

## Electric-quadrupole interaction at the Eu site in a high- $T_c$ superconductor $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$

Z. M. Stadnik, G. Stroink, and R. A. Dunlap

*Department of Physics, Dalhousie University, Halifax, Nova Scotia, Canada B3H 3J5*

(Received 18 January 1989)

The electric-quadrupole interactions at the Eu site in a high- $T_c$  superconductor  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  have been studied at 4.2 and 300 K with  $^{151}\text{Eu}$  Mössbauer spectroscopy. It is found that the quadrupole coupling constant is small and negative at both temperatures. This is at variance with the theoretical predictions published in the literature, which are based on calculations of the electric-field-gradient tensor using a point-charge model. The reasons for the failure of such calculations applied to various high- $T_c$  superconductors published in the literature are discussed.

### I. INTRODUCTION

Studies of electric-quadrupole interactions with nuclear quadrupole resonance (NQR), nuclear magnetic resonance (NMR), Mössbauer spectroscopy (MS), or perturbed angular correlations (PAC) provide valuable complementary information about the local structure, the local electronic states, and the chemical bonds associated with various ions in crystalline and amorphous compounds. In these studies one measures the quadrupole coupling constant  $eV_{zz}Q$ , where  $-e$  is the charge of the electron,  $V_{zz}$  is the principal component of the electric-field-gradient (EFG) tensor, and  $Q$  is the nuclear quadrupole moment.<sup>1</sup> Sometimes the asymmetry parameter  $\eta$  is also determined. By comparing the experimental values of  $V_{zz}$  and  $\eta$  with the calculated ones, it is possible in principle to test different theoretical models which attempt to describe local properties of an ion in a given system.

Mössbauer studies of high- $T_c$  superconductors have been performed using mainly  $^{57}\text{Fe}$  nuclei of Fe atoms substituting Cu atoms. The purpose of such studies has been to characterize local structure and the properties of Cu atoms. Since there are two crystallographically inequivalent Cu sites in 1:2:3 high- $T_c$  superconductors, and due to the fact that the substitution process of Cu by Fe atoms is preferential and leads to chemical disorder,  $^{57}\text{Fe}$  Mössbauer spectra are complex. Consequently, in spite of many claims in the literature,<sup>2-4</sup> it has not been possible as yet to make an unambiguous assignment of the observed Mössbauer subspectra to specific local configurations. Furthermore, since the majority of  $^{57}\text{Fe}$  MS experiments were performed on polycrystalline high- $T_c$  compounds, the sign of  $V_{zz}$  at the two Cu sites, whose knowledge is crucial for a comparison with the predictions of theoretical models, was not determined. In those few cases, when attempts have been made to determine the  $V_{zz}$  sign, contradictory results<sup>2-4</sup> were obtained (analysis of experimental data in Ref. 2 is superior to that in Refs. 3 and 4, and consequently, the  $V_{zz}$  sign given in Ref. 2 is more reliable than the one given in Refs. 3 and 4).

$\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$  ( $R$  is a rare-earth element) high- $T_c$  superconductors can be also studied with MS using Mössbauer nuclei of rare-earth (RE) elements. Here the situation is more straightforward. First, RE elements occupy only one crystallographic site, and consequently, Möss-

bauer spectra are essentially simpler. Second, Mössbauer RE elements constitute an integral part of these superconductors and, therefore, a substitution process is not necessary. It should be noted that although various RE ions do not influence appreciably the superconducting properties of  $\text{RBa}_2\text{Cu}_3\text{O}_{7-x}$  compounds, their presence is indispensable for the existence of these compounds. They can, therefore, be used as local probes to study possible changes of various characteristics of these compounds as a function of temperature, pressure, and other parameters. In this paper we are concerned with  $^{151}\text{Eu}$  MS studies of the high- $T_c$  superconductor  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ .

The first  $^{151}\text{Eu}$  MS experiments on  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  were aimed at determining the oxidation state of the Eu ions.<sup>5,6</sup> The  $^{151}\text{Eu}$  Mössbauer spectra, which at first glance appear to be in the form of a broadened single line, were fitted with a single Lorentzian. From the value of the isomer shift  $\delta$  it was concluded that Eu ions are, as could be expected, in a trivalent oxidation state.<sup>5,6</sup> The procedure of fitting  $^{151}\text{Eu}$  Mössbauer spectra with single Lorentzians was used in subsequent  $^{151}\text{Eu}$  Mössbauer studies of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  (Refs. 7 and 8) and other Eu-containing high- $T_c$  superconductors.<sup>9</sup> Such a fitting procedure is, however, a crude approximation and leads to the loss of valuable information on the EFG tensor.

The  $mmm$  point symmetry of the Eu site ( $1h$  site in Wyckoff's notation,  $Pmmm$  space group) in  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  requires that the EFG tensor exists and is not axially symmetric (the asymmetry parameter<sup>1</sup>  $\eta \neq 0$ ). Consequently,  $^{151}\text{Eu}$  Mössbauer spectra of Eu-containing 1:2:3 high- $T_c$  superconductors, which by eye inspection look like broadened single lines,<sup>5-9</sup> are in fact due to the presence of a small quadrupole interaction. As will be shown below, the absolute value of the quadrupole coupling constant and its sign can be determined unambiguously from an appropriate fit of a good-quality Mössbauer spectrum. This is an important observation, since  $^{151}\text{Eu}$  Mössbauer quadrupole spectra of polycrystalline samples,<sup>1,10</sup> as opposed to corresponding  $^{57}\text{Fe}$  spectra,<sup>11</sup> provide both the absolute value and the sign of  $V_{zz}$ . It is especially the knowledge of the  $V_{zz}$  sign which is essential for discriminating between different theoretical models used to calculate  $V_{zz}$ .

Calculations of the EFG tensor at the Eu site in  $\text{EuBa}_2\text{Cu}_3\text{O}_7$  have been recently performed, using an ionic

model of a crystal lattice, for two different distributions of nonstoichiometry holes among the Cu and O ions.<sup>12</sup> For both distributions the value of  $eV_{zz}Q_g$  ( $Q_g$  is the nuclear quadrupole moment of the ground state) turned out to be positive: 106 MHz (6.10 mm/s) for the nonstoichiometry holes distributed equally among the chain Cu and O ions, and 250 MHz (14.40 mm/s) for the nonstoichiometry holes shared equally among the Cu and O ions in the  $\text{CuO}_2$  plane. These calculated values were compared with the *absolute* value  $|eV_{zz}Q_g| = 125(10)$  MHz [7.20(0.56) mm/s] obtained experimentally.<sup>13</sup> On the basis of this comparison, which assumes a positive experimental value for  $eV_{zz}Q_g$ , it was concluded that there is a preference of the holes for the CuO chain.<sup>12</sup>

It will be shown in this paper that, contrary to the conclusion of the previous  $^{151}\text{Eu}$  MS study<sup>13</sup> of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$ , both the absolute value and the sign of  $eV_{zz}Q_g$  can be determined unambiguously from a good quality spectrum and its suitable analysis. The sign of  $eV_{zz}Q_g$  turns out to be negative at 4.2 and 300 K. Consequently, the calculated values of  $eV_{zz}Q_g$  (Ref. 12) are incorrect and the interpretation<sup>12</sup> based on the claimed agreement between theory and experiment is unjustified. The reasons for the incorrectness of the EFG calculations<sup>12,14,15</sup> at different sites in various high- $T_c$  superconductors will be discussed.

## II. EXPERIMENT

The polycrystalline compound  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  was prepared through a solid-state reaction of appropriate amounts of  $\text{Eu}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$ , each 99.99% pure. The actual preparation process consisted of grinding, pressing, and sintering several times under conditions similar to those described elsewhere.<sup>16</sup>

The resulting powder was characterized by a Siemens D500 x-ray diffractometer using  $\text{Cu } K\alpha$  radiation. Resistivity was measured by a standard four-probe method. Mössbauer measurements were conducted at 300 and 4.2 K using the 21.53 keV transition in  $^{151}\text{Eu}$ . The Mössbauer spectra were recorded with a Wissel II spectrometer, which was calibrated with an iron foil.<sup>17</sup> A sinusoidal reference signal was used, resulting in two mirror-image spectra that were folded. A newly purchased Amersham 100 mCi  $^{151}\text{Sm}(\text{SmF}_3)$  source was kept at room temperature. The surface density of the Mössbauer absorber was  $49.8 \text{ mg/cm}^2$ .

## III. RESULTS AND DISCUSSION

The x-ray-diffraction pattern of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  indicates a high-quality single-phase material possessing an orthorhombic structure. The values of the unit-cell parameters obtained from the fit,  $a = 3.840(2)$  Å,  $b = 3.905(2)$  Å, and  $c = 11.698(5)$  Å, are in a good agreement with the literature data.<sup>18</sup> The resistivity measurements gave the superconducting transition temperature  $T_c = 93.7(1)$  K, which refers to the resistive midpoint, and the transition width  $\Delta T_c = 0.6(1)$  K, which was deter-

mined from the 10% and 90% points of the resistive transition. The sharpness of the superconducting transition as measured by  $\Delta T_c$ , which is smaller than  $\Delta T_c$  reported for other polycrystalline  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  samples<sup>19</sup> and comparable to  $\Delta T_c$  for single crystals,<sup>20</sup> confirms the high quality of the sample produced.

$^{151}\text{Eu}$  Mössbauer spectra at 300 and 4.2 K appear, on casual inspection, as single lines. However, as a visual inspection of the fit to the 300-K spectrum using a single Lorentzian [Fig. 1(a)] shows, this does not describe properly the experimental spectrum. This is especially clearly reflected by the presence of structure in the plot of the difference between the experimental and fitted spectra shown in Fig. 1(b). The same behavior is observed for the 4.2-K spectrum. The failure of a single-line fit indicates that the experimental spectrum is due to the presence of a small quadrupole interaction. The values of  $\delta$  (relative to the source), the full linewidth at half maximum  $\Gamma$ , and  $\chi^2$  (defined as  $[\sum_{i=1}^k (y_i^{\text{expt}} - y_i^{\text{theor}})^2 / y_i^{\text{expt}}] / (k - m)$ , where  $k$  and  $m$  are, respectively, the number of experimental points and the number of fitted parameters) obtained from the single-line fits are 0.741(9) mm/s, 2.745(33) mm/s, and 1.741 for the 300-K spectrum, and 0.792(12) mm/s, 2.801(46) mm/s, and 1.469 for the 4.2-K spectrum. The natural linewidth for the 21.53 keV transition in

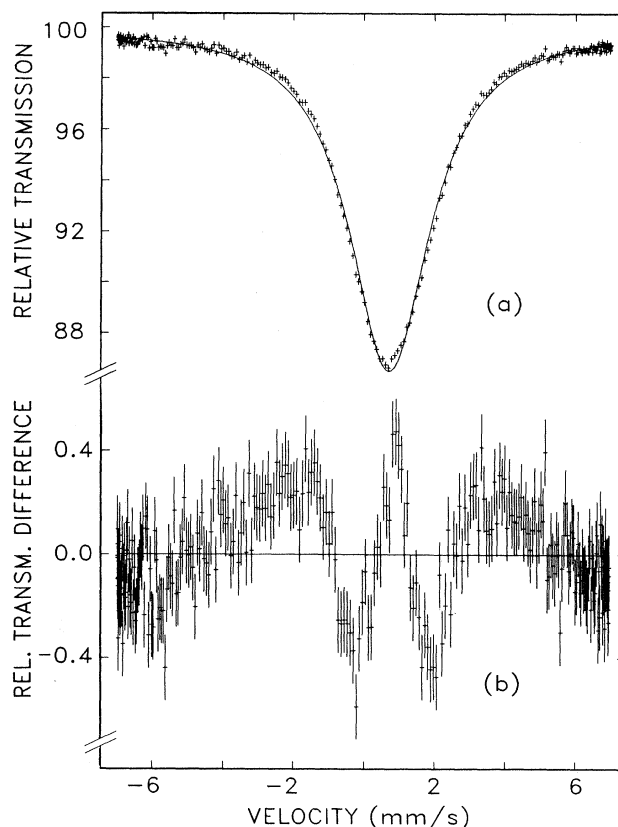


FIG. 1. (a)  $^{151}\text{Eu}$  Mössbauer spectrum of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  at 300 K. The solid line is a least-squares fit to a single Lorentzian. (b) Difference between the experimental and fitted spectra. The vertical bars indicate the statistical error.

$^{151}\text{Eu}$ ,  $\Gamma_{\text{nat}}$ , is equal to 1.31 mm/s.<sup>21</sup> However, the linewidth of the  $^{151}\text{Sm}(\text{SmF}_3)$  source is broader than  $\Gamma_{\text{nat}}$  due to the noncubic  $\text{SmF}_3$  source matrix. For the fresh source used in our experiments, the source linewidth was 2.14 mm/s. The difference of 0.605 mm/s between the  $\Gamma$  value obtained from a single-line fit of the 300-K spectrum of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  and the source linewidth is much larger than that expected from a finite absorber thickness line broadening.<sup>1,21</sup> This also indicates that the experimental line shape is the result of a small quadrupole interaction.

Using the method described by Shenoy and Dunlap,<sup>10</sup>  $^{151}\text{Eu}$  Mössbauer spectra of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  at 300 and 4.2 K were fitted with 12 component lines of the same linewidth, which are present for a nonaxially symmetric EFG tensor. The positions of the component lines depend on  $\delta$ ,  $eV_{zz}Q_g$ ,  $\eta$ , and the ratio  $R_Q = Q_e/Q_g$  of the excited and ground-state nuclear quadrupole moments, whereas their intensities are a function of  $\eta$ .<sup>10</sup> The value of  $R_Q$  is 1.312.<sup>21</sup>

As can be seen from Fig. 2(a), the fit assuming a nonzero quadrupole interaction describes satisfactorily the shape of the experimental spectrum. This is also shown in Fig. 2(b) by the lack of structure in the difference spec-

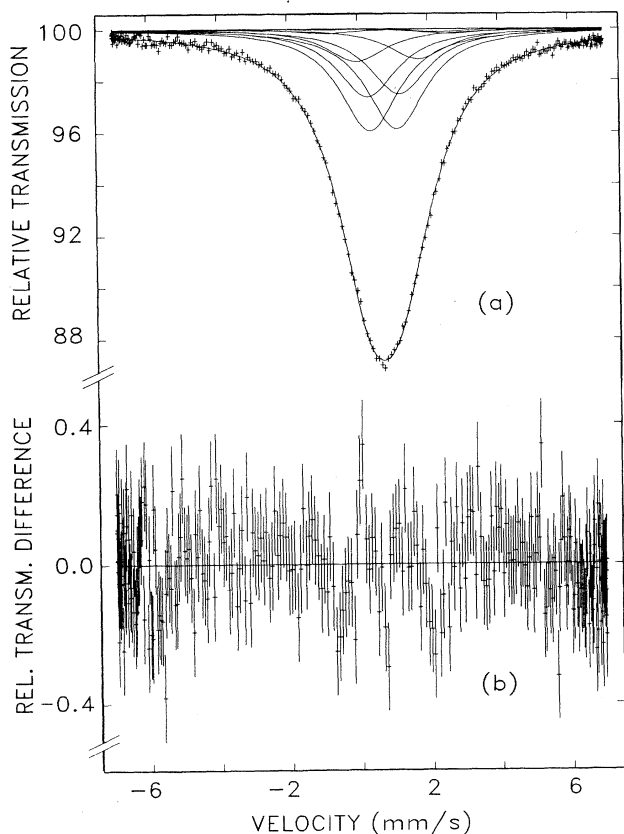


FIG. 2. (a)  $^{151}\text{Eu}$  Mössbauer spectrum of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  at 300 K. The solid line is a least-squares fit assuming a nonzero quadrupole interaction. The component lines are also shown. (b) Difference between the experimental and fitted spectra. The vertical bars indicate the statistical error.

trum. The parameters  $\delta$ ,  $eV_{zz}Q_g$ ,  $\eta$ ,  $\Gamma$ , and  $\chi^2$  obtained from the fit are 0.760(7) mm/s,  $-5.313(229)$  mm/s, 0.80(5), 2.286(58) mm/s, and 0.998 for the 300-K spectrum, and 0.824(12) mm/s,  $-5.726(325)$  mm/s, 0.70(5), 2.340(83) mm/s, and 1.051 for the 4.2 K spectrum. The fit assuming a nonzero quadrupole interaction is clearly superior to the single-line fit, as shown by significantly smaller values of  $\chi^2$  and as seen by visual inspection (Figs. 1 and 2). Also the  $\Gamma$  values obtained from the quadrupole fits are physically acceptable. We thus conclude that the quadrupole coupling constant at the Eu site in the high- $T_c$  superconductor  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  is small and negative, both at 300 and 4.2 K, and that its absolute value slightly increases with decreasing temperature.

In order to test the sensitivity of the fit to the sign of  $eV_{zz}Q_g$ , attempts were made to fit the  $^{151}\text{Eu}$  Mössbauer spectra with positive values of  $eV_{zz}Q_g$ . These attempts failed since the fits gave values of  $\chi^2$  much larger than the values obtained from the single-line fits and the difference spectra contained distinct structural features. The fits with negative values of  $eV_{zz}Q_g$  strongly depend on the value of  $\eta$ . This is demonstrated for the 300-K spectrum

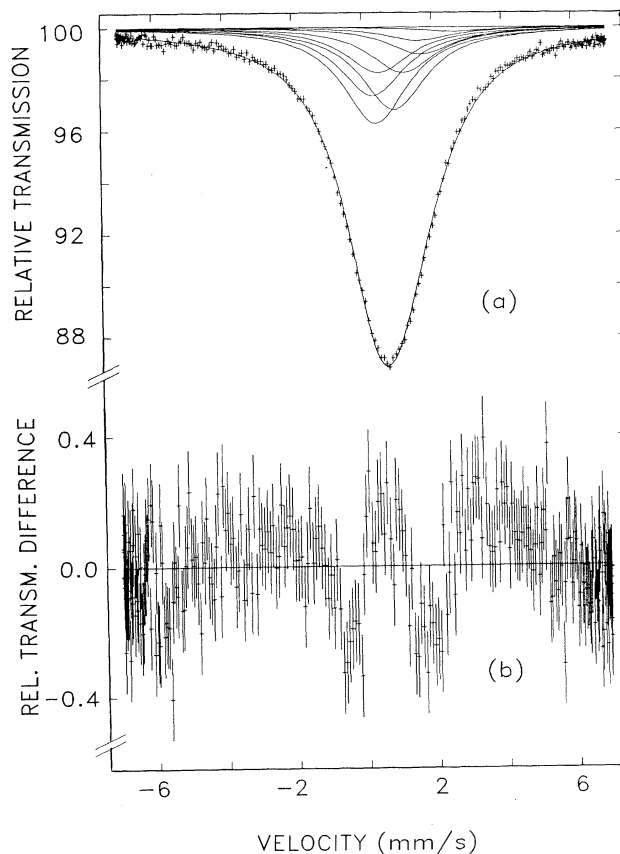


FIG. 3. (a)  $^{151}\text{Eu}$  Mössbauer spectrum of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  at 300 K. The solid line is a least-squares fit assuming a nonzero quadrupole interaction with the fixed value  $\eta=0$ . The component lines are also shown. (b) Difference between the experimental and fitted spectra. The vertical bars indicate the statistical error.

in Fig. 3(a), where the fit was made for the  $\eta$  value fixed to zero. This fit clearly fails as shown by the difference spectrum [Fig. 3(b)] and as evidenced by an increase of  $\chi^2$  to 1.191. These tests demonstrate the sensitivity of the shape of the  $^{151}\text{Eu}$  Mössbauer spectra to both the sign of  $eV_{zz}Q_g$  and the value of  $\eta$ .

The value of  $\delta$  confirms that Eu ions occur in the trivalent oxidation state.<sup>22</sup> The decrease of  $\delta$  on going from 4.2 to 300 K is caused by the second-order Doppler effect.<sup>1,21</sup>  $^{151}\text{Eu}$  MS studies of the perovskites  $\text{EuMO}_3$  ( $M = \text{Co, Cr, Mn, Fe, and Sc}$ ) showed<sup>23,24</sup> that  $eV_{zz}Q_g$  is small and negative. Since the crystallographic structure of the high- $T_c$  superconductor  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  is based on a perovskite structure, one can expect also a negative sign of  $eV_{zz}Q_g$  in this compound, which is indeed the case. This additionally confirms the correctness of the analysis presented above.

A negative sign of  $eV_{zz}Q_g$  at the Eu site in  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  found experimentally in this work is at variance with the positive sign obtained theoretically.<sup>12</sup> Also the negative  $V_{zz}$  value at the Cu(2) site in  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  determined experimentally<sup>2</sup> using  $^{57}\text{Fe}$  MS does not agree with the positive value predicted theoretically.<sup>12,14,15</sup> The reasons for the failure of the EFG calculations in the high- $T_c$  superconductors<sup>12,14,15</sup> to predict correctly the absolute value and the sign of  $V_{zz}$  are discussed below.

In general, the EFG tensor in an ionic compound consists of two contributions: one arising from the charge distribution of the surrounding ions in the crystal lattice (lattice contribution), and another arising from the electron distribution in incompletely filled electronic shells of the local probe (NQS, NMR, MS, or PAC) atom (valence contribution). Any component  $V_{ij}$  of the EFG tensor at a nuclear site may be written as

$$V_{ij} = (1 - \gamma_\infty)V_{ij}^{\text{lat}} + (1 - R)V_{ij}^{\text{val}}, \quad (1)$$

where  $\gamma_\infty$  and  $R$  are the Sternheimer antishielding and shielding factors, respectively.<sup>1</sup> For a calculation of the lattice contribution in ionic compounds, a point charge model is usually used. In this model a multipole expansion of the electric potential is used, and the monopole and the dipole contributions to  $V_{ij}$  are calculated (the higher than dipole contributions are usually negligibly small).<sup>25,26</sup> It has been shown for various ionic compounds that the dipole contribution to  $V_{ij}^{\text{lat}}$  cannot be neglected.<sup>11,25,26</sup> This contribution was not taken into account in the  $V_{ij}^{\text{lat}}$  calculations at various sites in the high- $T_c$  superconductors,<sup>12,14,15</sup> and this is the first probable cause of their disagreement with experiment. Second, the point charge model itself, which neglects charge transfer and covalency effects (always present to a larger or smaller degree in ionic compounds), is a very crude approximation of a real physical situation in these compounds. To use this model as the only theoretical basis for calculating  $V_{zz}^{\text{lat}}$  in the high- $T_c$  superconductors<sup>12,14,15</sup> for comparison with the experimental  $V_{zz}$ , which is necessary to discriminate between various hypothetical charge distributions on different ions, is obviously incorrect. If the point charge model is still being used in the literature,<sup>11,25,26</sup> it is only because of its simplicity and its ability to predict *qualitatively*, in certain cases, trends in the changes of  $V_{zz}$  with

composition for a given series of ionic compounds. Third, as discussed in detail in Ref. 26, there is a significant contribution to the EFG tensor in oxides [overlap contribution  $(1 - R)V_{ij}^{\text{ov}}$ ], which arises from the overlap distortion of the filled orbitals by the ligands. This contribution, which is more important for the Cu sites than for the RE sites (because of the shorter Cu-O distances in comparison to the R-O distances), was ignored in the  $V_{zz}$  calculations in the high- $T_c$  superconductors. This is another probable reason for their failure. Fourth, for the calculation of  $eV_{zz}Q_e$  at  $^{57}\text{Fe}$  nuclei in  $\text{YBa}_2(\text{Cu}_{1-x}\text{Fe}_x)_3\text{O}_{7-x}$  the values of  $Q_e$  used were  $0.213b$  (Ref. 12) and  $0.21b$  (Ref. 14). These values are incorrect. A theoretical analysis<sup>27</sup> of the Mössbauer data on  $\text{FeCl}_2$  and  $\text{FeBr}_2$  molecules trapped in an argon matrix, which involves the evaluation of the EFG tensor at  $^{57}\text{Fe}$  nuclei using electronic wave functions obtained by the first-principle unrestricted Hartree-Fock procedure, yields the value of  $0.082b$  for  $Q_e$ . This is substantially smaller than the previously accepted value of about  $0.20b$ . Subsequently, the new value of  $Q_e$  was supported by an independent line of reasoning based on nuclear physics experimental data and shell-model calculations.<sup>28</sup> Additional confirmation for the new value of  $Q_e$  came from the analysis of  $^{57}\text{Fe}$  quadrupole interaction data in transition-metal alloys,<sup>29</sup> and from covalency calculations in  $\alpha\text{-Fe}_2\text{O}_3$ .<sup>30</sup> Thus, the new value of  $Q_e$  is now firmly established and the use of the old  $Q_e$  value of about  $0.21b$  in the calculations of  $eV_{zz}Q_e$  in Fe-containing high- $T_c$  superconductors<sup>12,14</sup> leads to its overestimation by the factor of 2.6. Consequently, the claims<sup>12,14</sup> regarding the agreement between the calculated and experimental values of  $eV_{zz}Q_g$  based on the old value of  $Q_e$  are invalid.

Contrary to persisting beliefs, a calculation of the EFG tensor in solids is a complex and challenging theoretical endeavor. While experimental techniques for obtaining  $eV_{zz}Q$  are highly sophisticated, the theoretical understanding of the origin of the EFG tensor is poor. In fact, modern first-principle EFG calculations, which are necessary to make any meaningful comparison between experiment and theory, are rare, and those available were performed for simple systems.<sup>27,29-31</sup> First-principle EFG calculations in the high- $T_c$  superconductors, when available, will undoubtedly provide a better insight to the electronic structure and the charge distribution at various sites in these oxides. In view of the arguments presented above, the failure of the point charge model<sup>12,14,15</sup> to correctly calculate the EFG tensor in high- $T_c$  superconductors is hardly surprising.

#### IV. SUMMARY

$^{151}\text{Eu}$  Mössbauer spectra of a high-quality high- $T_c$  superconductor  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-x}$  were measured at 300 and 4.2 K. Their analysis shows that the sign of the quadrupole coupling constant  $eV_{zz}Q_g$  at the Eu site is negative. This is at variance with theoretical calculations of the EFG tensor, which predict a positive sign of  $eV_{zz}Q_g$ . The reasons for the failure of the EFG calculations in various high- $T_c$  superconductors were presented.

## ACKNOWLEDGMENTS

This work was supported by the Natural Sciences and Engineering Research Council of Canada. The technical assistance provided by Ben Fullerton is greatly appreciated.

- 
- <sup>1</sup>P. Gütllich, R. Link, and A. Trautwein, in *Inorganic Chemistry Concepts*, edited by M. Becke, Ch. K. Jørgensen, M. F. Lippert, S. J. Lippard, J. L. Margrave, K. Niedenzu, R. W. Parry, and H. Yamatera (Springer-Verlag, Berlin, 1978), Vol. 3.
- <sup>2</sup>R. A. Brand, Ch. Sauer, H. Lütgemeier, B. Rupp, and W. Zinn, *Physica C* **156**, 539 (1988).
- <sup>3</sup>M. Takano and Y. Takeda, *Jpn. J. Appl. Phys.* **26**, L1862 (1987).
- <sup>4</sup>S. Nasu, H. Kitagawa, Y. Oda, T. Kohara, T. Shinjo, K. Asayama, and F. E. Fujita, *Physica B* **148**, 484 (1987).
- <sup>5</sup>M. Eibschutz, D. W. Murphy, S. Sunshine, L. G. Van Uitert, S. M. Zahurak, and W. H. Grodkiewicz, *Phys. Rev. B* **35**, 8714 (1987).
- <sup>6</sup>J. M. D. Coey and K. Donnelly, *Z. Phys. B* **67**, 513 (1987).
- <sup>7</sup>G. Von Eynatten, K. Dransfeld, T. Ritter, and E. Bucher, *Hyper. Interact.* **42**, 1223 (1988).
- <sup>8</sup>A. Vértes, E. Kuzmann, Z. Homonnag, M. Gál, and K. Torkos, *Hyper. Interact.* **42**, 1247 (1988).
- <sup>9</sup>R. Nagarajan, A. K. Grover, S. K. Dhar, P. L. Paulose, V. Nagarajan, and E. V. Sampathkumaran, *Hyper. Interact.* **42**, 1227 (1988).
- <sup>10</sup>G. K. Shenoy and B. D. Dunlap, *Nucl. Instrum. Methods* **71**, 285 (1969).
- <sup>11</sup>Z. M. Stadnik and W. Zarek, *Phys. Rev. B* **34**, 1820 (1986).
- <sup>12</sup>F. J. Adrian, *Phys. Rev. B* **38**, 2426 (1988).
- <sup>13</sup>P. Boolchand, R. N.ENZWEILER, I. ZITKOVSKY, R. L. MENG, P. H. HOR, C. W. CHU, and C. Y. HUANG, *Solid State Commun.* **63**, 521 (1987).
- <sup>14</sup>R. Kamal, Lovleen, Sumanjit, B. R. Sood, and K. S. Sidhu, *Phys. Rev. B* **37**, 5928 (1988).
- <sup>15</sup>T. Shimizu, H. Yasuoka, T. Imai, T. Tsuda, T. Takabatake, Y. Nakazawa, and M. Ishikawa, *J. Phys. Soc. Jpn.* **57**, 2494 (1988).
- <sup>16</sup>R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, *Phys. Rev. Lett.* **58**, 1676 (1987).
- <sup>17</sup>J. P. Cali, *Natl. Bur. Stand., (U.S.) Misc. Publ. No. 1541* (U.S. GPO, Washington, D. C., 1971).
- <sup>18</sup>F. Hulliger and H. R. Ott, *Z. Phys. B* **67**, 291 (1987); Y. LePage, T. Siegrist, S. A. Sunshine, L. F. Schneemeyer, D. W. Murphy, S. M. Zahurak, J. V. Waszczak, W. R. McKinnon, J. M. Tarascon, G. W. Hull, and L. H. Greene, *Phys. Rev. B* **36**, 3617 (1987); H. Asano, K. Takita, H. Katoh, H. Akinaga, T. Ishigaki, M. Nishino, M. Imai, and K. Masuda, *Jpn. J. Appl. Phys.* **26**, L1410 (1987).
- <sup>19</sup>T. Tamegai, A. Watanabe, I. Oguro, and Y. Iye, *Jpn. J. Appl. Phys.* **26**, L1304 (1987); C. Jiang, Yu. Mei, S. M. Green, H. L. Luo, and C. Polis, *Z. Phys. B* **68**, 15 (1987).
- <sup>20</sup>M. Hikita, Y. Tajima, A. Katsui, and Y. Hidaka, *Phys. Rev. B* **36**, 7199 (1987); Y. Tajima, M. Hikita, T. Ishii, H. Fuke, K. Sugiyama, M. Date, A. Yamagishi, A. Katsui, Y. Hidaka, T. Iwata, and S. Tsurumi, *Phys. Rev. B* **37**, 7956 (1988).
- <sup>21</sup>J. G. Stevens, in *Handbook of Spectroscopy*, edited by J. W. Robinson (CRC, Boca Raton, Florida, 1981), Vol. III, p. 464.
- <sup>22</sup>E. R. Bauminger, G. M. Kalvius, and I. Nowik, in *Mössbauer Isomer Shifts*, edited by G. K. Shenoy and F. E. Wagner (North-Holland, Amsterdam, 1978), p. 661.
- <sup>23</sup>T. C. Gibb, *J. Chem. Soc., Dalton Trans.* 2245 (1981).
- <sup>24</sup>Z. M. Stadnik and E. de Boer, *Solid State Commun.* **50**, 335 (1984).
- <sup>25</sup>J. Teillet, Y. Calage, and F. Varret, *J. Phys. Chem. Solids* **43**, 863 (1982); J. Teillet and G. Coubion, *J. Phys. Chem. Solids* **46**, 559 (1985).
- <sup>26</sup>Z. M. Stadnik and B. F. Otterloo, *J. Solid State Chem.* **48**, 133 (1983); Z. M. Stadnik, *J. Phys. Chem. Solids* **45**, 311 (1984).
- <sup>27</sup>K. J. Duff, K. C. Mishra, and T. P. Das, *Phys. Rev. Lett.* **46**, 1611 (1981).
- <sup>28</sup>S. Vajda, G. D. Sprouse, M. H. Rafailovich, and J. W. Nosé, *Phys. Rev. Lett.* **47**, 1230 (1981); M. H. Rafailovich, E. Dafni, J. M. Brennan, and G. D. Sprouse, *Phys. Rev. C* **27**, 602 (1983).
- <sup>29</sup>R. E. Watson, R. M. Sternheimer, and L. H. Bennett, *Phys. Rev. B* **30**, 5209 (1984).
- <sup>30</sup>S. Nagel, *J. Phys. Chem. Solids* **46**, 905 (1985).
- <sup>31</sup>P. Blaha, K. Schwarz, and P. Herzig, *Phys. Rev. Lett.* **54**, 1192 (1985); P. Blaha, K. Schwarz, and P. H. Doderichs, *Phys. Rev. B* **37**, 2792 (1988).