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Solid State Section, Department of Physics, University of Athens[1]) *(a), Organic Chemistry, Department of Chemistry, University of Athens*[2]) *(b), and Democritos National Research Center for Physical Science, Athens*[3]) *(c)*

EPR Measurements on the Cu^{2+} Ion in the High-T_c Superconductors $MBa_2Cu_3O_{7-\delta}$

By

N. GUSKOS (a), C. A. LONDOS (a), CH. TRIKALINOS (a), S. M. PARASKEVAS (b), A. KOUFOUDAKIS (b), C. MITROS (b), H. GAMARI-SEALE (c), and D. NIARCHOS (c)

EPR studies are carried out on the polycrystalline high-T_c superconductors $MBa_2Cu_3O_{7-\delta}$ (M = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb and Lu). The onset of the superconducting transition is found to occur in the temperature range of 90 to 95 K (except for $LaBa_2Cu_3O_{7-\delta}$ where T_c = 50 K and $PrBa_2Cu_3O_{7-\delta}$ which is not superconducting for temperatures above 4.2 K). In all of these compounds an EPR spectrum of Cu^{2+} ions in the orthorhombic local symmetry, is observed. The signal intensities are found to depend strongly on the particular rare-earth ions of the lanthanide series which are substitutionally introduced into the host lattice of $YBa_2Cu_3O_{7-\delta}$, at Y-ions site. "Skin effect" is suggested to be the main cause of the observed changes in the intensity of EPR signals.

An polykristallinen Hoch-T_c-Suptraleitern $MBa_2Cu_3O_{7-\delta}$ (M = La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb und Lu) werden EPR-Untersuchungen durchgeführt. Der Einsatz des Supraleitungsübergangs tritt im Temperaturbereich von 90 bis 95 K (außer für $LaBa_2Cu_3O_{7-\delta}$, wo T_c = 50 K ist, und $PrBa_2Cu_3O_{7-\delta}$, das für Temperaturen oberhalb 4,2 K nicht supraleitend ist) auf. In allen diesen Verbindungen wird ein EPR-Spektrum von Cu^{2+}-Ionen mit lokaler rhombischer Symmetrie beobachtet. Die Signalintensitäten hängen stark von den speziellen Selten-Erd-Ionen der Lanthanserie ab, die substitutionell in das Wirtsgitter von $YBa_2Cu_3O_{7-\delta}$ auf Y-Ionenplätzen eingebaut werden. Es wird angenommen daß der „Skineffekt" die Hauptursache der beobachteten Änderungen in der Intensität der EPR-Signale ist.

1. Introduction

A large number of investigations on high-T_c superconductors of the type $YBa_2Cu_3O_{7-\delta}$ and $MBa_2Cu_3O_{7-\delta}$ (M rare-earth ions) using the EPR method have been reported, e.g. [1 to 7]. The majority of these investigations exhibit a characteristic EPR spectrum of Cu^{2+} ions with orthorhombic local symmetry. Up to now a number of authors have suggested that this spectrum of Cu^{2+} ions arises from other phases, e.g. green or tiny impurities [8 to 11]. Our room temperature (RT) EPR experiments in a number of powder HTS show that the observed resonance line could be attributed to Cu^{2+} ions possessing anisotropic g-tensor with orthorhombic symmetry.

In the present work, a report is given concerning the EPR studies of Cu^{2+} ions in $MBa_2Cu_3O_{7-\delta}$ (M = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb, and Lu) polycrystalline

[1]) Solonos str. 104, G-10680, Athens, Greece.
[2]) Naverinou str. 13A, G-10680 Athens, Greece.
[3]) Aghia Paraskevi, Attikis, G-15310 Athens, Greece.

samples and an attempt is made to understand why the intensities of these lines show significant differences between the various compounds. It is worth noticing that the substitute rare-earth ions in $YBa_2Cu_3O_{7-\delta}$ are expected to change the lattice parameters and presumably the density of states of the metallic phase at the Fermi level, a fact that could effect the intensity of the EPR signals.

2. Sample Preparation

The $MBa_2Cu_3O_{7-\delta}$ samples were prepared using the standard powder technique, by first mixing stoichiometric amounts of CuO, M_2O_3, and $BaCO_3$ (powders), followed by successive annealing in oxygen atmosphere and grinding. The procedure was performed in four 24 h steps at temperatures of 910, 920, 925, and 920 °C. In order to obtain the superconducting phases, the sintered samples, after the final grinding, were introduced into the furnace (920 °C, in flowing O_2) and cooled down to 500 °C, at which temperature they were left for 24 hs. Then, the furnace was turned off and the samples were slowly cooled down to RT.

3. Experimental Results and Discussion

Samples were characterized at RT with a Phillips X-ray powder diffractometer using CoKα radiation. The diffraction patterns showed that all samples consist of a single phase which could be indexed on the basis of an orthorhombic unit cell.

The magnetic measurements were carried out using a vibrating sample magnetometer in a field 0.02 T. The phase transition temperatures T_c for all our samples were found to be between 90 to 95 K except for the $LaBa_2Cu_3O_{7-\delta}$ sample, which has a significantly smaller T_c value around 50 K. Our EPR investigations of $LaBa_2Cu_3O_{7-\delta}$ material in the tetragonal phase have shown that inside this material various interaction could take place between two Cu ions of four Cu ions or even La ions bridging with O_2^- [12]. Presumably, the above interactions might be the cause of the lower transition temperature T_c in the superconducting state observed for $LaBa_2Cu_3O_{7-\delta}$ compared to the other rare-earth compounds. These interactions also affect the crystal structure causing difficulties in finding the exact lattice parameters of $LaBa_2Cu_3O_{7-\delta}$. The lattice parameters of $PrBa_2Cu_3O_{7-\delta}$ are not reported

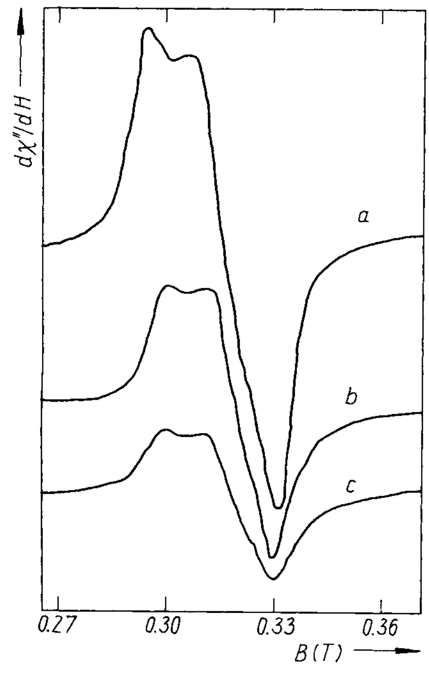

Fig. 1. The EPR spectrum of Cu^{2+} ions in ceramic powders of (a) $YBa_2Cu_3O_{7-\delta}$, (b) $EuBa_2Cu_3O_{7-\delta}$ and (c) $DyBa_2Cu_3O_{7-\delta}$

since XRD studies have shown the existence of two phases. Magnetic measurements have not shown the existence of any superconducting phase above 4.2 K for this material.

Magnetic measurements employing a field-cooled mode gave for the ratio $L = (-4\pi M/H)$ values indicating that the percentage of the superconducting phases were in the range of 20 to 30%.

RT powder EPR spectra were obtained with a Varian E-4 model X-band spectrometer operating at 9.4 GHz using 100 kHz field modulation. The modulation amplitude was chosen to be 1.2×10^{-3} T while the level of the microwave power on the sample was kept at 5 mW. The measurements were performed on powdered (50 mg) samples of cylindrical shape. At RT the high-T_c superconductors $MBa_2Cu_3O_{7-\delta}$ have shown the conventional EPR spectrum of powder samples, with an anisotropic **g**-tensor, which can be attributed to Cu^{2+} ions in orthorhombic symmetry (Fig. 1 and 2). The shape and the position of the lines agree very well with those reported in the literature for the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$. For all the samples the spin-Hamiltonian parameters have the same values: $g_x = 2.098(5)$, $g_y = 2.039(5)$, and $g_z = 2.232(5)$.

Comparison among different $MBa_2Cu_3O_{7-\delta}$ samples under similar conditions showed absolute EPR signal intensities widely differing by at least one order of magnitude.

For $GdBa_2Cu_3O_{7-\delta}$ an additional EPR line (Fig. 2) was recorded [13]. The linewidths ΔH and the spin-Hamiltonian parameter g derived are: $\Delta H = 0.2420(50)$ T and $g = 1.998(5)$. The experimental g-value of $GdBa_2Cu_3O_{7-\delta}$ corresponds closely to the value for S-state rare-earth ions, such as Eu^{2+} and Gd^{3+} [14]. This result is consistent with the assumption of trivalent cations which is reasonable for 123 superconductors [15, 16]. The EPR spectrum for Gd^{3+} ions for high-T_c superconductors has already been reported [1, 7]. It consists of one single, slightly asymmetric, line of width greater than 0.1 T. Our studies have shown that only in two cases single EPR line could be observed: on the samples with oxygen deficiency and on those with increased impurity concentrations [17]. The EPR spectra at RT of all our samples of high-T_c superconductors $GdBa_2Cu_3O_{7-\delta}$ (which are in the single orthorhombic phase) have shown a broad line which consists of the superposition of two lines arising from the Cu^{2+} and Gd^{3+} ions.

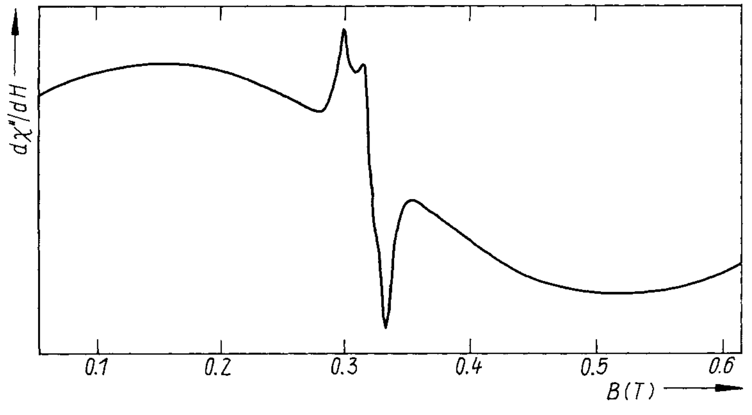

Fig. 2. The EPR spectra of divalent copper and trivalent gadolinium ions in polycrystalline $GdBa_2Cu_3O_{7-\delta}$

For the case of high-T_c superconductors $SmBa_2Cu_3O_{7-\delta}$ a single EPR line with g = 2.05 at 300 K has been reported [4]. Such a line was not detected in our experiments at RT. However, a similar line was observed at nitrogen temperature (NT) measurements on the sample $SmBa_2Cu_3O_{7-\delta}$.

The observed changes in the intensities of EPR lines of Cu^{2+} ions could be attributed to the so-called "skin effect" [13, 18, 19]. According to this effect the value of the sample that could be penetrated by microwave radiation decreases when the electrical conductivity increases. The relative intensities of the EPR signals is given [18] by the following relation:

$$I/I_0 = \{2\exp(-w) + [1 + \exp(-2w)]/w\}/[1 + \exp(-w)]^2 , \quad (1)$$

where $w = d/\delta$ (d being the thickness of the conducting sample), $\delta = (2/\mu_0\omega\sigma)^{1/2}$ is the skin depth, ω the frequency of microwave radiation, and σ the electrical conductivity. We used this relation to estimate the electrical conductivity from the changing relative intensity of the EPR signals. A value of 500 Ω^{-1} cm^{-1} is deduced for the electrical conductivity at RT for the high-T_c superconductor $YBa_2Cu_3O_{7-\delta}$ [20]. From (1) we can estimate the corresponding I/I_0 ratio. Assuming that I_0 is the same for all the $MBa_2Cu_3O_{7-\delta}$ compounds, the electrical conductivities are obtained (Table 1) using the values of I obtained from EPR signals (the dimension of the sample was d = 2 mm).

It is interesting to note that other researcher [10] have not observed an EPR signal arising from Cu^{2+} ions in single crystals of the above superconductors. We believe that the failure to observe the EPR spectrum is firstly due to the fact that the masses of the single crystals were small [2] and secondly because the electrical conductivity was so high that the microwave could not penetrate the whole volume of the sample.

Significantly enough great care should be taken during the preparation procedure of the above samples in avoiding the creation of other phases which could strongly influence the intensity of the EPR signal.

In conclusion, in all our samples of $MBa_2Cu_3O_{7-\delta}$ (M = Y, La, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Tm, Yb, and Lu) materials we have observed a characteristic EPR spectrum arising from the Cu^{2+} ions in the local orthorhombic symmetry. For the various substitutional rare-earth ions the intensities of the above spectrum significant changes appear. We have attributed these changes to the skin effect.

Table 1

compound	relative intensity I/I_0	σ (Ω^{-1} cm^{-1})
$YBa_2Cu_3O_{7-\delta}$	0.0281	500
$LaBa_2Cu_3O_{7-\delta}$	0.0439	198
$PrBa_2Cu_3O_{7-\delta}$	0.0081	5795
$NdBa_2Cu_3O_{7-\delta}$	0.0127	2357
$SmBa_2Cu_3O_{7-\delta}$	0.0154	1604
$EuBa_2Cu_3O_{7-\delta}$	0.0129	2285
$GdBa_2Cu_3O_{7-\delta}$	0.0211	856
$DyBa_2Cu_3O_{7-\delta}$	0.0090	4687
$HoBa_2Cu_3O_{7-\delta}$	0.0163	1452
$TmBa_2Cu_3O_{7-\delta}$	0.0251	603
$YbBa_2Cu_3O_{7-\delta}$	0.0132	2186
$LuBa_2Cu_3O_{7-\delta}$	0.0305	409

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References

[1] R. N. Schwartz, A. C. Pastor, R. C. Pastor, K. W. Kirby, and D. Rytz, Phys. Rev. **B36**, 8858 (1987).
[2] N. Guskos, Th. Leventouri, Ch. Trikalinos, and M. Calamiotou, phys. stat. sol. (b) **149**, K157 (1988).
[3] F. Mehran, S. E. Barnes, T. R. McGuire, T. R. Dinger, D. L. Kaiseserand, and F. Holzberg, Solid State Commun. **66**, 299 (1988).
[4] J. Dumas, B. Laayadi, R. Buder, J. Marcus, and C. Schlenker, Physica **C153–155**, 754 (1988).
[5] N. Guskos, Th. Leventouri, Ch. Trikalinos, M. Calamiotou, S. M. Paraskevas, J. Kuriata, and L. Sadlowski, phys. stat. sol. (b) **152**, K9 (1989).
[6] S. K. Misra and E. Misiak, J. Phys. Condensed Matter **1**, 9471 (1989).
[7] N. E. Alekseevski, A. V. Mitin, V. I. Nizhankovskii, I. A. Garifullin, N. N. Garifanov, G. G. Khaliullin, E. P. Khylbov, B. I. Kochelaev, and L. R. Tagirov, J. Low-Temp. Phys. **20**, 3041 (1989).
[8] G. J. Bowden, P. R. Ellistron, K. T. Wan, S. X. Dou, K. E. Easterling, A. Bourdillon, C. C. Sorrel, B. A. Cornell, and F. Separovic, J. Phys. **C20**, L545 (1987).
[9] I. Onyszkiewicz, M. Koralewski, P. Czarnecki, R. Micnas, and S. Robaszkiewicz, Physica **147B**, 166 (1987).
[10] J. Albino, O. de Aquiar, A. A. Menovski, J. van demm Berg, and H. B. Broom, J. Phys. **C21**, L237 (1988).
[11] S. K. Hoffman, B. Czyzyk, and J. Stankowski, Acta phys. Polon. A **77**, 621 (1990).
[12] N. Guskos, unpublished dates.
[13] N. Guskos, G. P. Triberis, M. Calamiotou, Ch. Trikalinos, A. Koufoudakis, C. Mitros, H. Gamari-Seale, and D. Niarchos, phys. stat. sol. (b) **162**, 243 (1990).
[14] A. Abragam and B. Bleaney, Electron Paramagnetic Resonance of Transition Ions, Clarendon Press, Oxford 1970.
[15] M. Eibschultz, D. M. Murphy, S. Sunshine, L. S. van Uitert, S. M. Zahurak, and W. H. Grodkiewicz, Phys. Rev. **B35**, 8714 (1987).
[16] S. Tanaka, S. Uchida, H. Tukagi, K. Kitazawa, K. Kishio, S. Tajima, and K. Fueki, MRS Anaheim Symp., USA, Mat. Res. Soc., Solid State, 1987 (p. 5).
[17] A. Koufoudakis, C. Mitros, H. Gamari-Seale, D. Niarchos, N. Guskos, M. Calamiotou, and Ch. Trikalinos, Book Abstracts, ICMC '90, Conf. High-T_c Superconductors, May 9 to 11 Garmisch-Partenkirchen, FRG.
[18] M. Godlewski, H. Przybilinska, and J. M. Langer, Appl. Phys. A **30**, 105 (1983).
[19] N. Guskos, J. Kuriata, and I. H. Salikhov, J. Phys. C **17**, 2175 (1984).
[20] E. Babic, Z. Marohnic, M. Prester, and N. Brnicevic, Phil. Mag. Letters **56**, 91 (1987).

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