Temperature dependence of the EPR linewidth of \( \text{Yb}^{3+} \) ions in \( \text{Y}_{0.99}\text{Yb}_{0.01}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{X} \) (6 \( \leq X \leq 7 \)) compounds: evidence for an anomaly near the superconducting transition

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Abstract
Electron paramagnetic resonance experiments on doped \( \text{Yb}^{3+} \) ions in \( \text{Y}_{0.99}\text{Yb}_{0.01}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{X} \) (6 \( \leq X \leq 7 \)) compounds with different oxygen contents have been made. We have observed a strong temperature dependence of the EPR linewidth in all the investigated samples caused by the Raman processes of spin–lattice relaxation. The spin–lattice relaxation rate anomaly revealed near \( T_C \) in the superconducting species can be assigned to the phonon density spectrum changes.

1. Introduction

\( \text{YBa}_2\text{Cu}_3\text{O}_X \) (\( \text{YBa}_2\text{Cu}_3\text{O}_7 \), \( \text{YBCO} \), 1-2-3) compounds are superconductors at \( X > 6.35 \) (\( T_C = 92 \) K for \( X = 7.0 \)), and they continue to be intensively studied by different spectroscopy methods such as inelastic neutron spectroscopy (INS), Mössbauer and Raman spectroscopy, nuclear magnetic (NMR) and electron paramagnetic resonance (EPR) methods \([1]\) in order to accumulate the data for a thorough understanding of the origin of high-temperature superconductivity (HTSC).

The behaviour of phonons in high-temperature superconductors is of great significance as dynamic lattice effects may play a relevant role in the mechanism of underlying superconductivity in these compounds. There are only a few publications on electron spin–lattice relaxation (SLR) processes in YBCO (see the review \([2]\) and references therein). The most direct and reliable pulse EPR techniques—electron spin-echo and pulsed saturation—are not applicable for this because of the very short relaxation times. These measurements, nevertheless, could give information about the spin–lattice relaxation mechanisms, the vibrational spectrum of the substance being studied, and their features.

In this paper, we present the spin–lattice relaxation rate measurements of doped \( \text{Yb}^{3+} \) ions from the temperature dependence of electron spin resonance linewidth in \( \text{Y}_{0.99}\text{Yb}_{0.01}\text{Ba}_{2}\text{Cu}_{3}\text{O}_{X} \) with different oxygen contents.

2. Experimental details

The polycrystalline powder \( \text{YBa}_2\text{Cu}_3\text{O}_X \) samples were prepared by the standard solid-state reaction technique. Appropriate proportions of \( \text{Y}_2\text{O}_3\), \( \text{BaCO}_3\), and \( \text{CuO} \) were dried at 400–500 °C, mixed and ground thoroughly into a fine powder. The \( \text{Yb}^{3+} \) dopants were added using an oxide \( \text{Yb}_2\text{O}_3 \) in a ratio \( \text{Yb}:\text{Y} = 1:100 \). These mixtures were converted to \( \text{RYBa}_2\text{Cu}_3\text{O}_7 \) by thermal treatment, after which the oxygen content was reduced to the specified value \( X \) by heating the samples. The exact value of \( X \) depends on the annealing procedure and was defined from the lattice parameter along the crystallographic \( c \)-axis \([3]\) using x-ray diffraction. Purity checking of our samples by means of x-ray phase analysis does not reveal that the proportion of impurity is less than 1%. The values of \( T_C \) for different \( X \) were determined from the temperature dependence of microwave absorption in a low magnetic field. In the present work, we have investigated four samples with different oxygen contents (see table 1).

It is very important to investigate single crystal samples of YBCO, because of their strong anisotropy. In this work, the YBCO powders were milled (size = 1–3 \( \mu \text{m} \)), then mixed...
with paraffin or epoxy resin and placed in a glass tube in a strong magnetic field (≥15 kG) to prepare the quasi-single-crystal samples. The c-axes of the individual crystallites were predominantly oriented along the direction C of the aligning magnetic field after hardening of epoxy resin. The EPR linewidth of the Yb³⁺ ions in the samples prepared by the aligning magnetic field after hardening of epoxy resin. The

**Table 1.** Critical and Debye temperatures, the minimal EPR linewidth ΔH_{pp} measured at temperatures T_{min}, effective g-values (estimated at T = 50 K), and the SLR parameter C against oxygen content X in YBa₂Cu₃Oₓ compounds.

| X   | T_C (K) | T_{min} (K) | ΔH_{pp} (G) | g   | Θ_D (K) | C (10⁻² s⁻¹ K⁻⁹) |
|-----|---------|-------------|-------------|-----|---------|------------------|
| 0.96| 85      | 55          | 95          | 3.07| 450     | 1.06             |
| 0.98| 65      | 45          | 90          | 3.11| 370     | 4.23             |
| 1.01| 40      | 25          | 75          | 3.18| 280     | 15.3             |
| 1.06| —       | 20          | 95          | 3.48| 250     | 50               |

*For the sample with X = 6.0 the perpendicular value of the g-tensor g₂l is given.

Figure 1 shows the EPR spectrum of Yb³⁺ ions in Y₀.₉₉Y₀.₀₁Ba₂Cu₃O₆.₆₇. In addition, the unavoidable intensive signal at g ≈ 2 in all investigated samples and low-field non-resonance signal of microwave absorption in the superconducting phase are detected. The effective values of the g-tensor and the minimal EPR linewidths of Yb³⁺ ions in the parallel (H // C) orientation are presented in table 1. The experimental g-values are in an excellent agreement with calculations using the crystalline electric field parameters as determined by inelastic neutron scattering [4, 5]. The integrated intensity of the EPR signal in the superconducting species increases with decreasing temperature below 80 K but more slowly than would be expected according to the Curie law.

Figure 2 shows the complicated temperature dependence of the Yb³⁺ EPR peak-to-peak linewidth ΔH_{pp} in YBa₂Cu₃O₆.₈₅ with a minimum at the temperature T_{min} and a small step of ΔH_{pp} near T_C. The EPR measurements on this sample at T < T_{min} have been discussed previously [6] and are not in the scope of the present paper. A rapid increase of ΔH_{pp} as T increases (non-linear, non-Korringa slope) in all investigated samples for T > T_{min} is very common for the rare-earth ions in single crystals (except for these with half-filled f-shell, e.g. Gd³⁺) and, as we have shown for Yb³⁺ and Er³⁺ probes in YBaCuO compounds [6-8], caused by the 4f-electron–phonon interaction only. To determine the dominating spin–lattice relaxation process we use the next approach.

The EPR linewidth caused only by the SLR, ΔH_{pp}^{SLR}, can be extracted from the experimentally measured EPR linewidth ΔH_{pp} by the relation [9]

\[
(\Delta H_{pp})^2 = \Delta H_{pp}^{SLR} \Delta H_{pp} + (\Delta H_{pp}^{min})^2.
\]

(1)

We take into account the fact that the EPR line has a Gaussian lineshape at g ≈ 2, and the Lorentzian lineshape is connected usually to the inhomogeneities of the crystal electric field (CEF) potential, and the Lorentzian lineshape is connected usually to the term ΔH_{pp}^{SLR}. The extracted data just slightly differ from those obtained by using the well-known expressions ΔH_{pp} = ΔH_{pp}^{Gaussian} + ΔH_{pp}^{min} for Lorentzian–Lorentzian or (ΔH_{pp})^2 = (ΔH_{pp}^{SLR})^2 + (ΔH_{pp}^{min})^2 for Gaussian–Gaussian convolutions, correspondingly [10].

The SLR rate T^{-1}_I can be expressed through ΔH_{pp}^{SLR} as follows [11]:

\[
T^{-1}_I (s^{-1}) = (\sqrt{2}/g\beta^2) \Delta H_{pp}^{Gaussian} (G) \\
= 7.62 \times 10^6 g \Delta H_{pp}^{SLR} (G),
\]

(2)

where β is the Bohr magneton, and h is Planck’s constant.

Figure 3 shows the temperature dependences of the SLR rate T^{-1}_I for samples with different oxygen contents. The relaxation rate T^{-1}_I of Yb³⁺ ions can be described approximately using formula [12]

\[
T^{-1}_I = CT^9 f(\Theta_D/T).
\]

(3)
MR Gafurov et al

Figure 3. SLR rates for Yb$^{3+}$ ions in YBa$_2$Cu$_3$O$_x$ with $X = 6.85$ (a), 6.67 (b), and 6.0 (c) derived from the EPR line broadening using equation (2). The data are presented in log–log scale.

Figure 4. Temperature dependence of the SLR rate of Yb$^{3+}$ ions in YBa$_2$Cu$_3$O$_{6.85}$. Dashed line—approximation using equation (3) with parameters listed in table 1. Solid lines—exponential approximation using equation (4) with $\Delta = 500$ K, $B_1 = 11.4 \times 10^{-11}$ s$^{-1}$ (below $T_C$), and $B_2 = 5.9 \times 10^{-11}$ s$^{-1}$ (above $T_C$). The data are presented in logarithmic scale.

The temperature dependence of $T_{1^{-1}}$ can alternatively be described as [16]

$$T_{1^{-1}} = B \exp(-\Delta_{SLR}/T)$$

(solid lines in figure 4). It manifests clearly the $T_C$ anomaly observed. For the sample with $X = 6.85$, for example, the factor $B$ decreases by a factor of approximately two with temperature ($B_1 \approx 11.4 \times 10^{-11}$ at $T < 80$ K and $B_2 \approx 5.9 \times 10^{-11}$ at $T > 100$ K with $\Delta_{SLR} = 500$ K). The lower the oxygen content is the weaker the SLR rate anomaly revealed. The exponential description in equation (4) may be assigned to the two-stage relaxation process via an intermediate energy level as well as to the Raman process with participation of some separated (optical, local, etc) vibrations in the crystal. The values of $\Delta_{SLR}$ are very close to those of $\Theta_D$ for all investigated samples and do not correlate with the energy of the first excited level of Yb$^{3+}$ ions in YBCO compounds ($\approx$1000 K [17], practically independent of oxygen content). Furthermore, for the two-step relaxation process with the Stark excitation energy of about 500 K, the order of magnitude of the pre-exponential factor $B$ should be approximately $10^{15}$. It is much more than $\approx 10^{12}$ estimated from our data. Therefore, we can exclude the two-stage relaxation process and conclude anew that the line broadening of Yb$^{3+}$ ions with temperature is caused by the Raman SLR process.

We have to note that the values of $\Delta_{SLR}$ (or $\Theta_D$) are in good correspondence with the peak positions in the Raman and inelastic neutron scattering spectra of high-$T_C$ YBCO compounds. For instance, the authors of [18] discuss the origin of the double peak observed near 300 cm$^{-1}$ ($\approx 430$ K) in NdBa$_2$Cu$_3$O$_7$. Pronounced enhancements of the spectral weight centred around 40 meV ($\approx 460$ K) for $X = 7.0, 33$ meV ($\approx 380$ K) for $X = 6.7$, and 25 meV ($\approx 290$ K) for $X = 6.5$ below $T_C$ in YBa$_2$Cu$_3$O$_x$ are revealed in [19] (cf with the values of $\Theta_D$ in table 1).

The anomaly of the spin–lattice relaxation rate near $T_C$ can be associated with the differences of the phonon spectrum

where $\int f(\Theta_D/T) \equiv f(z) \equiv I_8(z)/I_8(\infty)$, $I_8(z) = \int_0^\infty x^8 e^x/(e^x - 1)^2 dx$, $I_8(\infty) = 8!$ (dashed line in figure 4). This corresponds to the usual Raman SLR process with Debye approximation for lattice vibrations (and, therefore, the label $T_D^{-1}$ for the SLR rate in equation (3) is used). The magnitudes of the Debye characteristic temperature $\Theta_D$ and factor $C$ are listed in table 1. The values of $\Theta_D$ are in sufficiently good agreement with the data obtained from the specific heat capacity measurements [13] and calculations based on measurements of the elastic constants [14, 15].

A more detailed analysis is given in our previous paper [7], but we did not discuss the SLR rate anomaly near $T_C$ there.
of the YBaCuO host matrix in the superconducting and non-
superconducting states. For example, as it is shown in [20],
the phonon spectra density of the superconducting sample
with $X = 6.95$ at $T = 80$ K drastically differs from that
at $T = 290$ K, while there is no great difference for the
sample with $X = 6.35$. This is sensible for Yb$^{3+}$ ions because
practically the whole phonon spectrum is involved in the usual
Raman relaxation process. In addition, we have to note again
that a local peak in the vicinity of $40$ meV ($\approx 460$ K) was also
observed in [20] for the superconducting species.

We did not obtain the $T_C$ anomaly with Er$^{3+}$ doped ions
in $\text{Er}_{0.01} \text{Y}_{0.99} \text{Ba}_2 \text{Cu}_3 \text{O}_{6+X}$ compounds in our experiments [8].
This can also be understood in the framework of the above
approach. The line broadening of Er$^{3+}$ ions with temperature
is caused by the two-step resonance fluorescence SLR process.
The phonon density for the phonons with energy of 9–12 meV
(corresponding to Stark excitation energy $\Delta$ for Er$^{3+}$) involved
in the relaxation mechanism is approximately constant below
and above $T_C$ [20].

Our attempts to associate the anomaly with the small
changes of the sound velocity $\nu$ in the superconducting species
(see [21], for example) do not give any reasonable quantitative
or qualitative result, though the value $\nu$ appears as $\nu^{-10}$ in
the coefficient $C$ for the usual Raman and as $\nu^{-3}$ in the
coefficient $B$ for two-step processes, respectively. Although
the presumption could be right, it would be quite difficult to
explain the absence of the $T_C$ anomaly for Er$^{3+}$ ions.

4. Conclusion

Spin–lattice relaxation rate measurements of doped Yb$^{3+}$
ions from the temperature dependence of the electron spin
resonance linewidth in $\text{Y}_{0.99} \text{Yb}_{0.01} \text{Ba}_2 \text{Cu}_3 \text{O}_x$ with different
oxygen contents have been made. Near $T_C$ a small step in the
EPR linewidth and a corresponding anomaly in the $T_1^{-1}$
have been observed. The anomaly can be ascribed to
the phonon spectrum density changes of the YBaCuO host
matrix in the superconducting and non-superconducting states.
In this connection it might be interesting to carry out such
experiments with other rare-earth impurities and in other
frequency ranges.

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References

[1] Gshneider K A Jr, Eyring L and Maple M B (ed) 2000
Handbook on the Physics and Chemistry of Rare-Earths
vol 30 High Temperature Rare-Earths Superconductors–I
(Amsterdam: North-Holland)
Gshneider K A Jr, Eyring L and Maple M B (ed) 2001
Handbook on the Physics and Chemistry of Rare-Earths
vol 31 High Temperature Rare-Earths Superconductors–II
See also the recent publications and references therein
Sids Y, Pailh`es S, Keimer B, Bourges P, Ulrich C and
Regnault L P 2004 Phys. Status Solidi b 241 1204
Sherman E Ya, Ambrosch-Draxl C and Misochko O V 2002
Phys. Rev. B 65 140510
Carretta P, Lascialfari A, Rigamonti A, Tedesco P, Tedoldi F
and Larianov I A 2004 Phys. Rev. B 69 104512
Gafurov M R, Ivanshin V A, Kurkin I N, Rodionova M P,
Keller H, Gutmann M and Staub U 2003 J. Magn. Reson.
161 210
[2] Elschner B and Loidl A 2000 Electron paramagnetic resonance
in cuprate superconductors Handbook on the Physics and
Chemistry of Rare-Earths vol 30 High Temperature Rare-Earths
Superconductors–I ed K A Gshneider Jr, L Eyring and M B Maple
(Amsterdam: North-Holland)
[3] Jorgensen J D, Veal B W, Paullakas A P, Nowicki L J,
Craibtree G W, Claus H and Kwok W K 1990 Phys. Rev. B
41 1863
Mesot J, Allenspach P, Staub U, Furrer A, Mutka H, Osborn R
and Taylor A 1993 Phys. Rev. B 47 6027
[5] Misra S K, Chang Y and Festeiner J 1997 J. Phys. Chem.
58 1
Kurkin I N, Salikhov I Kh, Sedov L L, Teplov M A and
Zhdanov R Sh 1993 JETP 76 657
[8] Ivanshin V A, Kurkin I N, Gafurov M R, Salikhov I Kh,
Keller H and Gutmann M 2001 Physica C
[9] Dobryakov S N and Lebedev Ya S 1969 Sov. Phys.—Dokl.
13 873
[10] Stapleton H J and Brower K L 1969 Phys. Rev. Lett.
16 1668
[11] Antipin A A, Katyshev A N, Kurkin I N and Shekun L Ya
1967 Sov. Phys.—Solid State 9 3400
[12] Inderhees S E, Salamon M B, Friedmann T A and
Ginsberg D M 1987 J. Magn. Reson.
[13] Ledbetter H 1992 J. Magn. Reson. Sc. 7 2905
[14] Chaplot S L 1988 Phys. Rev. B 37 7435
[15] Abragam A and Bleaney B 1970 EPR of Transition Ions
(Oxford: Clarendon)
[16] Guillaume M, Allenspach P, Mesot J, Staub U, Furrer A,
Osborn R, Taylor A D, Stucki F and Untermaier P 1992
Solid State Commun. 81 999
[17] Heyen E T, Wegerer R, Schönher and Cardona M 1991
Phys. Rev. B 44 10195
[18] Fong H F, Keimer B, Milius D L and Aksay I A 1997 Phys.
Lett. 78 113
[19] Bar'yakhtar V G, Morozovsky A E, Pan V M, Pasechnik M V,
Vasil'kevich A A, Ivanitsky P G, Krotenko V T,
Maistrenko A N and Slisenko V I 1989 Physica C
[20] Bishop D J, Ramirez A P, Gammel P L, Batlogg B,
Rietman E A, Cava R J and Millis A J 1987 Phys. Rev. B
36 2401
[21] Bishop D J, Ramirez A P, Gammel P L, Batlogg B,
Rietman E A, Cava R J and Millis A J 1987 Phys. Rev. B
36 2408