

Mössbauer studies of Gd-doped bismuth-based ceramic superconductors

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Abstract. The results of ¹⁵⁵Gd Mössbauer studies (above 1.5 K) of the oxides, Bi_{3.5}Gd_{0.5}Ca₃Sr₃Cu₄O_y and Bi₂Sr₂Ca_{1-x}Gd_xCu₂O_y ($x = 0.25$ and 0.5) are reported. The observed electric quadrupolar split resonance patterns suggest that Gd ions prefer to occupy Ca site in both series. The spectral features give evidence for paramagnetic relaxation of isolated Gd ions at low temperatures.

Keywords: Gd-Mössbauer; ceramic superconductors.

1. Introduction

The bismuth-based ceramic superconducting system, Bi–Ca–Sr–Cu–O (Maeda *et al* 1988) seems to behave similar to the Y–Ba–Cu–O system (Wu *et al* 1987) as far as the influence of rare-earth substitution (partially at the Bi site) on superconductivity is concerned (Sampathkumaran *et al* 1988; Ikeda *et al* 1988). Our careful investigation of the series of compounds Bi_{4-x}RE_xCa₃Sr₃Cu₄O_y (with RE = La, Eu and Gd, $x \leq 0.5$) prepared under identical conditions shows that La suppresses the superconducting transition temperature (T_c) as well as the superconducting volume fraction of this Bi-based superconductor much faster than Eu and Gd substituents; in the latter two cases, there is practically no variation of T_c at all (≈ 65 K). This is contrary to expectations from magnetic pair-breaking effects in conventional superconductors, but in conformity with the knowledge on Y–Ba–Cu–O system. We explained this anomalous behaviour in terms of the influence of covalent mixing of extended $4f$ wavefunction. While arriving at this conclusion, we (Ikeda *et al* 1988) argued on the basis of lattice constant measurements that the attempts to replace Bi by RE result in the occupation of RE at the Ca site. In order to put our views on a firm ground, we have carried out ¹⁵⁵Gd Mössbauer measurements on Bi_{3.5}Gd_{0.5}Ca₃Sr₃Cu₄O_y ($T_c \approx 65$ K) as well as on Bi₂Sr₂Ca_{1-x}Gd_xCu₂O_y ($x = 0.25$ and 0.5 ; y -undetermined, $T_c \approx 80$ K and $T_c \approx 20$ K respectively). Preliminary results on some of these compounds have been communicated for publication (Wortmann *et al* 1989).

2. Experimental

The samples employed in the present investigation are the same as those used earlier (Sampathkumaran *et al* 1988, 1989). The ¹⁵⁵Gd Mössbauer experiments, using

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the 86.5 keV ($5/2 \rightarrow 3/2$) gamma resonance, were performed in standard geometry at various temperatures between 1.5 and 80 K on sintered pellets (600 mg/cm² thick), employing a liquid-helium cryostat and a sinusoidal Doppler drive for moving the source.

3. Results and discussion

Figure 1 displays ¹⁵⁵Gd-Mössbauer spectra of $\text{Bi}_{3.5}\text{Gd}_{0.5}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$ at various temperatures. The spectra reveal an electric-quadrupole-split hyperfine pattern typical for the ¹⁵⁵Gd Mössbauer resonance (Wortmann *et al* 1987, 1988). There is clearly a main narrow-split quadrupole doublet (marked A) and a wider split much weaker component (marked B) visible in the spectra of figure 1. We also checked our spectra for the absence of unreacted Gd_2O_3 in our specimen (to a few per cent) by taking into account the well-known Mössbauer spectrum of Gd_2O_3 (Cashion *et al* 1972) in the data analysis. From the careful least-squares fit analysis of the spectral shape of

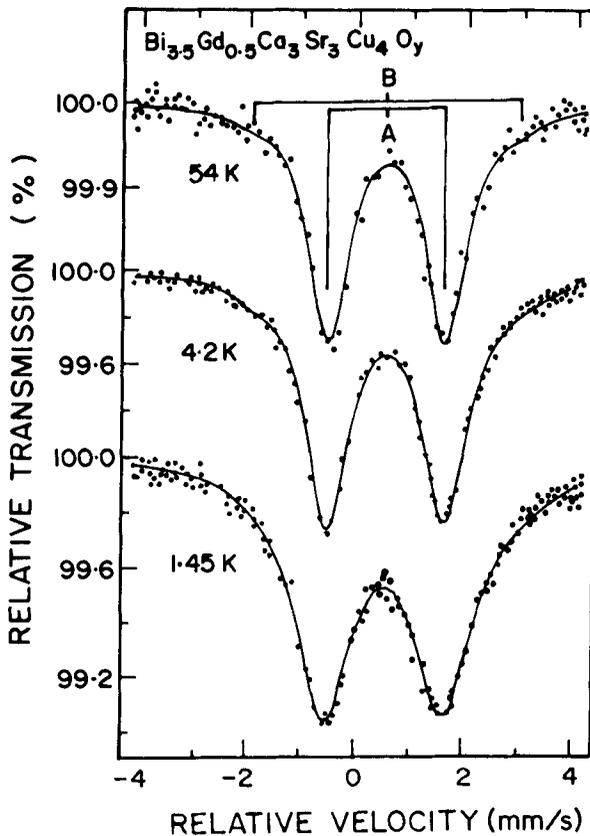


Figure 1. ¹⁵⁵Gd-Mössbauer absorption spectra $\text{Bi}_{3.5}\text{Gd}_{0.5}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$ at different temperatures. The intense doublet A indicating the splitting of the $l = 3/2$ ground state and the weak doublet B are indicated by vertical bars. The solid lines through the data points represent the results of least-square fits.

the dominant quadrupole doublet, A, we conclude that it consists of a superposition of at least three almost equally-split patterns, indicating a distribution of the electric field gradient by about 10% around the average value $V_{zz} = (-)8.3 \times 10^{17} \text{ V/cm}^2$. The relative weight of the weak quadrupole doublet, B, is about 6% and is characterized by $V_{zz} \approx 18.5 \times 10^{17} \text{ V/cm}^2$. The above values of V_{zz} were derived with $Q(3/2) = 1.59$ barn for the electric-quadrupole moment of the ^{155}Gd nuclear groundstate. The linewidth of the dominating doublet, A, exhibits an increase with decreasing temperature (FWHM at 80 K: 0.88(10) mm/s; at 54 K: 0.90(2) mm/s; at 10 K: 1.00(6) mm/s; at 4.2 K: 1.04(2) mm/s; and at 1.45 K: 1.40(4) mm/s) as is seen in figure 1, particularly for the low-temperature spectra. This indicates the presence of paramagnetic relaxation of relatively isolated Gd ions when compared with concentrated systems like Gd_2O_3 (Cashion *et al* 1973). The observed isomer shift for the doublet A, $S = 0.52$ mm/s, is identical to that of $\text{GdBa}_2\text{Cu}_3\text{O}_7$ (Wortmann *et al* 1987) and Gd_2O_3 (Cashion *et al* 1973). We also carried out Gd Mössbauer effect measurements on $\text{Bi}_{3.5}\text{Gd}_{0.5}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$ and we do not observe (not shown in figure) the doublet with $V_{zz} = 18.5 \times 10^{17} \text{ V/cm}^2$.

We now present the results of our investigation on the specimens $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Gd}_x\text{Cu}_2\text{O}_y$ in order to get an insight regarding the site occupation of Gd ions. The Gd Mössbauer spectra for two concentrations are shown in figures 2 and 3 at a few selected temperatures. For both the concentrations, essentially a single doublet is observed and the values of V_{zz} are: $-8.18(3) \times 10^{17} \text{ V/cm}^2$ for $x = 0.25$ and $-7.53(2) \times 10^{17} \text{ V/cm}^2$ for $x = 0.5$. The marginal difference in the values of V_{zz} between these two concentrations may be associated with the differences in the lattice para-

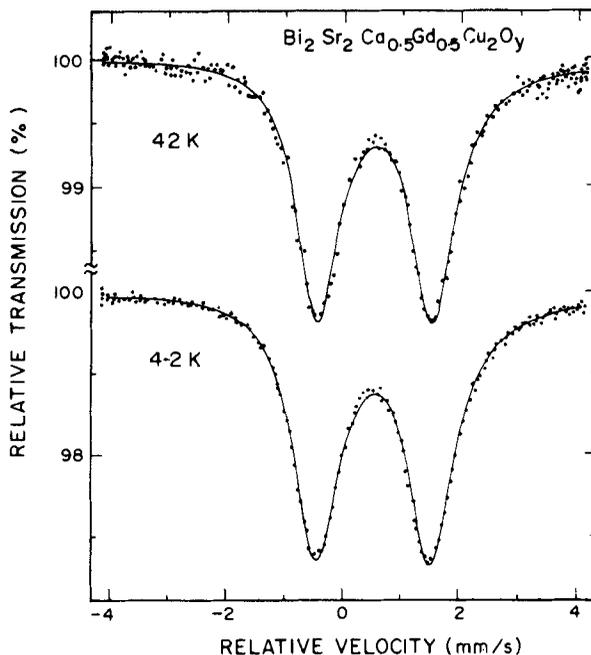


Figure 2. ^{155}Gd -Mössbauer absorption spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.5}\text{Gd}_{0.5}\text{Cu}_2\text{O}_y$ at different temperatures.

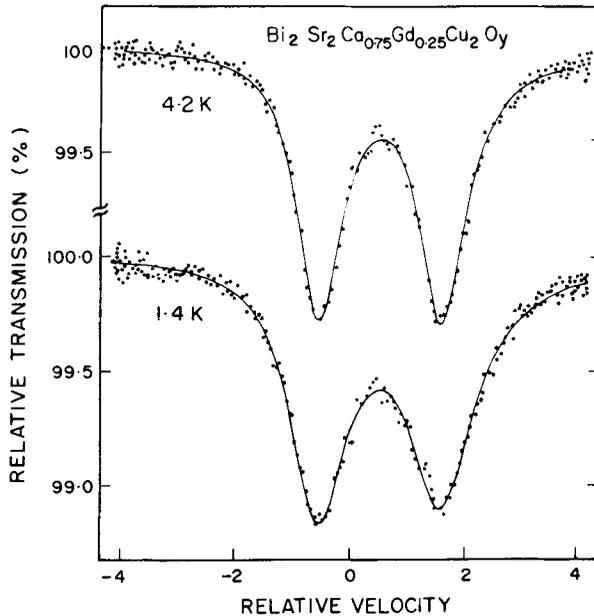


Figure 3. ^{155}Gd -Mössbauer absorption spectra of $\text{Bi}_2\text{Sr}_2\text{Ca}_{0.75}\text{Gd}_{0.25}\text{Cu}_2\text{O}_y$ at different temperatures.

eters, oxygen content, as well as carrier density concentration (Sampathkumaran *et al* 1989; Tamegai *et al* 1989). The essential point to be noted is that there is no evidence for the presence of another doublet in the Mössbauer spectra with a higher value of V_{zz} and that the value of V_{zz} for the intense component in $\text{Bi}_{3.5}\text{Gd}_{0.5}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$ is nearly the same as that observed in other specimens. Isomer shift values are also the same for all the specimens. These observations microscopically prove that the attempts to substitute Gd ion at the Bi site always result in the considerable occupation of this ion at the Ca site, in conformity with the conclusions from the lattice constants data (Ikeda *et al* 1989). The weaker component observed in $\text{Bi}_{3.5}\text{Gd}_{0.5}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$ may, therefore, arise from those Gd ions occupying Bi site. From the non-observation of this feature in $\text{Bi}_{3.7}\text{Gd}_{0.3}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$, we conclude that Gd initially prefers Ca site.

The occupation of Gd at the Ca site without depressing superconductivity (Sampathkumaran *et al* 1988) bears important consequences considering the crystallographic features of the Bi-based system. The Cu–O layers, which are presumably responsible for superconductivity, are the nearest to Ca(Gd) layer. Therefore, the partial occupation of Gd ions in Ca layers does not seem to influence superconductivity as monitored by susceptibility and microwave absorption studies (Sampathkumaran *et al* 1989). This then means that superconductivity is not suppressed by the magnetic moments of localized $4f$ electrons (in small concentrations) in this system. On the other hand, La doped in small concentrations under identical heat-treatment conditions depresses superconductivity (Sampathkumaran *et al* 1988; Ikeda *et al* 1988). This depression of T_c by La ions noted earlier by us may be attributed to the presence of more extended $4f$ electronic states hybridizing with the ligand band, as proposed for the first time (Ikeda *et al* 1988; Neukirch *et al* 1988). This idea

finds support in later investigations by various other groups (Kang *et al* 1989; Li *et al* 1989).

An analogous study was performed on an Eu-substituted Bi system, $\text{Bi}_{3.5}\text{Eu}_{0.5}\text{Ca}_3\text{Sr}_3\text{Cu}_4\text{O}_y$. We observed a single ^{151}Eu Mössbauer line with an isomer shift of $S = +0.70$ mm/s (with respect to the SmF_3 source) that is typical for insulating trivalent Eu compounds. The analysis of the broadened and slightly asymmetric resonance line in terms of an electric-quadrupole interaction (as expected from the Gd system) resulted in a negative electric-field gradient, $V_{zz} = -5.0(5) \times 10^{17}$ V/cm². The absolute value of $V_{zz}(\text{Eu})$ is roughly 2/3 of that observed for the Gd system. We expect that the chemical environment of substituted Eu is the same as that of substituted Gd. In case of Gd, there is no contribution of the 4f shell to V_{zz} due to the zero orbital angular momentum of the $S = 7/2$ spin state. Therefore, $V_{zz}(\text{Gd})$ represents exclusively the electric-field gradient of the lattice. The reduction of V_{zz} in the Eu system is then consistent with a small 4f contribution of the $J = 2$ higher lying state of the Eu^{3+} ion, which amounts to roughly 1/3 of V_{zz} (lattice) and has the opposite sign (Bauminger *et al* 1973; Wortmann 1988).

4. Acknowledgements

The authors thank Dr A Kolodziejczyk for his help in the initial stage of the Mössbauer measurements. One of the authors (EVS) would like to acknowledge the encouragement by Prof. R Vijayaraghavan. This work was supported by the Bundesminister für Forschung and Technologie, project no. 13N54842.

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