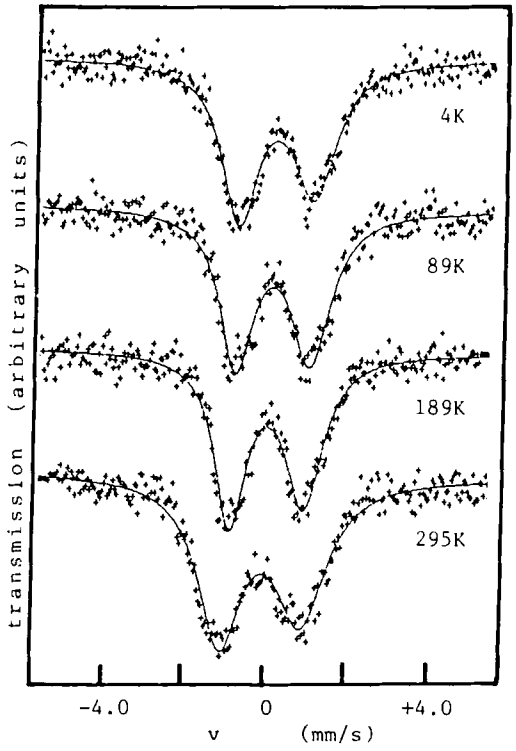

Fig. 1. ^{57}Fe Mössbauer spectra obtained with a split source for $GdBa_2Cu_3O_{7-y}$ as a function of temperature.

deviation from the calculated curve is suggestive of the phonon mode softening observed by Boolchand et al. [9] and Yen et al. [10] by ^{119}Sn Mössbauer spectroscopy in $EuBa_2Cu_3O_{7-y}$ and $YBa_2Cu_3O_{7-y}$, respectively. Other Mössbauer effect studies of phonon modes in high T_c superconductors have yielded variable results. Tsurin et al. [16] have not seen any anomalous behaviour of the recoil free fraction for ^{57}Fe in a Y-Ba-Cu-O superconductor. They have, however, seen evidence for softening of the phonon modes near T_c and a distinction between the Debye temperature of the low temperature phase (300 K). Cherepanov et al. [17] have seen clear evidence of phonon mode softening near T_c for ^{57}Fe in Y-Ba-Cu-O. They do not see any evidence of mode softening at lower temperatures and, as well, find an anomalously high value of the Debye temperature ~ 1450 K. Andrianov et al. [18] have measured the recoil free fraction for ^{119}Sn in Eu-Ba-Cu-O and have seen only a small anomaly near T_c, which they attribute to mode softening. Their measurements otherwise agree well with a Debye model with $\theta = 290$ K. While there is some evidence of mode softening from Fe and Sn probes in high T_c superconductors, the evidence shows considerable variation from one study to another. On the other hand, rare earth Mössbauer studies have shown no anomalies in the recoil free fraction and this is generally

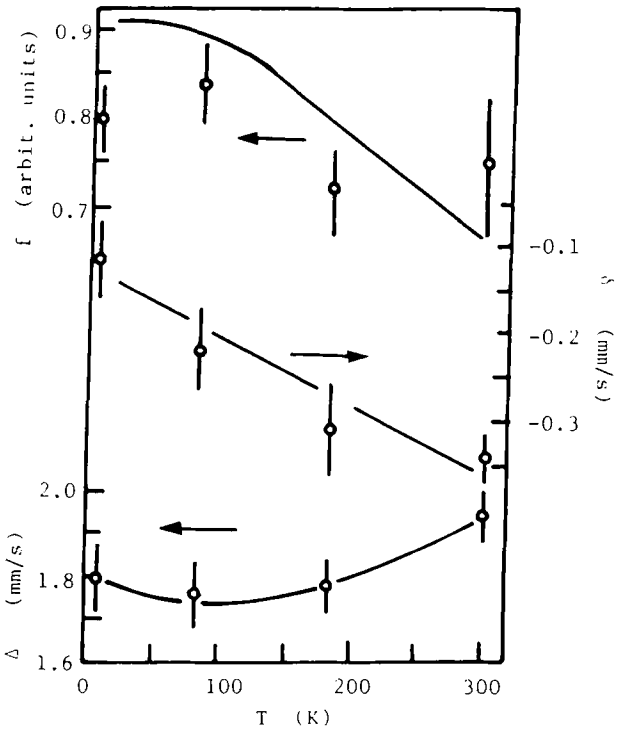

Fig. 2. Relative recoil-free fraction, f, isomer shift relative to room temperature α-Fe, δ, and mean quadrupole splitting, Δ, of ^{57}Fe in $GdBa_2Cu_3O_{7-y}$. The solid line represents the calculated f for a Debye temperature of 300 K.

viewed as due to differences in the vibrational modes for Cu-sites and rare earth sites [18].

In conclusion, we have seen that the quadrupole doublet nature of the ^{57}Mössbauer spectra of $GdBa_2Cu_3O_{7-y}$ is consistent with the lack of magnetic ordering down to 4 K and is expected for materials with sufficiently low concentration of potentially magnetic impurities. As well, the recoil free fraction is suggestive of the phonon mode softening at the transition metal sites observed by ^{119}Sn Mössbauer spectroscopy at low temperatures in similar systems.

Acknowledgements

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