ESR OF GdxEu1-xBa2Cu3O7-δ CERAMIC OXIDES

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ESR OF $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ CERAMIC OXIDES

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Abstract. – Electron spin resonance on Gd^{3+} ions in $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ are presented. The dependence of the g–factor and linewidth with the concentration of magnetic ions and temperature is discussed for superconducting and non superconducting samples with $\delta = 0$ and $\delta = 0.7$ respectively.

The magnetic behavior of materials can be studied with Magnetic Resonance Spectroscopy which provides information on the interaction of magnetic ions among themselves and between them and the crystal lattice. This information is conveyed mainly by two parameters: the g–factor and the linewidth of the resonance, ΔH. We report here experiments on ceramic powders of $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ in the range $0.02 \leq x \leq 1$. In this family of oxides non-magnetic Eu^{3+} ions are substituted for paramagnetic Gd^{3+} ions. In this system we can vary independently two parameters: the concentration of magnetic Gd^{3+} ions and the oxygen defficiency δ. For $\delta = 0$ this oxide shows high temperature superconductivity and antiferromagnetic ordering [1] at T_N=2.24 K for $x = 1$. The increase in δ suppresses the superconductivity without affecting the antiferromagnetic transition [2]. It has been shown also that the decrease in x depresses T_N at almost a linear rate [3].

Our samples were prepared in two sets: a first one, that we shall call oxygenated, was prepared by sintering a mixture of oxides at 950 °C in an oxygen atmosphere as described in [4]; a second one consist of pieces of samples of the first set that were subsequently heat treated at 530° for 3 hs in an argon flow [5]. We call this samples deoxygenated and, from the weight loss during the heat treatment, we have estimated $\delta = 0.7(1)$. All the samples were prepared for the ESR experiments by thoroughly grinding a mixture of the material with KCl in a 1:3 proportion, in order to avoid texture and attenuation effects.

All oxygenated samples were superconducting above 77 K while after deoxygenation none of them showed superconductivity down to 2 K. Calorimetric measurements, shown in figure 1, indicate that the magnetic transition remained unaffected by the heat treatment, in agreement with previous results [2].

The ESR experiments were made at x-band (9.5 GHz) between 4 K and room temperature. The measured g–factor for Gd^{3+} shows small departures from the free ion value $g = 1.992$, as shown in figure 2. At room temperature the average g–value for oxygenated samples is 1.98(3). For deoxygenated samples the g values are slightly higher. A possible source of this g–shift is the coupling of Gd ions to magnetic moments associated to the Cu ions present in the deoxygenated compound [6].

The observed ESR lineshape is assymetric, see figure 3. This assymetry is explained if take into account the two components of the resonance, centered at positive and negative magnetic fields, that overlap due to

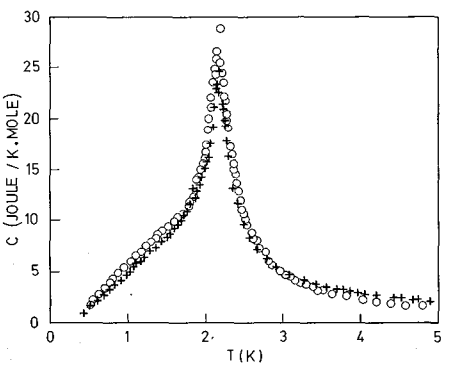

Fig. 1. – Specific heat of $GdBa_2Cu_3O_{7-\delta}$ showing the λ-type anomaly at the antiferromagnetic transition for (+) $\delta \simeq 0$ and (o) $\delta \simeq 0.7$.

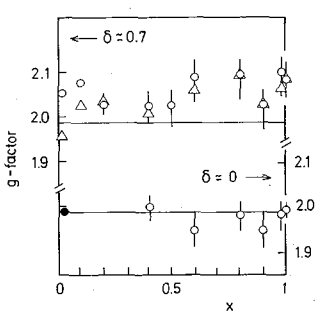

Fig. 2. – g–factor for Gd^{3+} ions in $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ as a function of the concentration x, measured at different temperatures: (o) 300 K and (△) 77 K. The solid circle corresponds to the g–factor measured at 35 GHz for a dilute sample ($x = 0.02$) in reference [4]. The continuous line indicates the Gd^{3+} free ions value $g = 1.992$.

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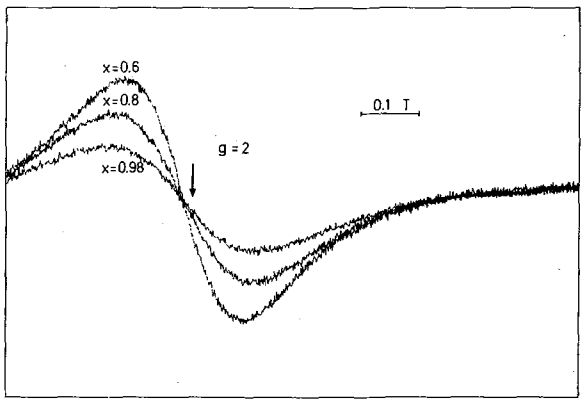

Fig. 3. – ESR spectra at 9.5 GHz for powdered samples of $Gd_xEu_{1-x}Ba_2Cu_3O_{6.3}$ taken at room temperature.

the large linewidth. This overlap also produces an apparent shift of the resonance maximum proportional to the linewidth. Corrections for this effect have been made to the $g-$values and linewidths.

The linewidth shows two different behaviors above and below liquid nitrogen temperatures. Between 85 K and 300 K the oxygenated samples showed [4] a very small increase with temperature $\Delta H/\Delta T \leq 1$ Gauss/K. After oxygen removal the high temperature linewidth remains almost unchanged.

The temperature independent contribution to the linewidth is strongly dependent on x, as shown in figure 4. This almost linear dependence is not expected in magnetic systems where the exchange interactions are clearly dominant [7]. In our system anisotropic interactions (dipolar and crystal field) are of the same order of magnitude as the exchange interactions [3]. Monte Carlo calculation of the high temperature limit of the dipolar contribution predicts a linear increase with x reaching an average peak-to-peak linewidth of about 0.3 Tesla for $x = 1$.

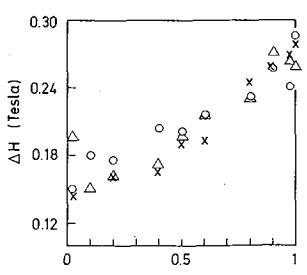

Fig. 4. – ESR linewidth for $Gd_xEu_{1-x}Ba_2Cu_3O_{7-\delta}$ *vs.* x for oxygenated and deoxygenated samples: (o) $\delta \simeq 0$ and $T = 300$ K; (×) $\delta = 0.7$ and $T = 300$ K; (△) $\delta \simeq 0.7$ and $T = 77$ K.

At low temperatures a significant linewidth increase is observed for $T \leq 30$ K as shown in figure 5. This behavior is characteristic of an antiferromagnetic system where anisotropic interactions are important [7]. The

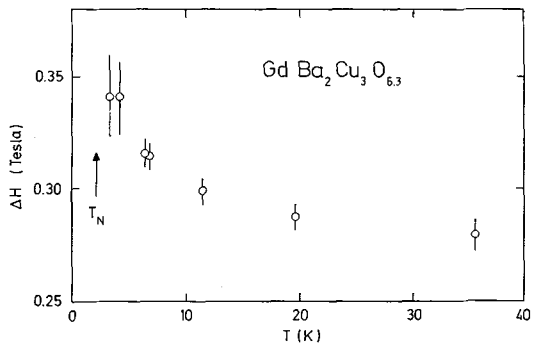

Fig. 5. – ESR linewidth for $GdBa_2Cu_3O_{6.3}$ *vs.* temperature.

fact that critical contributions to the linewidth appear at temperatures much higher than T_N is an indication of the low dimensionality of the magnetic interactions [7].

In conclusion we have observed a shift of the $g-$factor in deoxygenated samples probably related to the coupling to the magnetic moments associated to the Cu ions. The linewidth dependence with the concentration of Gd ions indicates the importance of dipolar couplings in these compounds. The low temperature increase of the linewidth well above T_N reflects the layered magnetic structure of the material. Our Monte Carlo calculations predict a highly anisotropic linewidth in the high temperature limit which is averaged in our ceramic powders. Single crystal studies are under way in order to study these effects.

[1] Willis, V. O., Fisk, Z., Thompson, J. D., Cheong, S. W., Aikin, R. M., Smith, J. L. and Zirngiebi, E., *J. Magn. Magn. Mater.* **67** (1987) L139.

[2] Dunlap, B. D., Slaski, M., Sungaila, Z., Hinks, D. G., Zhang, K., Segre, C., Malik, S. K. and Alp, E. E., *Phys. Rev. B* **37** (1988) 592.

[3] Causa, M. T., Dutrus, S. M., Fainstein, C., Nieva, G., Sanchez, R., Steren, L. B., Tovar, M., Zysler, R., Oseroff, S. B., Vier, D. C., Schultz, S., Fisk, Z. and Smith, J. L., *Physica C* **153-155** (1988) 188.

[4] Causa, M. T., Fainstein, C., Nieva, G., Sanchez, R., Steren, L. B., Tovar, M., Zysler, R., Vier, D. C., Schultz, S., Oseroff, S. B., Fisk, Z. and Smith, J. L., *Phys. Rev. B* **38** (1988) 257.

[5] Abriata, J. P. (private communication).

[6] Tranquada, J. M., Cox, D. F., Kunnmann, W., Moudden, H., Shirane, G., Suenaga, M., Zolliker, P., Vaknin, D., Sinha, S. K., Alvarez, M. S., Jacobson, A. J. and Johnston, D. C., *Phys. Rev. Lett.* **60** (1988) 156.

[7] Walsh, W. M., Birgeneau, R. J., Rupp, L. W. Jr. and Guggenheim, H. J., *Phys. Rev. B* **20** (1979) 4645.