Effect of a superconducting transition on the quantum luminescence yield of an adsorbed dye

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A new experimental method of studying superconductors, based on measuring the luminescence spectra of organic-dye molecules adsorbed at the surface of a superconductor, is proposed.

In the present letter we propose a new method of studying high-T_c superconductors. This method is based on studying the luminescence of organic dye molecules adsorbed on the surface of a high-T_c superconductor. The molecules are deposited by adsorption of a dye (erythrosine) from a 10^{-5} m/l solution for 40 min. The temperature dependence of the dye luminescence spectra is measured in the range $T \sim 4.2$–80 K as the molecules are photoexcited by a beam from a copper-vapor laser ($\lambda = 510$ nm). The temperature dependence of the magnetic susceptibility of the samples is recorded at the same time.

We have studied the surfaces of a bulk ceramic sample of YBaCuO ($T_c = 50$ K), of a YBaCuO epitaxial film ($T_c = 87$ K) and of an NbN film ($T_c = 13.5$ K).

Figure 1 shows the temperature dependence $\eta(T)$ of the quantum luminescence

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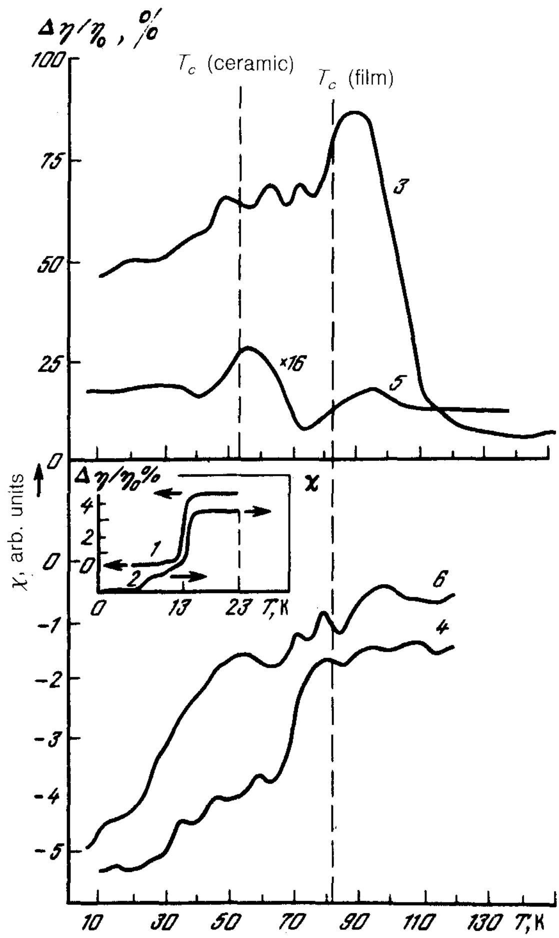

FIG. 1. Temperature dependence of the magnetic susceptibility χ (curves 2, 4, and 6) and of the quantum luminescence yield η of a dye adsorbed at the sample's surface—erythrosine $\Delta\eta/\eta_0 = (\eta - \eta_0)/\eta_0$ (η_0 is the quantum luminescence yield of the dye at $T = 180$ K) (curves 1, 3, and 5). Curves 1 and 2—NbN film; curves 3 and 4—film deposited on a $YBa_2Cu_3O_7$-MgO substrate; curves 5 and 6—$YBa_2Cu_3O_7$ ceramic.

yield of erythrosine molecules and of the magnetic susceptibility χ of the sample for an NbN film (curves 1 and 2), a YBaCuO film (curves 3 and 4), and a YBaCuO ceramic (curves 5 and 6). Let us analyze the results. In the case of an ordinary superconductor (NbN) the quantum luminescence yield $\eta(T)$ of the adsorbed molecules changes slightly ($\approx 5\%$) in an abrupt manner in the region of the phase transition, and the value of $\eta(T)$ is nearly constant above and below the transition point T_c. The difference in the values of $\eta(T)$ can be attributed to the change in the dielectric constant of the substrate as a result of the transition from the normal phase to the superconducting phase. We know[1] that the optical properties of the adsorbed molecules are determined to a large extent by the local field at the molecule, which in turn depends on the dielectric function of the adsorbent. The quantum luminescence yield is given by

$$\eta(T) = \int_0^\infty d\omega I(\omega, T) , \qquad (1)$$

where the luminescence lineshape is

$$I(\omega, T) = \frac{1}{\pi} \operatorname{Re} \int_0^\infty e^{-i(\omega - i\gamma)t} \operatorname{Tr}[\hat{\rho} \mathbf{P}(t) \mathbf{P}(0)]\, dt, \quad (\gamma > 0,\ \gamma \to 0). \tag{2}$$

Here the density matrix $\hat{\rho}$ of the system satisfies the equation

$$\partial \rho / \partial t = i[\mathcal{H}, \rho], \qquad \mathcal{H} = \mathcal{H}_0 + \mathcal{H}_\perp(\hat{\epsilon}),$$

where $\mathcal{H}_0$ is the Hamiltonian of the system without an interaction, $\mathcal{H}_1(\hat{\varepsilon})$ is the Hamiltonian of the interaction of molecules with the adsorbent and with each other, $\mathbf{P}(t) = \exp(i\mathcal{H}t)\mathbf{P}(0)\exp(-i\mathcal{H}t)$, $\mathbf{P}(0)$ is the operator of the dipole moment of a molecule, and ϵ is the dielectric function of the adsorbent. It thus follows that

$$\eta(T) = \eta(T, \hat{\epsilon}). \tag{3}$$

In high-T_c superconductors the situation is, as can be seen in Fig. 1, quite different. The curve of $\eta(T)$ for molecules adsorbed on a crystalline film of YBaCuO, whose behavior is nearly constant far from T_c, exhibits an unusual behavior over a rather broad temperature interval (≈ 40 K): the curve passes through a maximum at $T \approx 105$ K, undergoing an approximately 100% change.

In the case of molecules adsorbed by a YBaCuO ceramic there are two regions in which the $\eta(T)$ curve behaves in this manner: near $T \approx 90$ K and $T \approx 50$ K. This behavior is attributable to at least two phase transitions. At $T \approx 90$ K separate isolated regions of the sample undergo a transition to the superconducting phase. At $T \approx 55$ K there is a second transition at which the entire sample goes superconducting, as confirmed by the conductivity measurements.

The particular features of the behavior of the $\eta(T)$ curve can be linked to the following factors: first, because of the inhomogeneity of the adsorbent samples, the transition to the superconducting phase is slightly diffuse (over a 30-K temperature interval). Secondly, according to the fluctuation-dissipation theorem,[2] the dielectric function is determined by correlation functions of the current-current type:

$$\langle j_i j_j \rangle_{k, \omega, z} \sim \hat{C} \operatorname{Im} \overleftrightarrow{\epsilon}. \tag{4}$$

In the fluctuation region these correlation functions become anomalously large, so that the local field at the molecule changes sharply, causing $\eta(T)$ to behave peculiarly.

We notice that the fluctuation region in the high-T_c superconductors is inordinately broad. For a polycrystalline film of YBaCuO, for example, it amounts to ≈ 10 K, which apparently stems from a rather small coherence length of the high-T_c superconductors.[3]

The third factor, which ostensibly determines the anomalous behavior of $\eta(T)$ near T_c, may be that these systems undergo a structural phase transition, as suggested in Ref. 4.

The molecular-tag method proposed by us may therefore be a useful addition to the existing experimental methods of studying superconductors.

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