Vortex excitations above $T_c$ as revealed by ESR

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Using electron spin resonance (ESR) technique we have obtained data evidencing the existence of magnetic vortices in high-temperature superconductors at temperatures above the critical one $T_c$. We have studied magnetic excitations in $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ single crystals above $T_c$ with the method of surface spin decoration. The surface layer of diphenyl-picrylhydrazyl was used as a sensitive probe of magnetic field distortions. The temperature dependence of the ESR signal parameters has indicated that far above $T_c$ the magnetic flux of a sample is affected by the superconducting order parameter fluctuations while close to $T_c$ its changes are due to vortex-type excitations.

In recent years the evidences that Cooper pairs are formed at temperatures above the critical temperature $T_c$ have been obtained with the help of different methods, such as ARPES, NMR, Nernst effect, resistivity measurements, tunneling microscopy, etc. There are many indications that at $T > T_c$ the superconducting (SC) order parameter amplitude is not zero, while the phase coherence is absent. Some scenarios of the phase transition from the SC state to the normal one imply that upon crossing $T_c$ the phase coherence destroyed due to the rise of vortex excitations. Thus, it is suggested that the presence of vortices is the intrinsic property of the pseudogap state of high-temperature (HT) superconductors. The intensive Nernst signal was observed in many HTSC materials above $T_c$. This was related to the vortex motion, since it was responsible for the large Nernst effect in the type-II superconductors. Moreover, the vortex excitations are manifested in other studies, in particular in the measurements of the high-frequency conductivity. However, the vortex existence above $T_c$ is not generally recognized. In the literature, many different explanations of the large Nernst signal at high temperatures are proposed, namely, due to the SC fluctuation, without assuming thermally excited vortices; due to the unconventional charge density wave; due to the preformed pairs; due to the interference of the itinerant and localized-carrier contributions to the thermomagnetic transport.

To elucidate the underlying picture, new experimental data have to be obtained by means of a method sensitive to the local magnetic perturbations such as the Abrikosov vortices in the type-II superconductors. In this study we use electron spin resonance (ESR) of a thin paramagnetic layer precipitated on a surface of a superconductor (so-called "ESR-decoration") as such a method. This method was proposed in the work to study the Abrikosov vortex lattice which is formed when a HTSC material transfers to superconducting state upon lowering the temperature below $T_c$. The appearance of vortices results necessarily in the spread of the local magnetic fields both in the superconductor bulk and on its surface. In response to the local field dispersion, the ESR signal parameters (the resonance field value $H_R$ and the line width $\delta H$) of the paramagnetic substance deposited on the surface are changed. We use this technique to detect the possible local field perturbations due to the vortex excitations in the $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10}$ crystals at temperatures above $T_c$.

ESR is a powerful tool to study the local magnetic field distribution of any origin, in particular that due to the magnetic perturbations produced by the vortices. Its sensitivity depends on the ESR line width, the narrower the signal, the higher the resolution. Embedding spin probes in the form of paramagnetic ions results in a broad signal and lowers considerably the ESR resolution. To enhance the resolution, the organic free-radical compounds in the form of a surface layer are used as paramagnetic probes with a narrow ESR signal. In this study 2,2-diphenyl-1-picrylhydrazyl (DPPH) is used. It has a narrow Lorentzian ESR signal 1.2 Oe wide. Its resonance field at the spectrometer working frequency of 9.3 GHz is about 3300 Oe ($g = 2.0036$).

DPPH is deposited on a flat surface of a sample under study. The DPPH layer of required thickness was obtained by its precipitation from the solution in benzene. The layer thickness should meet two requirements. On the one hand, it should not be notably larger than the spatial period of the magnetic field variation on the sample surface. If the layer is thicker, the ESR signal is mainly due to DPPH which is not affected by the field inhomogeneity. The Abrikosov vortex lattice constant in the magnetic field of 3000 Oe and $T < T_c$ is estimated as about 80 nm. So the layer thickness should not exceed $100 \div 200$ nm. On the other hand, the DPPH layer less than 100 nm thick and with the area of several square millimeters does not provide the ESR signal inten-
sive enough for its analysis. Therefore the optimal layer thickness, which is sufficiently sensitive to the vortex perturbations of the magnetic field, has to be 150÷200 nm.

ESR spectra were recorded on a Bruker X-band BER-418s spectrometer with working frequency 9.2÷9.7 GHz and magnetic field modulation at a frequency 100 kHz. Signal proportional to the first derivatives of absorbed power was registered with the help of lock-in amplifier EG&G Model 5209. A sample was cooled with a helium gas flow inside a Dewar tube passing through the resonator. Resonance lines were recorded upon sweeping the applied field up. To increase the accuracy in determining the signal position, a small LiF crystal containing the dendrites of pure Li metal was mounted in a resonator along with a sample. Its ESR signal is about 0.1 Oe wide with $g = 2.00226$.

Single crystals of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ were used because they have the highest $T_c$ ($\sim 110$ K) among all Bi-based HTSC compounds. It allows us to eliminate the effect of possible impurity phases with $T_c$ higher than that of the main phase. The single crystals were grown with the travelling solvent floating zone technique. Approximate crystal dimensions are $1.5 \times 1.5 \times 0.1$ mm$^3$.

The superconducting transition was recorded in the measurements of the temperature dependence of ac-susceptibility at the frequency of 20 MHz. Its parameters are $T_{onset} = 111.6$ K and the width of 3 K.

The ESR spectra of the DPPH crystal and the DPPH layer and the conduction electron spin resonance (CESR) signal of the Li dendrite are shown in Fig.1. The spectrum (1) was obtained from the DPPH crystal which was then dissolved in benzene and deposited on a superconductor. Its signal has the following parameters: Lorentz shape, peak-to-peak line width $\delta H_{pp} = 1.2$ Oe, resonance field $H_R = 3322.4$ Oe at $\nu = 9317$ MHz. These parameters remain unchanged upon lowering the temperature from 300 to 30 K. The signal amplitude changes inversely proportional to the temperature. The CESR signal of the Li dendrite is of the Dyson shape with $\delta H_{pp} \simeq 0.1$ Oe and $H_R = 3325.0$ Oe. Its line width and resonance field are temperature-independent, but the shape changes and the amplitude decreases with lowering the temperature due to the decrease in the skin-layer thickness (see Fig.1 curves (2) - (5)).

The behavior of the ESR signal of the DPPH layer on the Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10}$ crystal is quite different. First of all, ESR signal shifts to higher fields. The shift depends on the crystal orientation in the applied magnetic field and temperature (Figs.1 and 2). Secondly, the signal broadens and its broadening depends on temperature as well. The signal changes are weak far from $T_c$ ($T > 120$ K), but they become observable close to the critical temperature, particularly below $T_c$.

The origin of the transformations of the surface-spin-layer EPR signal upon the SC transition of a HTSC sample was discussed in many publications (see, for example, Refs.16,18). These changes are induced by the distortions of the magnetic field on the SC surface and are due to three effects: (i) Meissner shielding leads to the field expulsion from the superconductor and thus enhances the field value close to it. (ii) The appearance of the Abrikosov vortex lattice forms a spatially-modulated field distribution both in the sample bulk and close to its surface outside. The modulation period is of the distance between vortices. The mean field value is considerably lower than that of the applied one. (iii) Any variation of the applied magnetic field results in the appearance of the vortex density gradients due to vortex pinning on the crystal structure imperfections. Thus the internal and surface field values can be both lower or higher than that of the applied one depending on the field variation direction (up or down, respectively). Figure 2 shows the field distribution inside and near an SC strip placed in the increasing magnetic field which is perpendicular ($H_a||c$) and parallel ($H_a||ab$) to the crystal plane surface coated by a DPPH layer. The field strength and vortex line density are proportional to the density of the field lines shown in Fig.3.

The above field distortions are reflected in the ESR spectrum of the DPPH layer. Namely, the decrease in the local field strength results in the signal shift towards higher fields, and the increase in the local field shifts the signal towards lower fields. The spatial variation of the field strength near the SC surface results in the broadening of the ESR line since different parts of the spin layer are in the fields of different strengths.

The temperature dependence of the resonance field of the DPPH layer is shown in Fig.2, for two orientations, parallel ($H_a||ab$) and perpendicular ($H_a||c$). As noted above, the $H^r_R$ and $H^p_R$ values differ from the reso-
nance field of the DPPH crystal and from each other. At \( \nu \approx 9315 \text{MHz} \) the resonance field of the DPPH crystal is 3321.4 Oe, while \( H^a_{R} = 3321.7 \text{Oe} \) and \( H^c_{R} = 3322.5 \text{Oe} \) when temperature is above 150 K. As the temperature approaches \( T_c \) from above, the resonance field increases. Below \( T_c \), the upward shift becomes very abrupt, \( \approx 0.2 \text{Oe/K} \).

When the applied field is perpendicular to the SC surface (\( H_a \parallel c \) in the present case), the local field distribution is determined by the field variations inside the vortex lattice and by the vortex density gradients. If the applied field increases as in the present case, then the internal field in the central part decreases due to the presence of vortices and their gradients (see Fig. 3). As the temperature is lowered, both contributions enhance rapidly and result in the larger upward shift. It is shown in many publications (see, for example, Refs. 18,23) that at \( T < T_c \) the surface-layer ESR signal shift \( \Delta H^c_{R} \) is unambiguously due to the formation of the vortex system and the vortex density gradients. Since the \( H^c_{R}(T) \) dependence does not disappear but extends to the temperatures above \( T_c \), one can assume that vortices exist in this temperature range.

A small but noticeable signal shift at \( T > 140 \text{K} \) has very a weak or even zero temperature dependence and is likely of another origin. The direction and value of the shift indicate the presence of the constant diamagnetic contribution to the magnetic field on the sample surface. This contribution correlates well with the magnetization measurements of the \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) crystal. It has been found at \( H_a \parallel c \) and from 110 to 120 K the \( 4\pi M \) magnitude was about 1 G. The authors attributed this magnetization to the Ginzburg-Landau fluctuation effect. There are no magnetization data on \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) at \( H_a \parallel ab \) in the literature. For the analysis we can use the susceptibility measurement results obtained for both orientation of the \( \text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_{10} \) crystal in the magnetic field. The authors found a noticeable contribution to the magnetic susceptibility (\( \Delta \chi \approx 10^{-5} \)) in the large temperature range from \( T_c \) to 300 K. This contribution, which was attributed to the thermal fluctuations of the SC order parameter amplitude, is not temperature-dependent but varies with orientation. The difference between \( \chi_{ab} \) and \( \chi_c \) is about \( 3 \cdot 10^{-5} \), which corresponds to \( 4\pi M \approx 0.1 \text{G} \). It is markedly smaller but comparable with the resonance field difference in our ESR measurements from 120 to 200 K: \( \Delta H_R \approx 0.9 \text{Oe} \). The disagreement can be due to both by the differing compound and by the different oxygen doping level. Thus the assumption that the ESR signal shift to higher fields at \( T > 120 \text{K} \) is due to the SC fluctuation contribution to the magnetization seems to be quite reasonable.

The \( H_R(T) \) dependence (both parallel and perpendicular) is similar to the \( M(T) \) dependence in Ref. 23. However, the authors connected the abrupt increase in the diamagnetic magnetization close to \( T_c \) (above and below) with the increased contribution of the SC order parameter fluctuations. It contradicts with our explanation of the resonance field behavior by the presence of vortices. The vortex character of the magnetic flux distortion is undoubtful since the presence of vortices (at least just below \( T_c \)) is experimentally proved by many methods of the vortex visualization, in particular by Bitter decoration, magnetic force microscopy, Lorentz microscopy, scanning Hall probe microscopy, scanning SQUID microscopy, etc. Therefore their existence
and the effect on magnetization below $T_c$ are beyond question. The fact, that the $H_R(T)$ function is continuous and monotonic at crossing $T_c$, suggests that below and above critical temperature the field distortion has the same origin - vortex excitations.

It should be noted that in the strict sense the vortex effect discussed above is only valid for $H_\| > H_c$. At $H_\| < H_c$, the vortex effect should be different (see Fig.3). Namely, the magnetic field expulsion due to the Meissner shielding results in the increase in the magnetic field strength on the surface spin-layer. The ESR signal should move to lower fields respectively. However, the observed shift is opposite. This observation can be explained taking into account the following. First, since the crystal thickness is by order of magnitude less than its plane dimension, the demagnetization factor is very small, $N_\parallel \ll 1$. So the field increase near the surface and the relative signal shift can not be considerable. Second, in the vortex state some of the vortex lines bend near the edges and run both through the surface perpendicular to applied field and through parallel surface with DPPH deposited on it (Fig.2b). The last effect has to result in weakening field strength with the corresponding ESR signal shift to higher fields. The signal shift below and slightly above $T_c$ suggests just vortex contribution to field distribution on the examined surface of the $Bi_2Sr_2Ca_2Cu_3O_{10}$ crystal. The temperature dependence of the ESR line width of the DPPH layer (Fig.2b), which is discussed below, suggests the same.

Note, that for both $H_\| > ab$ and $H_\| > c$ the $\delta H_{pp}(T)$ dependence is similar. The only difference is in its slope below $T_c$. Upon lowering temperature the line width is constant within the experimental error from 300 K down to $T' \approx 115$ K. An additional line broadening appears below $T''$ but above $T_c$, it increases with lowering temperature and is most pronounced when the sample transfers to the SC state. Taking into account the resonance field behavior (Fig.2a), the ESR signal broadening can be due to the appearance and development of the vortex structure as well. The $\delta H_{pp}(T)$ dependence reveals the onset of the additional broadening due to the vortex excitation by several degrees above $T_c$. The constant signal shift observed at higher temperatures is obviously due to the contribution from the superconducting order amplitude fluctuations which are uniformly distributed over the sample or averaged rapidly and do not result in the resonance line broadening. However, there is an experimental indication of the possibility of the nonuniform distribution of such fluctuations. In Ref.45 the diamagnetic regions larger than 10 $\mu m$ were revealed by the scanning SQUID microscopy technique in the $La_{2-x}Sr_xCuO_4$ thin films in the temperature range from $T_c$ to about $2T_c$. Such diamagnetic regions can be formed in $Bi_2Sr_2Ca_2Cu_3O_{10}$ crystals as well and produce the spin-layer signal broadening in the wide temperature range above $T_c$. But this is not observed. The situation can be explained by estimating the additional field due to the diamagnetic regions. According to Ref.45 the $B_{dia}^{loc}$ value near $T_c$ is about 5 $\mu T$ (0.05 G). It makes only 2.5% of the line width, that is within the experimental error. When the temperature is far above $T_c$ ($T \sim T_c + 40$ K), the addition $B_{dia}^{loc}$ becomes 5 times larger, but the fractional area of the diamagnetic regions at this temperature is one order of magnitude less than the total area. Such diamagnetic contribution is not detectable with our technique.

In conclusion, the surface-probe ESR study of the features of the magnetic state of the $Bi_2Sr_2Ca_2Cu_3O_{10}$ single crystal in the vicinity of a critical temperature reveals the presence of the magnetic flux disturbances on the crystal surface at $T > T_c$. The temperature dependence of the ESR signal shift and line width at $T \geq T_c$ is the same as that observed upon the formation of the vortex system in the superconducting material. This supports the hypothesis that the vortex excitations exist in the normal state of a superconductor, that is, above $T_c$.

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