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Probing electronic density of states and magnetic interactions at the rare-earth site in $ErBa_2Cu_3O_7$

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By exploiting the 4f-shell properties of Er in the high-T_c superconductor $ErBa_2Cu_3O_7$, we find by inelastic magnetic neutron scattering that the electrostatic field around the rare-earth site is anomalously large. Above T_c there exists considerable magnetic interaction between the conduction electrons and the rare-earth's 4f shell: $N(E_F)J_{ex}=0.025$. This interaction is lost in the superconducting state. The ground-state magnetic moment of Er in the host lattice is $\mu_{eff}=5.3\mu_B$.

One of the unique properties of the Y-Ba-Cu-O high-T_c superconductor is that substitution of yttrium by ions of the isochemical rare-earth (RE) series, having local magnetic 4f moments, does not change the superconducting phase transition temperature T_c considerably.[1] Most importantly, these local moments, which are both theoretically and experimentally well understood, render it possible to probe the physical environment of the new high-T_c materials on a local, atomic scale. Of particular interest is the detailed mechanism of high-T_c superconductivity and its coexistence with magnetism in the oxide systems.

This work explores the actual role of the RE in the framework of the R-Ba-Cu-O system (where R is a rare earth), especially with regard to interactions of the RE ion with the superconducting electrons. This is achieved by taking advantage of the well-known splitting effect of the RE Hund's-rule ground state in metallic crystal fields (CF) and measuring it by inelastic, magnetic neutron scattering. For $ErBa_2Cu_3O_7$, we determine explicitly at the RE site the product $N(E_F)J_{ex}$, where $N(E_F)$ is the density of states at the Fermi level and J_{ex} is the exchange integral. Above T_c, $N(E_F)J_{ex}=0.025$, an unexpectedly high value, while below T_c $N(E_F)J_{ex}=0$. The observed CF splitting of Er in this system is anomalously high.

Inelastic, magnetic neutron scattering experiments were performed on polycrystalline $ErBa_2Cu_3O_7$ using the high-resolution time-of-flight spectrometer HRMECS at the Intense Pulsed Neutron Source at Argonne National Laboratory. The samples were prepared using a modification[2] of a standard procedure.[3] According to x-ray data no impurity phase could be detected, indicating that a large fraction of the sample is single phase. The samples exhibited a sharp drop of the magnetization at $T_c=90$ K with a Meissner effect of 44% for $T\rightarrow 0$.[2] According to far-infrared spectroscopy[4] and tunneling experiments[5] on $YBa_2Cu_3O_7$, the superconducting gap width is $2\Delta(0)=(3-5)k_BT_c=23-39$ meV. In order to observe CF splittings below this gap the incoming energy was chosen to be $E_0=45$ meV (the direct observation of excitations across the superconducting gap is forbidden by selection rules). Data were taken from $ErBa_2Cu_3O_7$ at $T=12$, 82, 90, 100, and 300 K. Additional background measurements and a vanadium run allow the data to be corrected and placed on an absolute scale.

Figure 1 shows such corrected spectra for $ErBa_2Cu_3O_7$ at $T=12$, 90, and 300 K for the energy-loss side of the neutrons up to 15 meV energy transfer. The mean scattering angle is $\theta=12.2°$ which corresponds to a momentum transfer $Q=0.56$ Å^{-1} at $\Delta E=10$ meV in this low-Q spectra. Clearly, two merging inelastic transitions are observed at $\delta_1=9.53$ meV and $\delta_2=11.00$ meV. We have clear evidence that these excitations are of magnetic origin. Firstly, the intensity of each line is *decreasing* with increasing temperature, characteristic of magnetic excitations from the CF ground state (phonon excitations would show increasing intensities with increasing T). Secondly, according to their form factor, these excitations diminish to virtually zero in a medium-Q spectrum (mean scattering angle $\theta=114.7°$ corresponding to $Q=6.9$ Å^{-1} at $\Delta E=10$ meV) at $T=12$ K, in contrast to phonon lines which would have intensified roughly proportional to Q^2.

With the same experimental setup, spectra were also taken with $E_0=250$ meV in order to look for CF excitations *above* the superconducting gap as shown in Fig. 2. We found another excitation in $ErBa_2Cu_3O_7$ at $\delta_3=78.5$ meV (Fig. 2, upper part), which, following the same reasoning given above, must be a magnetic one from the ground state. For comparison, we have included in Fig. 2 also the CF transitions δ_1 and δ_2 as seen in the 45 meV spectra (the two peaks observed in Fig. 1 appear in Fig. 2 as only one peak due to the different resolution). Although the matrix elements of the low- and high-energy transitions are comparable in their absolute value (see Fig. 3) the intensity of the excitation at 78 meV is strongly reduced due to the higher Q ($Q=2.7$ Å^{-1} at $\Delta E=78$ meV) via the magnetic form factor. At room temperature (Fig. 2, lower part) another excitation emerges at $\delta_4=60.0$ meV apparently arising from an excited CF level. No other inelastic magnetic transition could be observed for energy transfers lower than 220 meV, except

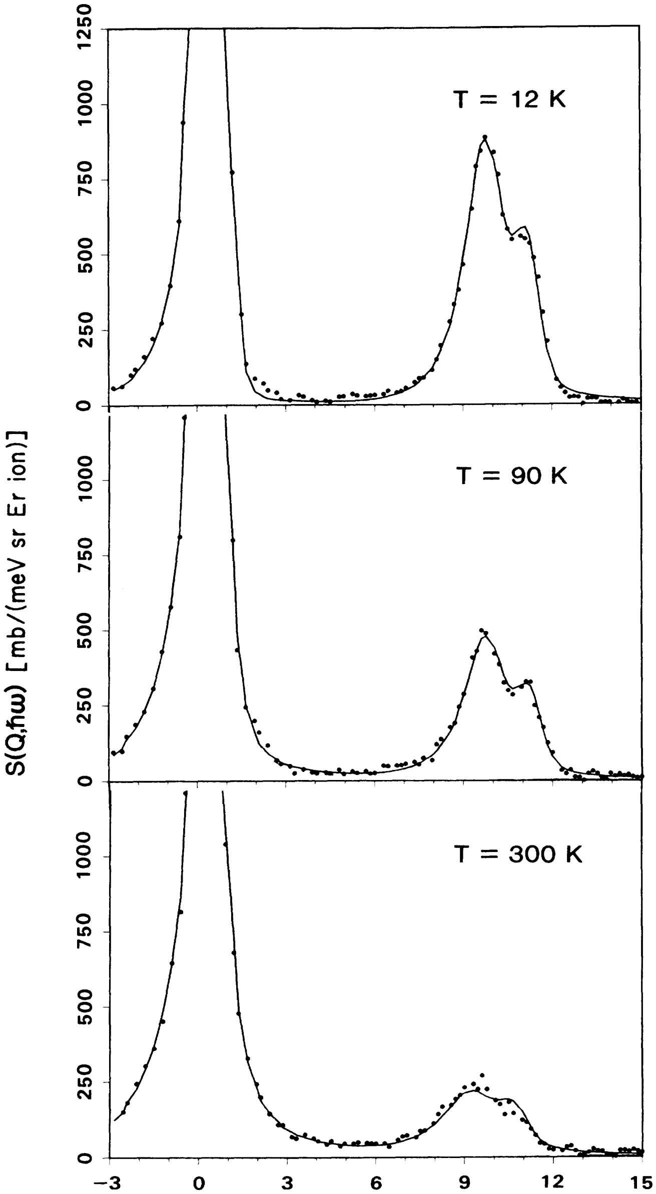

FIG. 1. The scattering function of $ErBa_2Cu_3O_7$ with $E_0=45$ meV. The full line is a fit to the spectrum.

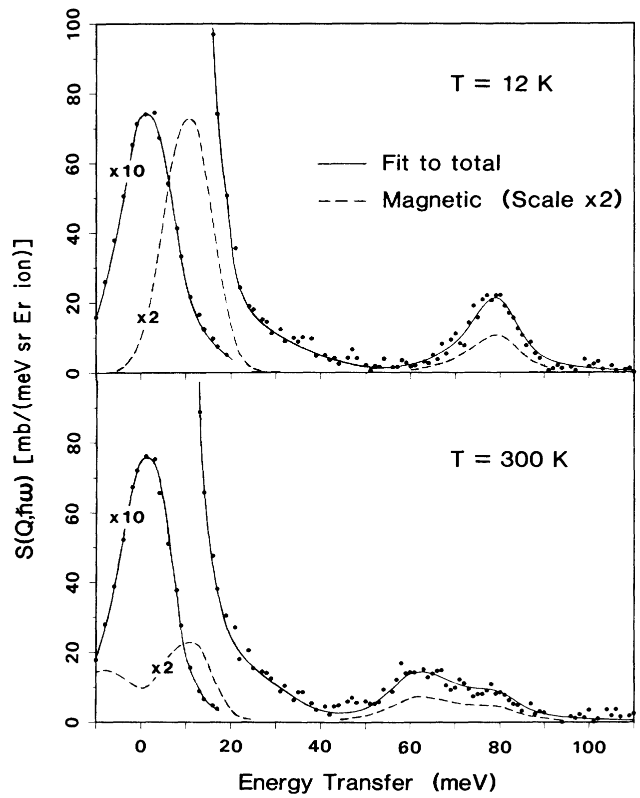

FIG. 2. Same as Fig. 1, except with $E_0=250$ meV. The broken line represents only the magnetic scattering. Note vertical scale changes.

optical phonon states at 23, 45, 65, and 81 meV.

We now turn to an analysis of our experimental results. Having found only four distinct CF transitions, it is practically impossible to derive the entire CF scheme with its eight doubly degenerate CF levels, either by deducing the nine independent CF parameters[6] [Er has orthorhombic ($mmm=D_{2h}$) site symmetry] or directly from the observed transition energies and matrix elements. However, from the specific decrease of the intensity of the transition at 9.53 meV and from the occurrence of $\delta_4=60.0$ meV at elevated temperatures it follows that there must be at least one more CF level at $\delta_3-\delta_4=18.5$ meV. From this knowledge and from the observed ground-state transitions at 9.53, 11.0, and 78.5 meV one is able to account for about two-thirds of the CF scheme, which is sufficient to reveal its most important attributes: the ground-state properties, the low-lying excitations and the overall splitting. Since we have found all excitations from the ground state, we may calculate its elastic matrix element from the sum rule that all matrix elements connected to it should yield $2/3J(J+1)=42.5$. This gives 13.3 for the elastic matrix element or $\mu_{\text{eff}}=5.3\mu_B$ for the *isotropic* moment of the ground state of Er in the host lattice.

The CF splitting in RE ions, which is the lifting of the degeneracy of the Hund's-rule ground state due to local electrostatic fields, is a well-known effect and usually of order 5–10 meV in a metallic, and 10–50 meV in an ionic environment. The observed total splitting of about 78 meV is therefore an extremely high value. It indicates that the electrostatic field around the RE site in $RBa_2Cu_3O_7$ is anomalously large. In an effort to understand the origin of the large splitting, and to investigate the possibility of using it as a probe of the charge states of the Cu and O ions in this system, we have performed calculations of the CF splitting of Er^{3+} in this environment using a point-charge model.[7] This model assigns a nominal charge to each ion in the crystal. The splitting of the degenerate Hund's-rule ground state of Er^{3+} is then considered to arise entirely from the electrostatic field due to

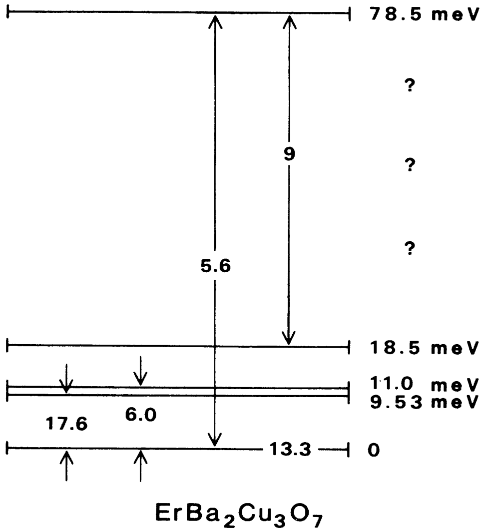

FIG. 3. Parts of the crystal-field scheme of $ErBa_2Cu_3O_7$ as derived from inelastic neutron scattering. The numbers attached to the transitions indicate the magnetic dipole matrix element $\frac{1}{3}[(\langle\Gamma_i|J_x|\Gamma_j\rangle)^2+(\langle\Gamma_i|J_y|\Gamma_j\rangle)^2+(\langle\Gamma_i|J_z|\Gamma_j\rangle)^2]$. Each question mark indicates a questionable location of one crystal-field level.

this array of point charges. We have included shielding of the CF[8] by orbital Er electrons by interpolation of the shielding constants for Pr and Tm.[9] Because the conduction-electron density seems too low in this system to significantly screen long-range fields, no further dielectric screening such as metallic screening of the CF was included. Infinite lattice sums were performed by a generalization of the Ewald summation technique.[10] The expectation values of r^n for the Er $4f$ states were taken from the relativistic Hartree-Fock calculations of Freeman and Deslaux.[11]

In the calculation the Er ions were assumed to substitute into the Y positions in the structure determined from neutron scattering diffraction[12] for $YBa_2Cu_3O_7$ (similar results are obtained using the structure proposed by Reller, Bednorz, and Müller[13]). For any physically reasonable assignment of charge to the Cu and O ions in the system, we are unable to suitably match the experimentally observed CF level sequence and CF matrix elements. Surprisingly, even the experimentally observed total CF splitting is not obtainable with this model. For example, by assigning Cu^{3+}, O^{2-} in the two-dimensional Cu—O layers, we obtain a total splitting of only 39 meV. Many other charge assignments were tested but in no case could we find allowed magnetic dipole transitions to states more than 10 meV above the ground state or an overall CF splitting greater than 40 meV. We have also considered a model where we placed point charges with up to one elementary unit at the bond positions in order to simulate the effects of bond charges (or covalency) in the Cu—O layers. This does not appreciably affect the prior results, in fact it *reduces* the overall splitting by up to 10 meV. Crude point-charge models often fail to describe details of the observed CF splittings, but it is surprising that here such a model fails to account even for the gross splitting. Hence, we believe that there are unconventional effects, in the $RBa_2Cu_3O_7$ which are responsible for this unusually high total splitting.

An analysis of the temperature dependence of the linewidth of the inelastic excitation at $\delta_1=9.53$ meV allows an explicit determination of the density of conduction electrons at the Fermi surface $N(E_F)$ and the exchange integral J_{ex} both above and below T_c. According to BCS theory, the condensation of free conduction electrons into Cooper pairs below T_c should influence any transition probability, such as for electron-phonon scattering, electron-electron scattering (exchange and coulomb), ultrasonic attenuation, NMR, and ir absorption.[14] With inelastic neutron scattering, anomalies in the acoustic phonon excitation energies and phonon life time [Nb_3Se (Ref. 15) and metallic Nb (Ref. 16)], and in the lifetimes of $4f$ levels[17,18] have been observed. Both effects feature a sudden drop of the corresponding linewidths at T_c. This effect stems from the transition of the free conduction electrons with their capability of continuous electron-hole pair excitation energies above T_c, to the state of Cooper pairs with excitation gap $2\Delta(T)$ below T_c. In particular for Re ions diluted into a superconducting matrix several different cases have to be considered.[13] If $\delta_{CF}>2\Delta(0)$, the magnetic moment of the transition is always able to cause pair breaking on the Cooper pairs. No discontinuity is expected in the temperature dependence of the corresponding linewidth. The situation is different for $\delta_{CF}<2\Delta(0)$. For $T>T_c$, the electron-hole excitation scattering always gives rise to a linear temperature dependence (Koringa law). For $\delta_{CF}>2\Delta(T)$, i.e., for temperatures just below T_c, theory predicts that the high density of states just above 2Δ first leads to a initial *increase* in the CF linewidth. For decreasing temperatures $\delta_{CF}<2\Delta(T)$ and the rapid decrease of thermally excited quasiparticles above 2Δ yields a corresponding rapid exponential *decrease* of the linewidth down to $\Gamma=0$ at $T=0$. It is this exponential decay of the linewidth which seems to be characteristic of the temperature dependence of certain CF levels in a superconductor, as observed for example in $La_{1-x}Tb_xAl_2$.[16]

In $ErBa_2Cu_3O_7$ the lowest CF excitation $\delta_1=9.53$ meV $<2\Delta(0)\simeq30$ meV, and therefore is suitable to study the aforementioned, predicted effect. In Fig. 4 we have plotted the intrinsic linewidth half-width at half maximum (HWHM) of this excitation at the five different temperatures measured. For comparison, the resolution width (HWHM) at $\Delta E=10$ meV is 0.50 meV as derived from the vanadium spectrum. The observed intrinsic width is of exactly the same magnitude and hence well discernible from the resolution width. $N(E_F)J_{ex}$ is related to the observed slope of Γ by the familiar Koringa law

$$\Delta\Gamma=4\pi[N(E_F)J_{ex}]^2(g_J-1)^2J(J+1)\Delta T$$

from which we derive $N(E_F)J_{ex}=0.025$ for $T>T_c$. This value is derived under the conventional assumption that there is negligible linewidth broadening due to aspherical Coulomb or phonon scattering, so that the given figure is only an upper limit. Obviously, the linewidth at $T=82$ K falls below the straight Koringa line, whereas that at

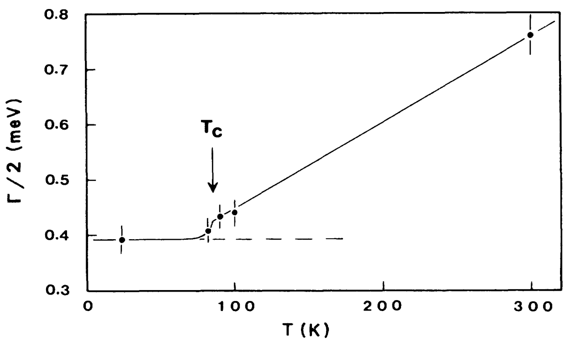

FIG. 4. The temperature dependence of the linewidth of the crystal-field transition at 9.53 meV in $ErBa_2Cu_3O_7$.

$T=12$ K is located far above, indicating a small and sudden drop in the linewidth at T_c and a zero slope plus a high residual linewidth of $\Gamma_0=0.39$ meV below T_c. We note that it is both the small drop in Γ *and* the rapid drop of its slope to zero value that proves the exchange mechanism with the conduction electrons is disrupted, i.e., $N(E_F)J_{ex}=0$ for $T<T_c$. The high residual linewidth supports the observation of structural analysis by elastic neutron scattering[12] that the oxygen sites O(2) around the Y site are only partially occupied so that every Er ion senses a CF being slightly different from each other. The observed transition line therefore resembles a distribution of δ-shaped CF transitions centered at 9.53 meV having a standard deviation equal to the observed residual width.

Interestingly enough, the discontinuous effects at T_c signal that, contrary to the structural considerations, there is a considerable overlap between the free conduction electrons and Cooper pairs and the 4*f* electrons, which makes it questionable whether the superconducting electrons are indeed closely confined to the linear Cu–O chains, or whether these chains are only the superconducting trails through the lattice. We also mention that the vanishing exchange interaction below T_c demonstrates that the magnetic dipole interaction between the RE ions is the sole origin of the small magnetic ordering temperatures in these systems, as observed for instance in $GdBa_2Cu_3O_7$ or $ErBa_2Cu_3O_7$.[19,20]

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