Effect of energy gap in the high-T_c superconductor $Tm_{0.1}Y_{0.9}Ba_2Cu_3O_{6.9}$ on the widths of the transitions between the levels of the crystal field

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The temperature dependence of the width of the transitions between the levels of a crystal field in a high-T_c superconductor $Tm_{0.1}Y_{0.9}Ba_2Cu_3O_{6.9}$ was studied by the inelastic-neutron-scattering method. At $T < T_c$ the widths of the transitions were found to decrease because of the appearance of an energy gap as a result of transition to the superconducting state. The constant which is a measure of the s–f coupling is estimated to be $\rho' = 0.025 \pm 0.005$.

The relaxation of localized $4f$ magnetic moment in metals due to the coupling with the conduction electrons (the s–f coupling) manifests itself in the broadening of peaks in the spectra of inelastic magnetic scattering of neutrons in the transitions between the levels of the basic multiplet, split by a crystal electric field (CEF), of a rare-earth metal ion.[1] In the superconducting state this relaxation mechanism may cause a Cooper pair to break [the spin of one of the electrons which forms a Cooper pair flips $(\mathbf{k}\uparrow - \mathbf{k}\downarrow)$] if the energy of the transition between the CEF levels (ϵ) is larger than the energy gap $2\Delta(\mathrm{T})$. If the condition $2\Delta(T) < \epsilon$ is satisfied, the appearance of an energy gap in a first approximation has no effect on the temperature dependence of the transition width. If $2\Delta(T) > \epsilon$, the excitation energy ϵ is not large enough to break a Cooper pair. As a result, the relaxation channel due to the *s–f* coupling will be in effect, causing the widths of the corresponding peaks to decrease below T_c in the spectra of the inelastic magnetic scattering of neutrons.[2]

In the present letter we report the results of an experimental study of the temperature dependence of the widths of the transitions between the CEF levels. The results were obtained by the inelastic magnetic neutron scattering method in a high-T_c superconductor $\mathrm{Tm_{0.1}Y_{0.9}Ba_2Cu_3O_{6.9}}$ (Tm:YBCO). The basic multiplet $^3\mathrm{He}_6$ of a Tm^{+3} ion in a crystal electric field, of orthorhombic symmetry, is split into thirteen singlets Γ_i: $4\times\Gamma_1$, $3\times\Gamma_2$, $3\times\Gamma_3$, and $3\times\Gamma_4$. The low-lying states of Tm^{+3} ion in YBCO are characterized by the ground level Γ_3 and two first excited levels Γ_4 and Γ_2 at energies of 11.8 meV and 14.2 meV. Between them, two intense dipole transitions from the ground level are resolved. This circumstance makes the Tm:YBCO system very useful in the study of the temperature dependence of the widths of the transitions between the CEF levels, since the spectra of inelastic magnetic scattering of neutrons contain two, slightly overlapping, intense, inelastic peaks at 11.8- and 14.2-meV momentum transfer. The effect of *4f–4f* coupling on the CEF transition widths can be eliminated by means of a 10% substitution of thulium for yttrium.

X-ray and neutron-diffraction experiments showed that the Tm:YBCO sample is a single-phase sample with a superconducting transition temperature $T_c = 92$ K and a transition width $\Delta T_c = 2$ K. The inelastic neutron scattering experiments were carried out with a NET spectrometer[3] which was set up at the ISIS pulsed source of the Rutherford–Appleton Laboratory, in Great Brittain. The incident neutron energy was 35 meV and the resolution of the elastic line was 0.3 meV (half-width at half maximum). The angle at which the scattered neutrons were recorded was $\phi = 5^\circ$, and the momentum transfer for the transfer region 8-16 meV ranged from 0.6 $\mathrm{\AA}^{-1}$ to 1.12 $\mathrm{\AA}^{-1}$. A 100-g sample, placed in a thin-walled aluminum holder filled with helium for optimum thermal contact, was attached to the cold finger of a closed-cycle refrigerator which allowed the temperature to be varied between 15 K and 300 K.

Figure 1 shows fragments of three spectra of inelastic scattering of neutrons at temperatures of 125 K (above T_c), 90 K (near T_c), and 35 K (below T_c). The following circumstances were taken into account in the analysis of the experimental data: (a) Since the peaks at $\epsilon_1 = 11.8$ meV and $\epsilon_2 = 14.2$ meV are caused by the transitions from the ground level, the ratio of their intensities is equal to the ratio of the squares of the matrix elements of the operator $J_\perp$ $(I_2/I_1 = 0.83)$ and does not depend on the temperature. (b) At high temperatures $(T > 100$ K) the spectra exhibit only a slight contribution from the scattering in the CEF transitions from the excited levels. This circumstance was taken into account on the basis of the parameter values of the CEF Hamiltonian. (c) The resolution function which was convoluted with the model scattering law as a set of Lorentzians was determined from the data on the

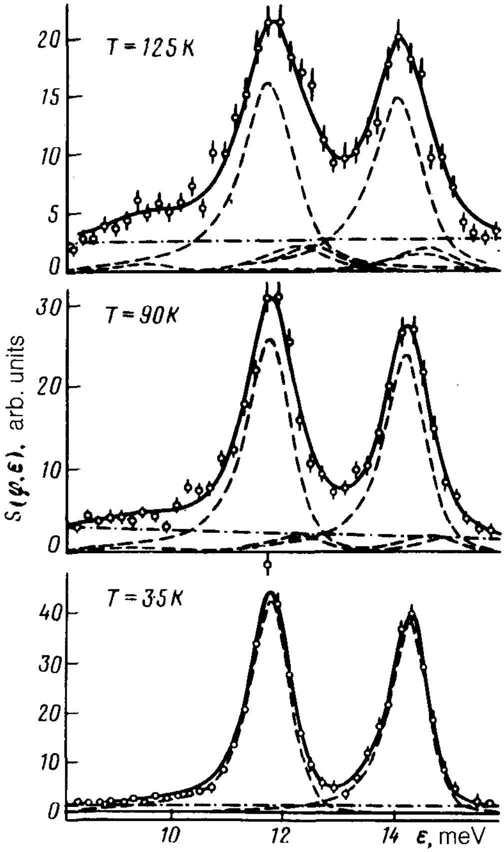

FIG. 1. Fragments of spectra of inelastic neutron scattering (points) in the energy-transfer interval between 8 meV and 16 meV. The curves are explained in the text proper.

scattering by vanadium. The background was approximated by a straight line beyond the interval that contains the magnetic response.

We ultimately had three independent parameters: the widths of the two transitions (half-width at half maximum) from the ground level and the peak intensity at $\epsilon_1 = 11.8$ meV.

The solid line in Fig. 1 represents an approximation of the experimental spectra by the method of least squares, the dashed line represents separate spectral components, and the dot-dashed line is the background. The results of the measurement of the transition widths are shown in Fig. 2. The vertical arrow shows the position of the superconducting transition temperature. We see that at $T < 70$ K the linewidth does not depend on the temperature and amounts to $\Gamma_0 = 0.05$ meV. At $T > T_c$ and near T_c the transitions between the CEF levels broaden considerably. Such a behavior of the temperature dependence of the width stems from the appearance of the relaxation channel: at $T > T_c$ electron-hole pairs are created because of the closing of the energy gap. The residual width Γ_0 apparently is attributable to the static inhomogeneities which are associated with oxygen deficiency ($\delta = 0.1$), for example. Figure 3 is a plot of the temperature dependence of the transition rate at $\epsilon = 11.8$ meV. The solid line is

CEF levels. Using expression (1) (the least-squares method) to approximate the transition width at $T > T_c$ (the solid line in Fig. 2), we estimate the value of the parameter characterizing the strength of the *s–f* coupling, $\rho' = N(0)J_{ex} = 0.025 \pm 0.005$, consistent with the value of ρ' for the $ErBa_2Cu_3O_7$ compound.[4] It should be noted that the parameter ρ' for high-T_c compounds is not a small parameter and corresponds in order of magnitude to ρ' for a metallic superconductor[5] Tb:$LaAl_2$ ($T_c = 3.2$ K; $\rho = 0.034$).

At $T < T_c$ the experimental points in Fig. 2 lie below the theoretical curve. Clearly, in the superconducting state we have $N(0) \approx 0$ (or it at least decreases dramatically in comparison with that in the normal state) if it is assumed that Γ_0 is not a consequence of the *s–f* coupling (as suggested by the fact that the width does not depend on the temperature below 70 K). We note in conclusion that the more accurate measurements of the temperature dependence of the widths of the transitions between the CEF levels near T_c, which we are planning to carry out, may allow us to determine the size of the energy gap $2\Delta(0)$ (to find this gap, we must determine experimentally the law governing the decrease of the width below T_c). At the currently available experimental accuracy we can use only the lower limit for $2\Delta(0) > 14.2$ meV.

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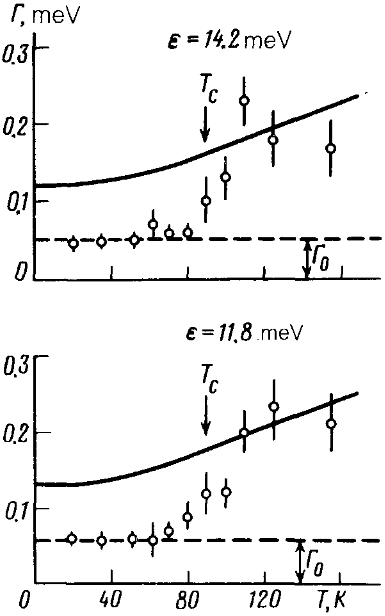

FIG. 2. Temperature dependence of the half-width at half maximum for the transitions between the CEF levels at energy transfer of 14.2 meV and 11.8 meV.

a calculation of the ground-state population in the CEF model. $\rho(\mathrm{T}) = Z(\mathrm{T})^{1}$ [$Z(T)$ is the statistical sum]. This calculation is normalized to allow for the experimentally determined intensity at $T = 20$ K. A good agreement of the theoretical curve and the experimental points in this figure suggests that there are no systematic experimental errors in the measurements and analysis of the experimental data.

In the normal state ($T > T_c$) the width of the transition between CEF levels in the case of two singlets is described by the expression[1]

$$\Gamma = 4\pi M^2 (N(O)J_{ex})^2 (g_J - 1)^2 \delta \,\mathrm{cth}\, \frac{\delta}{2T}, \qquad (1)$$

where $M = \langle m|J|n\rangle$, $N(0)$ is the state density at the Fermi level, J_{ex} is the exchange integral of the s–f coupling, g_J is the Lande factor, and δ is the spacing between the

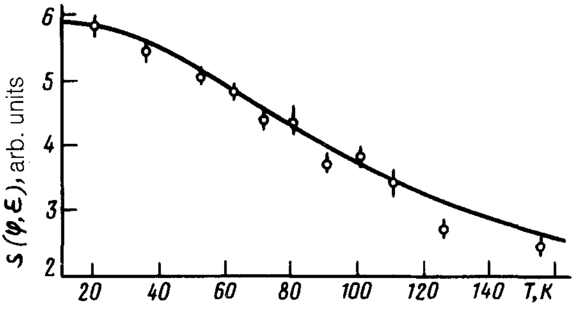

FIG. 3. Temperature dependence of the transition at 11.8 meV (points); the solid line represents calculation based on the CEF model.