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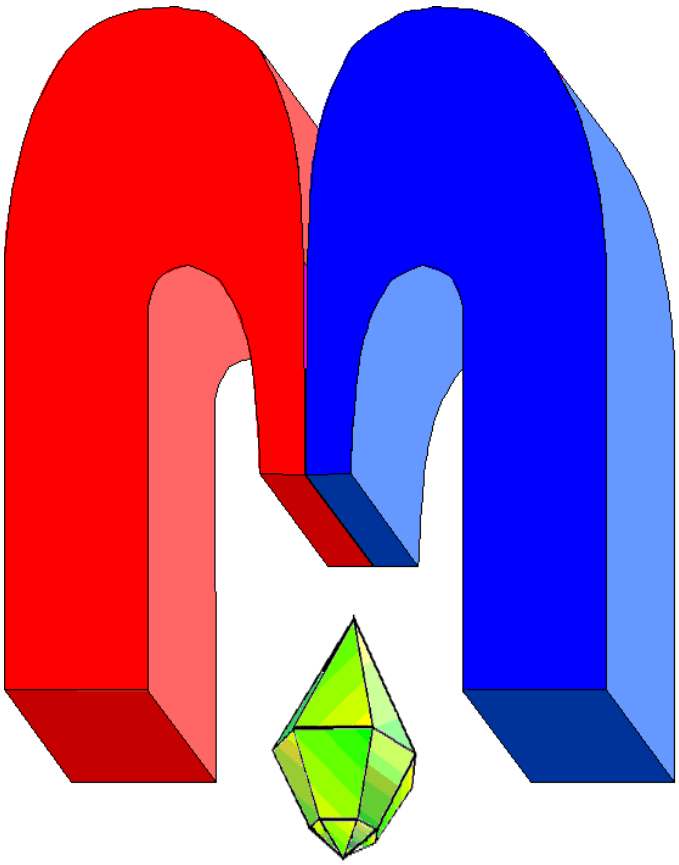

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* In Kazan University the Electron Paramagnetic Resonance (EPR) was discovered by Zavoisky E.K. in 1944.

Exponential temperature dependence of the Yb^{3+} relaxation in $Y_{0.98}Yb_{0.02}Ba_2Cu_3O_x$ †

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The relaxation of Yb^{3+} in $YBa_2Cu_3O_x$ ($x = 6.1$ and 6.4) was studied using Electron Paramagnetic Resonance (EPR). In these samples the Yb^{3+} relaxation is dominated by a phonon mechanism. It was shown that the conventional Raman two-phonon process involving acoustic phonons can not describe the temperature dependence of the Yb^{3+} relaxation. Instead, the Raman process involving optical phonons or an Orbach-like process via the excited vibronic levels of Cu^{2+} ions with energy $\Omega = 500(50)$ K is responsible for the phononic part of the Yb^{3+} relaxation in $YBa_2Cu_3O_x$. The present results provide clear experimental evidence that optical phonons or local vibrations are the dominant source of spin-lattice relaxation at sufficiently high temperatures, which cannot be described by the traditional approach using the Debye approximation.

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The spin-lattice relaxation rate of paramagnetic ions doped in materials provides important information on fluctuating electric and magnetic fields and has been widely used in solid state physics. The theory of electron spin-lattice relaxation in nonconducting solids was elaborated in classical papers of Heitler and Teller [1], Kronig [2], and Van Vleck [3]. They showed that the mechanism of relaxation consists of modulation of the crystal electric field by the lattice vibrations. The thermal vibrations in these models were considered in the Debye approximation. Whereas the low-frequency end of the phonon spectrum in crystals may be approximated by a simple Debye spectrum, the more dense high-frequency portion associated with optical phonons should be active at high temperatures in multiple phonon spin-lattice relaxation processes. To our knowledge, the first explicit treatment of the optic vibrations in the two-phonon Raman relaxation process was done by Kochelaev for nuclear quadrupole relaxation [4]. He showed that the optical vibrations can be the dominant source of relaxation at room temperatures with almost an exponential temperature dependence due to the narrow range of frequencies for these modes. Experimental studies of nuclear spin-lattice relaxation confirmed this prediction, showing that it is necessary to take into account optical modes in order to explain the temperature dependence of the nuclear quadrupole relaxation rate [5, 6]. Later, also Huang theoretically studied the electron spin-lattice relaxation and found that under certain conditions the optical phonon relaxation process may dominate the conventional acoustic phonon relaxation [7]. However, the importance of the optical phonon contribution in the spin-lattice relaxation was not acknowledged by the Electron Paramagnetic Resonance (EPR) community. In fact there are

†This paper is originally written by authors on the occasion of eightieth birthday of Professor Boris I. Kochelaev.

only a very few experimental publications in EPR, where the optical phonon contribution was taken into account to explain spin-lattice relaxation data [8,9]. It is remarkable that in the classical textbook of magnetic resonance by Abragam and Bleaney [10] the contribution of optical phonons to spin relaxation is not mentioned. Even in a more recent book concerning EPR there is a statement: "It is only the acoustic modes that are involved in spin-lattice relaxation" [11].

Here we report results of an EPR study of the Yb^{3+} relaxation in $YBa_2Cu_3O_x$ samples with oxygen content $x = 6.1$ and 6.4. In these samples the Yb^{3+} relaxation is dominated by a phonon mechanism. The temperature dependence of this relaxation was determined by measuring the Yb^{3+} EPR linewidth in a broad temperature range. The obtained results clearly demonstrate that the traditional Raman mechanism using the Debye approximation cannot describe the phononic contribution to relaxation. Instead, the Raman process involving optical phonons or an Orbach-like process via the excited vibronic levels of Cu^{2+} ions with energy $\Omega = 500(50)$ K is responsible for the phononic part of the Yb^{3+} relaxation in $YBa_2Cu_3O_x$.

The polycrystalline samples of $Y_{1-y}Yb_yBa_2Cu_3O_x$ with $x = 6.1$ and 6.4 were prepared by the standard solid state reaction. The as-prepared samples were oxidized in oxygen atmosphere at 500^{o}C. The required oxygen content in the samples was adjusted by gettering in a closed ampoule with metallic copper (850° C, 10 h; cooling 10° C/h). The dilute level of the Yb doping ($y = 0.02$) was chosen in order to minimize broadening effects from Yb-Yb interactions and at the same time to obtain a sufficiently strong EPR signal. The EPR measurements were performed with an X-band BRUKER EMX spectrometer equipped with an Oxford Instruments helium flow cryostat. In order to avoid a signal distortion due to skin effects, the samples were ground and the powder was suspended in epoxy. The c-axes grain-orientation was obtained by placing the samples in a 9 T magnetic field until the epoxy hardened.

The rare-earth site in $YBa_2Cu_3O_x$ is eight-fold coordinated by oxygens lying in the CuO_2 bilayers. In this case the eight-fold degeneracy of the ground-state multiplet $^2F_{7/2}$ of the Yb^{3+} ions ($4f^{13}$) is split by the crystal electric field with either a Γ_7 or a Γ_6 ground state doublet [10]. Generally, this splitting is large enough so that only the lowest lying doublet is appreciably populated. So, EPR signals should be observed only for this doublet. In fact, the observed EPR spectra of Yb^{3+} in $Y_{0.98}Yb_{0.02}Ba_2Cu_3O_x$ can be described with an effective spin $S = 1/2$ and anisotropic g values [12]. In the sample with oxygen content $x = 6.4$ the anisotropic g values $g_\parallel = 3.13(3)$ and $g_\perp = 3.49(3)$ are observed at $T = 40$ K. The average value $\bar{g} = 3.37$ is close to $g = 3.43$ expected for the isolated Γ_7 ground doublet [10].

Fig. 1 shows typical EPR spectra for the $x = 6.4$ sample at different temperatures with the magnetic field applied perpendicular to the c-axis direction. The EPR lines in the $g \approx 2$ region are due to Cu^{2+} defect centers, which are always present in $YBa_2Cu_3O_{6+x}$ [13]. The Yb^{3+} EPR spectrum at 37 K is rather complex, with a dominant central line and shoulders on each side, which are due to partially resolved hyperfine components from ytterbium isotopes with nonzero nuclear spin. In Fig. 1 one can see that with icreasing temperature the Yb^{3+} EPR line broadens and the multiple-line structure of the Yb spectra gradually merges into one line which continues to broaden with temperature. This broadening is due to the Yb relaxation and is the subject of the present study.

The anisotropic nature of the Yb^{3+} signal, the partially resolved hyperfine structure and the non-ideal grain alignment, make it very difficult to accurately model the complex shape of the Yb EPR spectra and its evolution with temperature. In order to extract the linewidth related to relaxation, we used a similar approach as used in inelastic neutron scattering studies

of rare-earth relaxation in cuprates [14]. This method is based on the assumption that the observed line shape consists of two components: a temperature-independent residual function due to inhomogeneous broadening and a temperature-dependent function related to relaxational broadening. The exact function used to describe the residual line shape is not important. We used a sum of several Lorentzians to model the inhomogeneous broadening at low temperatures, where relaxational broadening is negligible. The line drawn through the 37 K data in Fig. 1 represents the residual function. Having established the residual function, we kept it fixed at all temperatures and fitted the data at higher-temperature by convolving the residual function with the broadening function of Lorentzian shape. The center, width, and amplitude of the broadening function were the only variable parameters. The resulting fits are shown in Fig. 1

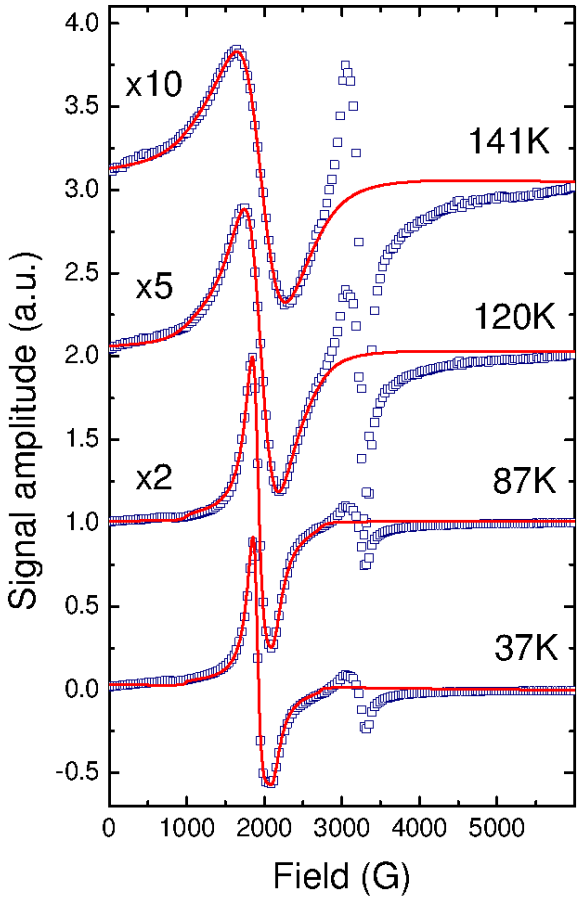

Figure 1. (Color online) EPR spectra in grain oriented $Y_{0.98}Yb_{0.02}Ba_2Cu_3O_{6.4}$ at different temperatures for the magnetic field direction perpendicular to the crystal c-axis. The solid lines are fits to the data, and include relaxation as described in the text.

Our detailed EPR studies have shown that in superconducting $YBa_2Cu_3O_x$ samples both electronic and phononic processes contribute to the Yb^{3+} relaxation [12]. The electronic contribution to relaxation decreases with decreasing x. Below $x = 6.4$ the electronic contribution is negligible and the Yb^{3+} relaxation is dominated by a phonon mechanism. We observed that the temperature dependence of the relaxation rate follows closely the exponential function $C\exp(-\Delta/T)$ in both samples ($x = 6.1$ and 6.4) with $\Delta \simeq 500(50)$ K. This is demonstrated in Fig. 2 for the sample with $x = 6.4$, where the relaxation rate is plotted on a logarithmic scale versus inverse temperature. Such an exponential dependence is expected for the Orbach relaxation process via an excited intermediate energy level [15]. In this case Δ corresponds to the separation between the ground state doublet and the excited level. According to inelastic neutron scattering experiments the first excited energy level of Yb in $YBa_2Cu_3O_7$ is about 1000 K above the ground state doublet [16]. Since there is no excited crystal field energy level with $\Delta \sim 500$ K, the traditional Orbach relaxation mechanism can be excluded.

Another possible relaxation mechanism is the Raman two-phonon process involving acoustic phonons with the following temperature dependence in the case of a Kramers doublet [10]:

$$T_1^{-1}(T) = CT^9 \int_0^{\Theta_D/T} z^8 e^z/(e^z-1)^2 dz. \quad (1)$$

We found that this expression describes the temperature dependence of the relaxation rate quite well, as shown by the dashed line in Fig. 2. However, the Debye temperature $\Theta_D = 650(20)$ K obtained from the fit is too large compared to $\Theta_D = 300$ K reported for low-doped $YBa_2Cu_3O_x$ [17].

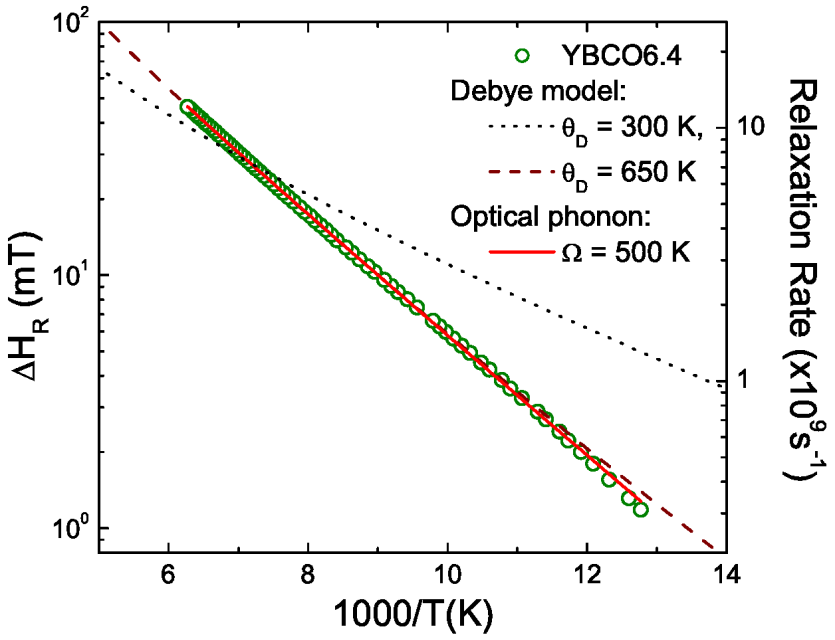

Figure 2. (Color online) Temperature dependence of the relaxation linewidth ΔH_R in $Y_{0.98}Yb_{0.02}Ba_2Cu_3O_{6.4}$ plotted on a logarithmic scale versus inverse temperature. The solid line is a best fit to Eq. (2). The dashed and dotted lines represent the best fits using Eq. (1) with $\Theta_D = 650\,\mathrm{K}$ and 300 K, respectively.

The dotted line in Fig. 2, calculated with $\Theta_D = 300\,\mathrm{K}$ clearly does not fit the data and shows that a conventional Raman process involving acoustic phonons cannot explain the temperature dependence of the Yb^{3+} relaxation rate in $YBa_2Cu_3O_x$. It was already mentioned in the introduction that in the vast majority of publications concerning spin relaxation, experimental results are interpreted using the Debye model with a linear dispersion law. The optical modes are taken into account only by extending the acoustical modes beyond the Brillouin zone with the Debye temperature Θ_D defined by the total degree of freedom of the lattice. Moreover, using this approach in many publications the authors attempted to extract the Debye temperature from the temperature dependence of the spin-lattice relaxation rate. The dashed line in Fig. 2 shows that in principle it is possible to fit experimental results with such a model, however Θ_D extracted from this fit has nothing to do with the real Debye temperature of the material. Therefore, although the Debye model is reasonable to describe the heat capacity properties, our results show that it may be misleading for the spin-lattice relaxation at relatively high temperatures. It is a consequence not only of a completely different dispersion law of optical phonons with a narrow band of frequencies, but also due to very different amplitudes and relative phases of neighboring ions vibrations in comparison with acoustical modes.

For a Raman process with the participation of some local vibrations or optical phonons

$$T_1^{-1}(T) = C\exp(\Omega/T)/[\exp(\Omega/T) - 1]^2, \tag{2}$$

where Ω is the optical phonon frequency [4,7]. The solid line in Fig. 2 represents a best fit to the data using Eq. (2) with $\Omega \simeq 500(50)$ K. This indicates that the Raman process involving optical phonons describes well the phonon contribution to the Yb^{3+} spin-lattice relaxation. Optical phonons within this energy range exist in $YBa_2Cu_3O_x$: (i) in-plane bond-bending (500-560 K) and (ii) out of plane B_{1g} (470 K) phonons [18,19]. Preliminary theoretical calculations taking

into account in-plane optical phonons have been performed in order to compare the contribution of acoustical and optical phonons to the Yb^{3+} spin relaxation in $YBa_2Cu_3O_x$. It was found that the optical phonon contribution to relaxation in the temperature range 60-140 K is at least one order of magnitude higher than the contribution from acoustical phonons [20]. Additional theoretical calculations are necessary in order to determine which of the two optical phonon modes (in-plane bond-bending or out of plane B_{1g}) mostly contributes to the Yb^{3+} spin-lattice relaxation.

Finally, it is interesting to note that an exponential temperature dependence of the spin relaxation rate was also observed in an EPR study of crystals containing Jahn-Teller (JT) transition metal ions [21, 22]. In this case relaxation also takes place due to an Orbach-like process via the excited vibronic levels of the JT ion (localized Slonczewski modes) [23]. It would be interesting to search for localized vibronic modes in cuprates using inelastic neutron scattering. Such vibronic modes could lead to the observed exponential temperature dependence of the relaxation rate in $YBa_2Cu_3O_x$ if the Yb^{3+} spin relaxation occurs due to coupling to the vibrations of surrounding CuO_6 complexes since Cu^{2+} is a strong JT ion.

To summarize, we studied the temperature dependence of the Yb^{3+} EPR linewidth in $YBa_2Cu_3O_x$ with oxygen content $x = 6.1$ and 6.4. It was shown that the Raman process involving optical phonons or an Orbach-like process via the excited vibronic levels of Cu^{2+} ions with energy ~ 500 K is responsible for the phononic part of the Yb^{3+} relaxation in $YBa_2Cu_3O_{6+x}$. Our results demonstrate that optical phonons or local vibrations may provide a dominant contribution to spin-lattice relaxation of paramagnetic ions at sufficiently high temperatures, which cannot be accounted for by the traditional approach using the Debye approximation.

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