Evidence for Extreme Gap Anisotropy in $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ from Neutron Spectroscopy of Ho^{3+}

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We have measured by neutron spectroscopy the relaxation behavior of the 0.5 meV ground state crystal field transition of Ho^{3+} in $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$. We studied the intrinsic linewidth Γ and peak position over the temperature range 1.5–160 K. The data show an anomaly at ~115 K consistent with the formation of an energy gap. We extrapolate the normal state linewidth Γ_n to lower temperatures, and hence evaluate the reduced relaxation rate Γ/Γ_n. Both Γ/Γ_n and the peak position show a significant increase with temperature well below T_c characteristic of a high degree of gap anisotropy. [S0031-9007(96)00956-8]

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The formation of an energy gap $2\Delta_{\boldsymbol{q}}(T)$ in a superconductor causes changes to the low energy excitations which can enlighten us as to the nature of the pairing interaction. Among the many techniques which have been employed to study excitations in $YBa_2Cu_3O_{6+x}$, inelastic neutron scattering [1] has given us an overall view of the magnetic dynamics on the CuO_2 planes through the imaginary part of the generalized susceptibility, $\chi''(\boldsymbol{q},\omega)$, while relaxation methods, especially nuclear resonance (NMR and NQR) measurements of the static susceptibility $\chi(\boldsymbol{q},\omega \approx 0)$, have been prominent in the debate concerning the symmetry of the order parameter [2]. Of particular interest are the observed temperature variations of the nuclear relaxation rates and shifts in the superconducting state [3–5], which have been analyzed in detail to assess various models for the energy gap [6].

In this Letter we study the gap in $YBa_2Cu_3O_7$ by a relaxation method that is similar in principle to nuclear relaxation, but which works in zero field and which probes $\chi(\boldsymbol{q},\omega)$ on a meV energy scale, 6 orders of magnitude larger than NMR or NQR. These conditions avoid the difficulties with nuclear resonance measurements in the superconducting state caused by the need to apply external static (NMR) and radio frequency (NMR and NQR) electromagnetic fields. The nuclear relaxation rate, for example, which at temperatures $T \ll T_c$ is very slow, must be corrected for low frequency relaxation effects such as the motion of flux lines and the distribution of internal fields due to screening currents [5].

Our method involves the measurement by neutron scattering of a transition between Ho^{3+} energy levels in $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ split by the local crystal field (CF). The CF transition energy and intrinsic linewidth vary with temperature, and these changes are essentially a reflection of the density of excitations at the transition frequency ω_{CF}. The first observation of CF linewidth changes due to superconductivity was made on $La_{1-x}Tb_xAl_2$ [7], and subsequent investigations on superconducting cuprates have revealed interesting effects when $\hbar\omega_{\mathrm{CF}} \approx 10$ meV [8]. The gap anisotropy, however, is most directly probed when $\hbar\omega_{\mathrm{CF}} \ll 2\Delta_{\mathrm{max}}(0)$. This condition is satisfied in the present experiment because we studied an excitation with $\hbar\omega_{\mathrm{CF}} \approx 0.5$ meV, some 50 to 100 times smaller than reported values of $2\Delta_{\mathrm{max}}(0)$. In this case the relaxation at low temperatures ($T < T_c/2$) is of particular importance because the gap is independent of temperature. We developed the methods used here in a preliminary study [9] performed on the IRIS spectrometer at the ISIS neutron facility. In that work we concentrated on the temperature region around T_c, and used two different Ho concentrations. Here we give a much more complete set of data measured in a consistent way on a single sample, and explore the low temperature region ($T < T_c/2$) in detail for the first time. Our data are consistent with the notion of a highly anisotropic gap.

The data were measured on the high resolution, time-of-flight spectrometer IN5 at the Institut Laue-Langevin. During the measurements the powder sample was contained in a cylindrical Al can mounted inside a ^{4}He cryostat. The choppers were configured so as to give an incident wavelength of 0.7 nm, and an energy resolution of 0.040 meV for the elastic peak. On the neutron energy loss side of the elastic peak, the energy resolution is better, and improves with increasing energy transfer. It is in this domain that we studied the CF excitation. In order to estimate the nonmagnetic scattering, we collected spectra at several different temperatures from an identically prepared sample of $YBa_2Cu_3O_7$. These background spectra were averaged, taking account of their weak temperature variation, and subtracted from the data before further analysis.

Figure 1 shows energy spectra measured at several temperatures to illustrate the scale of the observed broadening

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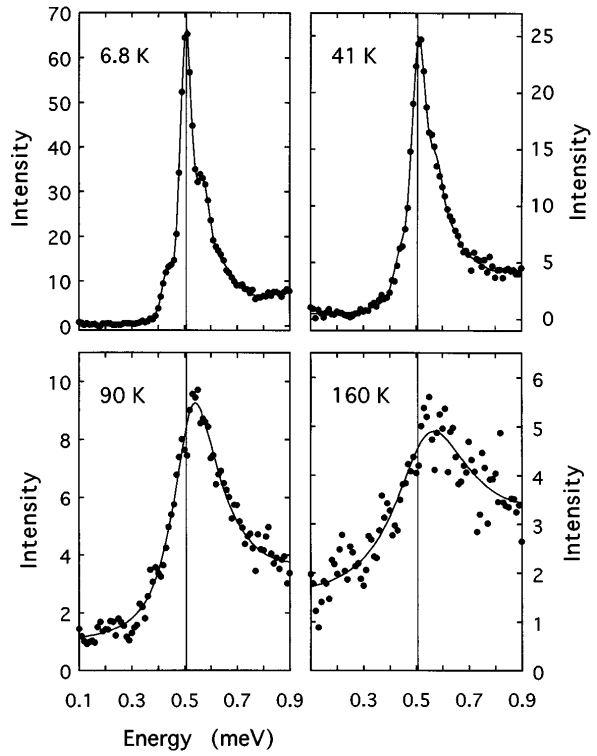

FIG. 1. Inelastic neutron scattering spectra of the ground state to first excited state CF transition of Ho^{3+} in $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ in the energy range 0.1 to 0.9 meV. The data have been corrected for the non-Ho^{3+} scattering. The vertical line is a reference for the peak position at 6.8 K. The calculated curves are fits to the data, and include the relaxation as described in the text. The counting time for each spectrum was 8 h.

and shift. Although the CF transition is between two singlets, the low temperature peak shape is seen to be rather complex, comprising a dominant central peak with shoulders on each side, and a tail on the higher energy side. The side peaks have been discussed in terms of exchange coupling between pairs of Ho^{3+} ions on adjacent sites [10], and their magnitude is reduced if a lower Ho:Y ratio is used [11]. The desire for an uncomplicated line shape, however, must be moderated by the associated loss in signal due to dilution, and our choice of a 10% Ho:Y ratio was a compromise between these two factors.

The key assumption on which our analysis is based is that the observed line shape arises from Ho^{3+} ions distributed in slightly different local environments, but *subject to the same relaxation processes.* In this case, the spectrum measured at a particular temperature is given by the convolution of a broadening function characteristic of that temperature and the residual line shape at absolute zero. Hence, the relaxation can be described by a single broadening function whose position, width, and amplitude depend on temperature. To facilitate the convolutions we constructed the residual out of a sum of Gaussians. We then convolved it with a Lorentzian broadening function, and combined the result with the Bose factor in the standard way to satisfy detailed balance.

We first of all analyzed all the data with a 1.5 K spectrum as the reference. There was virtually no relaxation between 1.5 and 20 K, but a close comparison of data measured at 1.5 and 6.8 K revealed very small changes in the relative intensities of the two "dimer" peaks. Between 6.8 and 20 K, however, the shape of the spectra were all identical within the statistical precision. We henceforth took the 6.8 K data as the reference and repeated the analysis. To within experimental error, the results were the same as before. Thus, while we cannot explain the very low temperature behavior of the two side peaks, we can be certain they have no influence on the results within the bounds of experimental error. This is to be expected since most of the spectral weight is contained in the central peak.

The line drawn through the 6.8 K data in Fig. 1 is the residual function, and the lines superimposed on the other data in Fig. 1 were obtained from the residual by a least-squares fit in which the center, width, and amplitude of the broadening function, together with an additional flat background, were the only variable parameters. The flat background did not vary systematically with temperature, and was included only to allow for inaccuracies in the background estimate. The spectra shown in Fig. 1 reveal an enhancement in intensity with temperature on the right side of the peak, an effect caused by transitions between thermally excited CF levels which overlap into our window. This extra intensity has a negligible effect on the analysis below 50 K, and causes only minor deviations at higher temperatures, but was included in the model so as to allow fitting over the full energy range at all temperatures. We calculated this scattering from the known CF wave functions [12], and verified its shape by comparison with the energy gain scattering, which extends out to greater (negative) energies. Good fits were obtained at all temperatures, with χ^2 values of between 1 and 2 in the fitting range 0.1 to 0.9 meV.

Figures 2(a)–2(c) display the temperature variation of the intrinsic width Γ (HWHM) of the broadening function, the peak shift relative to 6.8 K, and the integrated intensity normalized to unity at absolute zero. The relaxation rate ($\propto\Gamma$) is seen to increase very slowly with temperature at first, then more so up to $T_m \approx 115$ K where the variation becomes roughly linear. The peak shift shows a more marked initial increase with T than does Γ, but flattens out above T_m. The decrease in the integrated intensity with temperature, Fig. 2(c), arises from the depopulation of the CF ground state into higher levels. To within experimental error the points follow the curve calculated from the CF levels [12], and this confirms our calculation of the amount of scattering from thermally excited levels.

In general, the damping of a CF transition in a metal does not follow the Korringa law ($\Gamma \propto T$) familiar with

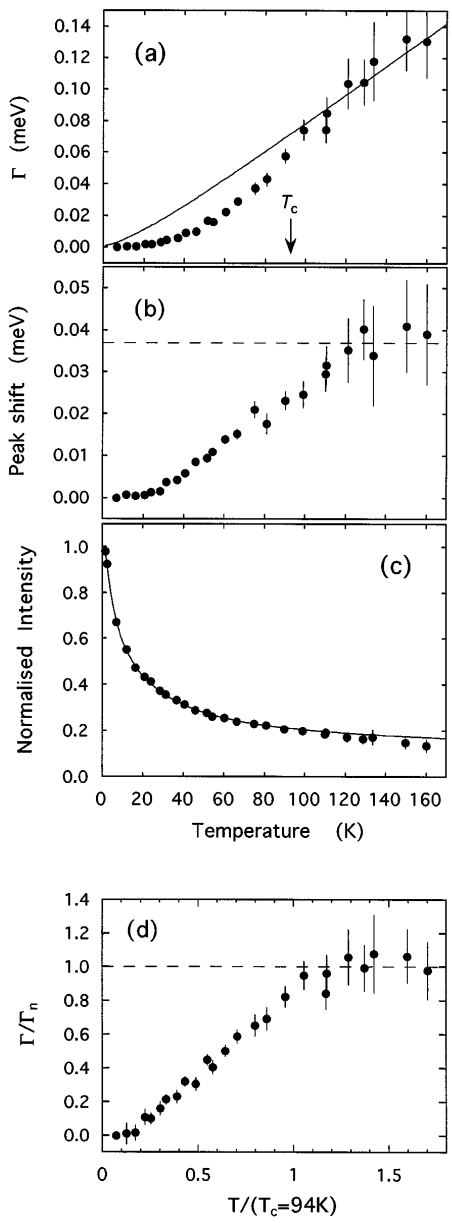

FIG. 2. Temperature variation of (a) the intrinsic linewidth, (b) the peak shift, (c) the measured and calculated integrated intensity, and (d) the reduced linewidth. The reduced linewidth is the ratio of the measured linewidth [the data points in (a)] to the normal state linewidth calculated from Eq. (1) with coupling constant $J_{ex}N(0) = 0.0036$ [the line in (a)]. The reduced temperature axis in (d) corresponds to the same range of temperature as in (a)–(c).

nuclear relaxation. This is because the transition energy is often comparable to k_BT, and because contributions arise from relaxation pathways involving higher lying CF levels. The theory of Becker, Fulde, and Keller (BFK) [13] may be used to calculate the relaxation by exchange scattering for an arbitrary CF splitting. For the case when the CF levels do not overlap, the linewidth of a transition between the ground state (0) and the first excited state (1) is

$$\Gamma = 2J_{ex}^2\Big[M_{01}^2 \coth(\beta\hbar\omega_1/2)\chi''(\omega_1) + \sum_{t>1}\Big(M_{0t}^2\,\frac{\chi''(\omega_t)}{e^{\beta\hbar\omega_t}-1} + M_{1t}^2\,\frac{\chi''(\omega_t-\omega_1)}{e^{\beta\hbar(\omega_t-\omega_1)}-1}\Big)\Big], \quad (1)$$

where $\hbar\omega_t$ is the energy of level t relative to the ground state, M_{ij}^2 is the squared matrix element of the angular momentum operator, J_{ex} is the exchange constant between the localized $4f$ moment and the quasiparticles, and $\beta = 1/k_BT$. $\chi''(\omega)$ is the same local susceptibility as used in nuclear relaxation, i.e., the Brillouin zone sum of $|A(\boldsymbol{q})|^2\chi''(\boldsymbol{q},\omega)$, where $\chi''(\boldsymbol{q},\omega)$ is the dynamic susceptibility probed by neutron scattering and $A(\boldsymbol{q})$ is a geometrical factor which takes account of the local structure around the lanthanide ion [2]. It will be seen from Eq. (1) that Γ samples $\chi''(\boldsymbol{q},\omega)$ at several energies, the main one being that of the direct transition, $\omega_1 = \omega_{CF}$. In $Ho_{0.1}Y_{0.9}Ba_2Cu_3O_7$ the ω_{CF} term dominates at low temperatures ($T < 20$ K), but virtual transitions to higher levels ($1.8 < \hbar\omega_t < 11.5$ meV) contribute increasingly at higher temperatures, accounting for approximately half the total relaxation above 120 K [9].

For a noninteracting Fermi liquid $\chi''(\omega) = \pi N(0)^2\omega$, where $N(0)$ is the density of states at the Fermi energy, and we will use this form to calculate the normal state linewidth Γ_n even though the normal state of $YBa_2Cu_3O_7$ is still under discussion. The use of a Fermi liquid model in the present problem is justified by ^{89}Y NMR observations [14] which show that the ^{89}Y relaxation rate is close to the noninteracting limit in the normal state and obeys the Korringa law. Furthermore, although $\chi''(\boldsymbol{q},\omega)$ is strongly enhanced around $\boldsymbol{q} = (\pi/a, \pi/b)$ by antiferromagnetic spin fluctuations [1], these are largely filtered out by $A(\boldsymbol{q})$, the $\boldsymbol{q}$ dependence of which reflects that the Y(Ho) site is at a center of symmetry of the fluctuations [2].

In Fig. 2(a) we show $\Gamma_n(T)$ calculated from Eq. (1), with CF energy levels and matrix elements from the literature [12] and $J_{ex}N(0) = 0.0036$. The corresponding expression for the peak shift is less simple, but we estimate the normal state shift to be much smaller (and in the opposite sense) to that observed here. In Fig. 2(d) we plot the ratio $\Gamma(T)/\Gamma_n(T)$. For temperatures $k_BT > \hbar\omega_{CF}$ this ratio becomes relatively insensitive to the details of the CF spectrum. The temperature variation arises from the suppression of $\chi''(\boldsymbol{q},\omega \approx \omega_{CF})$ due to the formation of the gap $2\Delta_{\boldsymbol{q}}(T)$, and will include coherence factors which reflect that the CF relaxation by exchange scattering is odd under time reversal [15].

The functional form of Γ/Γ_n is analogous to the nuclear relaxation quantity $1/T_1T$, the only difference being in the energy scales probed by the two techniques ($\hbar\omega_{CF} \gg \mu_N B$). The CF peak shift relates in a similar way to the Knight shift K. The limiting forms for $1/T_1T$ and K at low temperatures have been discussed for different

orbital pairing models [6]. In the standard BCS theory, with an isotropic gap of magnitude $2\Delta(0) = 3.52k_BT_c$, the low temperature ($T < T_c/2$) relaxation rate and peak shift vary as $\exp[-\Delta(0)/k_BT]$. This is manifestly inconsistent with the behaviors depicted in Figs. 2(b) and 2(d), which reveal a roughly linear increase in the relaxation of the CF excitation, well in excess of the experimental sensitivity, starting at approximately $T/T_c = 0.2$. Rather, these observations require the existence of a significant density of low energy excitations at temperatures as low as 20 K, and this points toward the need for an unconventional pairing model characterized by a highly anisotropic gap function, consistent with the results of many recent experiments [16].

Nuclear relaxation studies of $YBa_2Cu_3O_7$ have been compared extensively with different gap function models [6], and a similar analysis of the present data could yield important information on $\chi(\boldsymbol{q}, \omega)$ in the superconducting state. We refrain, however, from drawing any conclusions from the static susceptibility predictions for nuclear data because $\chi(\boldsymbol{q}, \omega)$ at our characteristic energy ($\sim$0.5 meV) may have a different $\boldsymbol{q}$ and temperature dependence to $\chi(\boldsymbol{q}, 0)$. For example, we observe changes occurring in the relaxation at $T_m > T_c$, reminiscent of the spin gap behavior observed in $\chi''(\boldsymbol{q}, \omega)$ directly by inelastic neutron scattering [1] and in previous CF relaxation data [8], but not in NMR studies.

The important contribution of this work to the field of cuprate superconductivity is in showing that significant relaxation occurs at low temperatures at energies which are intermediate between zero and the maximum gap energy. By probing on this energy scale, we avoid the potential problems associated with very low frequency measurements. Our results support the need for a highly anisotropic gap, and we hope that calculations of the relaxation at intermediate energies for specific models might be available in the near future.

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