



# STUDY OF THE ELECTRIC FIELD GRADIENT IN EuBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub> ( $\delta \approx 0$ AND $\delta \approx 1$ ) BY <sup>151</sup>Eu MÖSSBAUER SPECTROSCOPY

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P. Chaudouët, J. Sénateur, F. Weiss, P. de Réotier, P. Vulliet, et al.. STUDY OF THE ELECTRIC FIELD GRADIENT IN EuBa<sub>2</sub>Cu<sub>3</sub>O<sub>7- $\delta$</sub>  ( $\delta \approx 0$  AND  $\delta \approx 1$ ) BY <sup>151</sup>Eu MÖSSBAUER SPECTROSCOPY. Journal de Physique Colloques, 1988, 49 (C8), pp.C8-2161-C8-2162. 10.1051/jphyscol:19888968 . jpa-00229256

**HAL Id: jpa-00229256**

**<https://hal.science/jpa-00229256>**

Submitted on 4 Feb 2008

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## STUDY OF THE ELECTRIC FIELD GRADIENT IN $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ( $\delta \simeq 0$ AND $\delta \simeq 1$ ) BY $^{151}\text{Eu}$ MÖSSBAUER SPECTROSCOPY

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**Abstract.** - We have measured the quadrupole interaction parameter and the asymmetry coefficient at the  $^{151}\text{Eu}$  Mössbauer nucleus for  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$ ,  $\delta \simeq 0$  and  $\delta \simeq 1$ . The measurements have been extended up to 420 K and 600 K respectively. From the temperature dependence of the electric field gradient parameter  $V_{zz}^{\text{Eu}}$  and the isomer shift we deduce that the contribution of the excited electronic state of  $\text{Eu}^{3+}$  to the measured parameters is stronger in the superconducting than in the semiconducting oxide.

A number of groups have already published results obtained by  $^{151}\text{Eu}$  Mössbauer spectroscopy on  $\text{EuBa}_2\text{Cu}_3\text{O}_7$  [1] but only recently data have been presented on the temperature dependence of the quadrupole interaction parameter and the isomer shift for  $\text{EuBa}_2\text{Cu}_3\text{O}_{4-\delta}$ ,  $\delta \simeq 0$  and  $\delta \simeq 1$  [2]. The measurements were performed up to 420 K and 600 K for the  $\delta \simeq 0$  and  $\delta \simeq 1$  compound respectively. Here we give a first approach to the analysis of these data.

In these compounds the electric quadrupole interaction is unresolved [1] but a careful analysis shows that the Mössbauer spectra can not be fitted by a simple Lorentzian line and that a quadrupole interaction does exist. Our samples were very thin ( $3.6 \text{ mg/cm}^2$  of  $^{151}\text{Eu}$ ) in order to avoid saturation effects. This point was carefully examined by transmission-integral fits to the spectra. The line width of a single line was for all the spectra  $2.04$  (3) mm/s. The value of the component of the electric field gradient (EFG) along the main axis,  $V_{zz}^{\text{Eu}}$ , was deduced from the measured quadrupole interaction parameter using the quadrupole moments given in reference [3]. The asymmetry parameter  $\eta$  was temperature independent with  $\eta = 0.77$  (8),  $0.84$  (8) for the  $\delta \simeq 0$  and  $\delta \simeq 1$  compounds respectively. In the figure 1 we present the temperature dependence of  $(-V_{zz}^{\text{Eu}})$  and the isomer shift (IS) for the two compounds. At first sight the non-monotonous temperature dependence for the superconducting oxide ( $\delta \simeq 0$ ) is surprising. This type of behaviour has already been seen for  $\text{Eu}_2\text{Ti}_2\text{O}_7$  and has been attributed to the contribution of the electronic state  $J = 2$  of  $\text{Eu}^{3+}$  to the EFG [4].

The continuous line on the IS data for the two compounds is a fit to a Debye model with a Debye temperature of 290 K. This fit works perfectly well only for the semiconducting compound. It is remarkable that the deviation from the fit for the superconducting oxide occurs at the same temperature as the min-

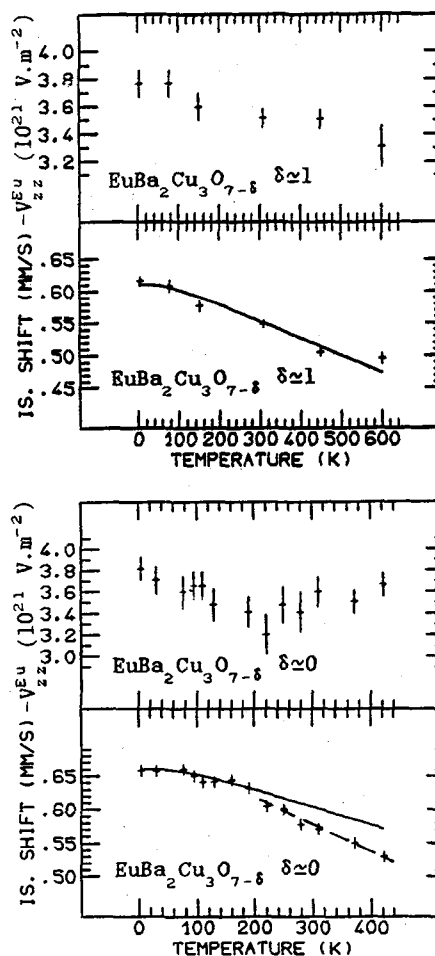


Fig. 1. - Temperature dependence of  $(-V_{zz}^{\text{Eu}})$  and the isomer shift (IS) of  $\text{EuBa}_2\text{Cu}_3\text{O}_{7-\delta}$  for  $\delta \simeq 1$  and  $\delta \simeq 0$ . The continuous line on the IS data is the result of the Debye model with a Debye temperature of 290 K. The dashed line in the high temperature IS data for  $\delta \simeq 0$  has a slope of  $\simeq -4.0 \times 10^{-4} \text{ mm.s}^{-1}.\text{K}^{-1}$ .

imum in  $(-V_{zz})$ . The IS curves describe the effect of the second order Doppler shift (SOD) for a particular model. But the misfit which is seen starting at  $\simeq 200$  K can not be attributed to any SOD because the minimum slope which is model independent can only be  $-2.75 \times 10^{-4} \text{ mm.s}^{-1}.\text{K}^{-1}$  whereas our data have a slope of  $\simeq -4.0 \times 10^{-4} \text{ mm.s}^{-1}.\text{K}^{-1}$ . We attribute this extra IS to the excited electronic states  $J = 1, J = 2$  of  $\text{Eu}^{3+}$ . Our data show that the mixing of these states to the  $J = 0$  ground state decreases the s-electron density at the Eu nucleus. Because we do not see any deviation from the Debye model for the semiconducting oxide we deduce that in this case the mixing is negligible.

The Mössbauer spectroscopy provides a measurement of the EFG tensor  $V_{ij}$  at the nucleus which in our case is the sum of two tensors, one representing the effect of the lattice and the conduction electrons and one taking into account that 4f electron shell. If we suppose that the main axis of both tensor are parallel we can write:

$$V_{zz}^{\text{Eu}} = V_{zz,\text{lat}} + V_{zz,4f} \quad (1)$$

$V_{zz,\text{lat}}$  can be taken directly from the  $^{155}\text{Gd}$  Mössbauer measurement because the only contribution to the EFG for this nucleus comes from the lattice and the conduction electrons. Using the quadrupole moments given in reference [6, 7] we obtain at 42 K:  $V_{zz,\text{lat}} = -6.00$  (15) and  $-5.32(2) \times 10^{21} \text{ V.m}^{-2}$  for the  $\delta \simeq 0$  and  $\delta \simeq 1$  oxides respectively (2,5). Therefore we can deduce  $V_{zz,4f}$  and compare to the result of Elliott (8) who has computed the EFG due to the polarization of the 4f orbitals by an axial crystalline field potential. This theory takes into account only the mixing of the  $|J = 2, m = 0\rangle$  state to the  $|J = 0\rangle$  ground state. At low temperature

$$V_{zz,4f} = \frac{32}{75} e \langle r^{-3} \rangle (1 - R) \frac{V_2^0}{\Delta_2} \quad (2)$$

$\Delta_2$  is the energy of the  $|J = 2, 0\rangle$  state and  $V_2^0$  is the crystalline field potential parameter which can be expressed in term of  $V_{zz,\text{lat}}$  as follows

$$V_{zz,\text{lat}} = -4V_2^0 (1 - \gamma_\infty) / (1 - \sigma_2) \langle r^2 \rangle \quad (3)$$

Using the parameters  $R$ ,  $\langle r^{-3} \rangle$ ,  $\Delta_2$ ,  $\gamma_\infty$ ,  $\sigma_2$ , and  $\langle r^2 \rangle$  given in reference [4] and our data at 4.2 K for the superconducting oxide we deduce from equations (1) and (2) a value of  $V_2^0$  which agrees with the value deduced from the  $^{155}\text{Gd}$  measurement and equation (3). But we find a discrepancy of 20 % for the  $\delta \simeq 1$  compound. In fact equations (1), (2) and (3) imply that

$$(V_{zz}^{\text{Eu}} / V_{zz}^{\text{Gd}})_{\delta=0} = (V_{zz}^{\text{Eu}} / V_{zz}^{\text{Gd}})_{\delta=1}.$$

This is not seen experimentally. But we must remember that our model is crude: for instance it takes into account only the mixing of the  $|J = 2, m = 0\rangle$  state and suppose that  $V_{zz,4f}$  has the same main axis as  $V_{zz,\text{lat}}$ . A complete theoretical analysis is under way which should explain the minimum seen  $(-V_{zz}^{\text{Eu}})$  [4]. But it is clear from the present analysis that the differences seen between the two oxides is due to the excited electronic state of  $\text{Eu}^{3+}$ . These states should give a Van-Vleck contribution to the magnetic susceptibility.

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