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1999 J. Phys.: Condens. Matter 11 L59

(http://iopscience.iop.org/0953-8984/11/9/001)

J. Phys.: Condens. Matter **11** (1999) L59–L64. Printed in the UK PII: S0953-8984(99)01150-9

LETTER TO THE EDITOR

Difficulty of probing the superconducting gap with relaxation measurements on 4f crystal-field transitions with neutron scattering

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Received 22 January 1999

Abstract. Inelastic neutron scattering results on the temperature dependence of the quasi-elastic crystal-field transition of Tb in $YBa_2Cu_3O_{7-\delta}$ for samples with $\delta = 0.03$ (metallic, superconducting) and $\delta = 0.9$ (insulating) are presented. The linewidth as a function of temperature does not show an anomaly at the superconducting transition temperature T_c and follows a $1/(\exp(\Delta/T) - 1)$ law with Δ the energy difference from an excited crystal-field state. The relaxation of the 4f magnetic moments can be described in terms of simple Orbach processes originating from the magneto-elastic interaction with lattice vibrations. These results, when put into context with reported measurements on the linewidth of crystal-field excitations and EPR, imply that previous neutron measurements must be re-examined.

Recently, there has been a considerable effort to obtain information on the superconducting gap [1] and the pseudo-gap [2] in high-T_c superconductors. Inelastic neutron scattering has been widely used to obtain information on the gaps by studying the temperature dependence of the linewidth of crystalline-electric-field (CEF) transitions [3–18]. With this technique it is possible to obtain results similar to those obtained with NMR. Whereas NMR probes the imaginary part of the spin susceptibility $\chi(\omega)$ for $\omega \geqslant 0$, inelastic neutron scattering for CEF transitions probes χ at the energy Δ of the CEF transition. Anomalies below T_c or T^* (the temperature at which the pseudo-gap opens) have variously been interpreted as an energy gap in the spin excitation spectrum of CuO_2 planes [18], as an indication of d-wave symmetry of a superconducting gap [8] and as the appearance of a pseudo-gap [3, 4, 7].

The sensitivity of the 4f electrons as a probe for studying the superconducting state has been nicely demonstrated for the BCS-type superconductor Tb:LaAl [19]. The experiments were based on the careful determination of a linewidth $\Gamma(T)$ of a CEF transition as a function of temperature. Above the temperature of interest (T_c, T^*), Γ is believed to follow a Korringa law due to the s–f interaction with a normal Fermi liquid, leading for $T \gg \Delta$ to a linear dependence of $\Gamma(T)$. The deviation from a linear temperature dependence at low temperatures is then interpreted in terms of the opening of a gap and the associated reduction in the damping associated with the formation of the superconducting state. Such experiments require a relevant exchange integral for the conduction electrons and the 4f moments, implying the presence of carriers at the rare-earth site. Whereas almost all reported results on cuprates are based on this interpretation, a study of the quasi-elastic CEF transition in $Pb_2Sr_2Tb_{1-x}Ca_xCu_3O_8$, which

exhibits a high antiferromagnetic Néel temperature of the Tb sublattice of 4 K ($T_c = 71$ K) [20], found neither a linear $\Gamma(T)$ nor any anomalies in $\Gamma(T)$.

We report here $\Gamma(T)$ studies of the quasi-elastic line of Tb in $YBa_2Cu_3O_{7-\delta}$ for small amounts of Tb. No anomalies are found in $\Gamma(T)$, but it approximately follows a $1/(\exp(\Delta/T)-1)$ dependence. Such a behaviour is predicted if lattice vibrations are involved in the relaxation process (Orbach process). We show that such a model is also able to predict $\Gamma(T)$ for the CEF transitions of Ho substituted in $YBa_2Cu_3O_{7-\delta}$ [8]. Therefore, these earlier experiments should be re-examined as regards the dominant contribution of relaxation processes involving the lattice vibrations.

$Y_{1-x}Tb_xBa_2Cu_3O_{7-\delta}$ ($x = 0.01$, 0.02, 0.05 and 0.1) samples were prepared by either the standard solid-state reaction technique (grinding, pelletizing, sintering) or by the sol–gel method [21]. They were characterized by powder x-ray diffraction and magnetization measurements and were found to be single phase with a T_c of 91 K for the fully oxygenated compounds. Some samples were studied in more detail by powder neutron diffraction and x-ray absorption, and these measurements indicate that Tb is incorporated in the trivalent oxidation state [22], similarly to Tb in $Pb_2Sr_2Tb_{1-x}Ca_xCu_3O_8$ [23]. The inelastic neutron scattering experiments were carried out at the high-resolution back-scattering spectrometer IRIS of the ISIS neutron spallation source at the Rutherford Appleton Laboratory, the time-of-flight spectrometer IN5 on a cold-neutron guide at the Institut Laue–Langevin in Grenoble and the newly built triple-axis spectrometer Drüchal of the SINQ neutron spallation source at the Paul Scherrer Institute in Switzerland. With IRIS, both mica and graphite 002 analysers were used, resulting in resolutions of 1 and 15 μeV, respectively. At IN5, an incident neutron energy of 3.27 meV was chosen, resulting in an energy resolution of 0.11 meV. Drüchal was operated with a constant incident energy of 3.7 meV or a constant final energy of 4.7 meV, yielding a resolution of 0.14 or 0.2 meV, respectively. For the measurements on Drüchal, a cooled Be filter was inserted in either the incoming or the outgoing beam.

Figure 1 shows typical energy spectra of $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_{7-\delta}$ ($\delta = 0.03$) taken at IRIS and IN5 for two different temperatures. The spectra contain two components: an incoherent nuclear contribution described by the resolution function (elastic line) and a magnetic quasi-elastic (QE) contribution with a Lorentzian lineshape. The absence of the QE contribution in the pure $YBa_2Cu_3O_{7-\delta}$ analogue confirms the magnetic origin of this contribution. The QE component is due to a very strong CEF transition (9 μ_B) between the ground state and the first excited state, predicted to lie at 5 μeV [22]. However, this small splitting has not been observed, even with 1 μeV resolution. Therefore, the ground state can be described as an effective doublet, as for Tb in $Pb_2Sr_2Tb_{1-x}Ca_xCu_3O_8$ [23].

A Lorentzian convolved with the instrumental resolution function has been used to describe the QE contribution. In order to reduce the number of parameters, the ratio between the integrated intensities of the elastic line and the Lorentzian has been kept constant at the value determined at elevated temperature. The absence of observable excited-state transitions at elevated temperatures supports such a constraint. In addition, a constant background has been included, which does not change significantly with temperature.

Figure 2 shows the temperature dependence of the QE linewidth for the superconducting sample with $x = 0.1$ and $\delta = 0.03$. The linewidth does not show any anomaly as a function of temperature. The temperature dependence for the non-metallic, non-superconducting compound ($x = 0.1$ and $\delta = 0.9$) is similar. In addition, the experiments on the more dilute Tb compounds ($x = 0.05$) show a very similar behaviour, indicating that a single-ion effect is responsible for $\Gamma(T)$. It is obvious that the temperature dependence cannot be described by the Korringa law, i.e. an interaction between the 4f electrons and a Fermi liquid (s–f interaction). The Korringa law predicts $\Gamma(T)$ to be proportional to $(J_{ex}N(0))^2T$ for a QE line with the s–f

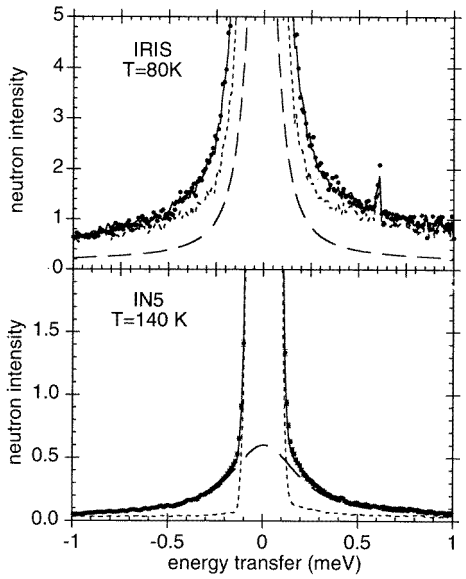

Figure 1. Energy spectra of neutrons scattered from $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_{7-\delta}$ ($\delta = 0.03$). Upper part: $T = 80$ K, IRIS; lower part: $T = 140$ K, IN5. The dashed curve corresponds to the magnetic contribution (a Lorentzian convolved with the resolution function), the dotted curve to the incoherent scattering (the resolution function) and the solid curve to the fit.

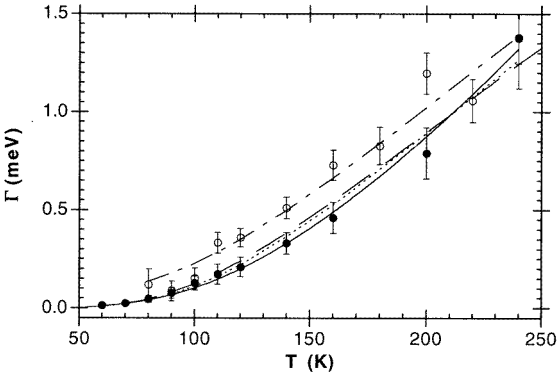

Figure 2. The temperature dependence of the linewidth (full width at half-maximum) of the quasi-elastic line of Tb in $Y_{0.9}Tb_{0.1}Ba_2Cu_3O_{7-\delta}$ (filled circles, dotted, dashed and full curves for $\delta = 0.03$ and open circles and chain curve for $\delta = 0.9$). The full, dashed and chain curves correspond to the fit and the dotted curve to the extrapolation from the Er EPR results (see the text). For the dotted curve, the observed crystalline-electric-field energy of $\Delta_2 = 36.7$ as observed in reference [23] has been used.

exchange integral J_{ex} and the density of states at the Fermi level $N(0)$. A linear dependence at elevated temperatures would lead to a zero-crossing of $\Gamma(T)$ at approximately 50 K, which is unphysical. The s–f interaction further predicts a strongly reduced $\Gamma(T)$ for the non-metallic $\delta = 0.9$ analogue, in contrast to the observation (see figure 2). However, a $1/(\exp(\Delta/T) - 1)$ temperature dependence, as predicted for Orbach processes arising from the magneto-elastic interaction [24], nicely describes $\Gamma(T)$ (figure 2).

The linewidth, which is directly related to the relaxation rate T_{i0}^{-1}, can be expressed for Orbach spin-relaxation processes as [24]

$$\Gamma = \hbar \sum_i T_{i0}^{-1} = \frac{3}{2\pi\rho v^5 \hbar} \sum_i \frac{\Delta_i}{\hbar} M_i^2 \frac{1}{e^{\Delta_i/k_B T} - 1} = \sum_i B_i \frac{1}{e^{\Delta_i/k_B T} - 1}. \quad (1)$$

Here, v is the sound velocity, ρ is the density of the material, Δ_i is the CEF splitting between the ground state and the ith state and M_i is the matrix element which couples these two states. This matrix element is a weighted sum of $|\langle 0|O_n^m|i\rangle|^2$ terms†, where the O_n^m correspond to Stevens operators, and $\langle 0|$ and $|i\rangle$ correspond to the wave functions of the ground and the ith state, respectively. This is a good approximation if Δ_i is less than the Debye energy (350–400 K) [21]. The wave function and the CEF splitting of the rare-earth ions in these cuprates are well known [25]. It is, however, very difficult to obtain reliable values for the prefactors of the $|\langle 0|O_n^m|i\rangle|^2$ terms, which leaves the B_i as fitting parameters. Because the relaxation is due to the population of excited states with energies Δ_i, $\Gamma(T)$ for Tb can be modelled with just the two lowest-lying groups of CEF states at $\Delta_1 = 19$ meV (four states) and $\Delta_2 = 39.5$ meV (two states) taken from reference [22]. The population of the higher-lying states is very small, which may lead to a small modification of the temperature dependence at the highest temperatures. This model is in excellent agreement with $\Gamma(T)$, resulting in values for B_1 and B_2 of 0.23 and 6.7 meV, respectively. For the insulating $\delta = 0.9$ compound, the extrapolation of the energy level scheme from Er and Ho leads to $\Delta_1 = 10$ meV and $\Delta_2 = 38$ meV and the corresponding fit leads to values of B_1 and B_2 of 0.42 and 3.8 meV (figure 2).

An exponential temperature dependence of the relaxation time has also been found in recent electron paramagnetic resonance (EPR) studies of Er^{3+} in $YBa_2Cu_3O_{7-\delta}$, which have also been interpreted in terms of Orbach processes [21, 26]. Our results, together with these EPR studies, indicate that the relaxation is dominated by the interaction with lattice vibrations and not that with the conduction electrons. The addition of a small Korringa contribution to $\Gamma(T)$ does not result in a significantly improved fit to the data. A Korringa law can only be observed when the relaxation processes involving the lattice vibrations are missing due to the absence of excited CEF levels, as is the case for Gd, with a degenerate s ground state. Indeed, in EPR studies of Gd in $YBa_2Cu_3O_{7-\delta}$ a linear temperature dependence of the relaxation time was observed above T_c [27], leading to a value of $(J_{ex}N(0))^2$ which is more than an order of magnitude smaller than those obtained from inelastic neutron scattering experiments on CEF transitions [3, 8, 18]. The dominant contribution of Orbach processes to $\Gamma(T)$ for CEF transitions may also explain why, in the case of Tm^{3+}, $\Gamma(T)$ is larger for the non-metallic compound than for the metallic one [18]. Again, the Korringa-type relaxation is expected to be zero for the insulating $\delta = 0.9$ compound and the relaxation due to the ordered Cu ions is expected to be very small.

For Ho^{3+}, $\Gamma(T)$ has been studied in great detail for the lowest CEF transition by Boothroyd *et al* [8] and is shown in figure 3. The deviation of $\Gamma(T)$ from the Korringa law (the solid curve) has been interpreted as an indication of d-wave symmetry of the gap. The broadening of the CEF transition below T_c would indicate an interaction of the 4f electrons with low-lying excitations close to the Fermi surface. However, our calculation based on Orbach processes accurately describes the observed $\Gamma(T)$ without introducing a reduced relaxation due to the opening of a d-wave gap (figure 3). This result strongly supports the idea that in these cuprates the relaxations of CEF transitions are generally dominated by relaxation processes involving lattice vibrations. This view is also consistent with the very low carrier density found from Y nuclear quadrupole resonance (NQR) [28] at the Y site. We note that when using the

† *Note added in proof.* Detailed considerations to evaluate these matrix elements are in progress.

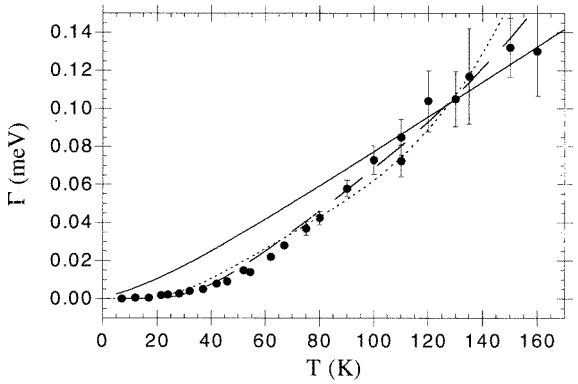

Figure 3. The temperature dependence of the half-width at half-maximum of the first excited crystal-field transition of Ho^{3+} in $Y_{0.9}Ho_{0.1}Ba_2Cu_3O_{7-\delta}$, taken from reference [8]. The solid curve corresponds to the Korringa law, as explained in [8], the dashed curve to the fit and the dotted curve to the extrapolation from EPR, as explained in the text.

extrapolation from the Er EPR data with the prefactor of equation (1) and the matrix element M taken as $|\langle 0|J|i\rangle|^2$, good agreement with the observed $\Gamma(T)$ is obtained (figures 2 and 3).

In conclusion, we present inelastic neutron scattering results on the quasi-elastic line of Tb in $YBa_2Cu_3O_{7-\delta}$. The extracted linewidth $\Gamma(T)$, which is proportional to a relaxation rate T_{i0}^{-1} of the 4f electrons, can be described by a simple $1/(\exp(\Delta/T) - 1)$ law. The relaxation processes can be directly ascribed to the interaction of excited CEF transitions with lattice vibrations. We show that such an interpretation also describes the results obtained on Ho^{3+} [8]. These results, together with those from EPR, indicate that the interactions with the conduction electrons are negligible and that the interactions with the lattice vibrations are responsible for the relaxation behaviour of the 4f electrons. Therefore, the inelastic neutron scattering results which claim to probe the superconducting gap or the pseudo-gap should be re-examined in terms of Orbach processes.

We would like to acknowledge helpful discussions with B D Patterson and R Abela and the technical assistance of W Henggeler and F Altorfer during the experiments performed at SINQ.

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