

Electron paramagnetic resonance of copper centres in potassium tantalate single crystals

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 6855

(<http://iopscience.iop.org/0953-8984/14/27/309>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.96

The article was downloaded on 18/05/2010 at 12:14

Please note that [terms and conditions apply](#).

Electron paramagnetic resonance of copper centres in potassium tantalate single crystals

A G Badalyan¹, P G Baranov¹, D V Azamat¹, V A Trepakov¹,
C B Azzoni², P Galinetto², M C Mozzati², L Jastrabik³ and J Rosa³

¹ Ioffe Physico-Technical Institute, 26 Polytekhnicheskaya Str., St Petersburg 194021, Russia

² INFN-Dipartimento di Fisica 'A Volta', I-27100 Pavia, Italy

³ Institute of Physics, AS CR, 18221 Prague, Czech Republic

E-mail: Andrey.Badalyan@pop.ioffe.rssi.ru

Received 26 December 2001

Published 28 June 2002

Online at stacks.iop.org/JPhysCM/14/6855

Abstract

Electron paramagnetic resonance (EPR) of exchange-coupled pairs of Cu^{2+} ions was observed in $\text{KTaO}_3:\text{Cu}$, $\text{K}_{1-x}\text{Li}_x\text{TaO}_3:\text{Cu}$ and $\text{K}_{1-x}\text{Li}_x\text{Ta}_{1-y}\text{Nb}_y\text{O}_3:\text{Cu}$ single crystals. The spectra are typical of centres with $S = 1$ and tetragonal symmetry with the pair axis parallel to the [100], [010] or [001] directions. The angular and temperature dependences of the signals have been studied. The experimental results are explained in terms of a pair centre model, which consists of a chain of two equivalent copper ions and three oxygen vacancies. The two copper ions occupy neighbouring tantalum sites and one of the oxygen vacancies lies between them, the chain running in the (100) direction. Ferromagnetic exchange coupling takes place between the copper ions, as confirmed by the thermal behaviour of the corresponding EPR spectra.

1. Introduction

KTaO_3 (KTO) single crystals have an ideal perovskite structure and, if appropriately doped with various impurities, constitute an object of considerable interest for quite a number of attractive applications. EPR in KTaO_3 has been used to study a variety of dopants–transition metal ions. These extensive studies furnished much information about the defect structure and the interaction between ions and ligands and structural pair defects, e.g., of impurity ion–vacancy type [1]. In particular, early EPR studies of Cu-doped KTO [2, 3] dealt with axial Cu^{2+} single centres. The first observation of exchange-coupled Cu^{2+} – Cu^{2+} pair centres was recently reported in [4].

The KTaO_3 cubic perovskite structure can be visualized as a cube with six oxygen ions at face centres, a tantalum ion at the body centre and eight potassium ions at the corners. During crystal growth, copper ions substitute Ta^{5+} in the octahedral position and oxygen vacancies are required to neutralize the extra charge of Ta^{5+} . Divalent copper has $3d^9$ configuration. In

the octahedral crystal field, the 2D ground state of Cu^{2+} splits into an orbital doublet E_g and an orbital triplet T_{2g} , with the doublet lying at lower energy. The degeneracy of the doublet state is removed by tetragonal distortion of the Cu^{2+} environment. The oxygen vacancies associated with the Cu^{2+} ions can reduce the local cubic symmetry to a tetragonal one, with the tetragonal axis parallel to the (100) direction. Two axial Cu^{2+} centres have been observed with different g -values and SHF constants [4].

As long as the concentration of the copper impurities is small, only two types of single Cu^{2+} ion EPR spectra are observed. At high enough Cu^{2+} doping level, exchange-coupled Cu^{2+} - Cu^{2+} pairs can be formed because of the higher probability of occupation by two Cu^{2+} ions of adjacent octahedral sites. The interaction between the ions of such a pair gives rise to EPR spectra entirely different from those of isolated ions [4]. In the following sections, fine, hyperfine (HF) and superhyperfine (SHF) structures of the pair spectrum are described and the results are discussed in terms of the model of two adjacent Cu^{2+} ions sharing an oxygen vacancy and interacting via direct exchange. The importance of studying copper-doped $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ crystals is associated with the attractive modern applications of this material for electro-holography devices [5, 6]. Another important point of interest in exchange-coupled pairs of copper in KTO is that this crystal has a simple perovskite structure similar to that of cuprate superconductors [7, 8].

2. Experimental details

Single crystals of copper-doped $KTaO_3$, $K_{1-x}Li_xTaO_3$ and $K_{1-x}Li_xTa_{1-y}Nb_yO_3$ were grown by spontaneous crystallization in a platinum crucible at the Ioffe Physico-Technical Institute in St Petersburg and by top-seed solution method at the Department of Applied Physics of the Hebrew University in Jerusalem. The molar concentration of copper in the melting stock ranged from 0.05 to 4.0%. The EPR spectra were recorded with X- and Q-band spectrometers. The angular dependences were measured by rotating a sample about the [100] and [110] crystallographic axes perpendicularly to the direction of the magnetic field B . A helium-flow cryostat was used to investigate the temperature dependence of the EPR signals in the range 3.5–300 K.

3. Results and discussion

3.1. Single Cu^{2+} ions

A typical X-band EPR spectrum of Cu^{2+} single ions in a KTO single crystal at 300 K is shown in figure 1. This spectrum is well described by the spin Hamiltonian for axial centres:

$$H = \mu_B B \tilde{g} S + S \tilde{A} I + \sum_{i=1}^N S \tilde{a}_i I_i \quad (1)$$

where $S = 1/2$, the first term is the Zeeman interaction, the second and third terms are the HF and SHF interactions, μ_B is the Bohr magneton, \tilde{g} is the g -tensor, \tilde{A} is the HF interaction tensor, I is the nuclear spin of copper and \tilde{a}_i is the SHF interaction tensor with nuclear spin I_i of tantalum ions. Since the stable isotopes ^{63}Cu (69.2%) and ^{65}Cu (30.8%) have the same nuclear spin $I = 3/2$ and only a small difference exists between their nuclear magnetic moments, the isotope splitting is undetectable in our EPR spectra.

We observed two single Cu^{2+} centres, $Cu^{2+}(1)$ and $Cu^{2+}(2)$, whose spin Hamiltonian parameters at 300 K are listed in table 1. These values are close to those obtained in [4]. The g -values suggest that the Cu^{2+} ions are in the $|x^2 - y^2\rangle$ state which leads to elongation

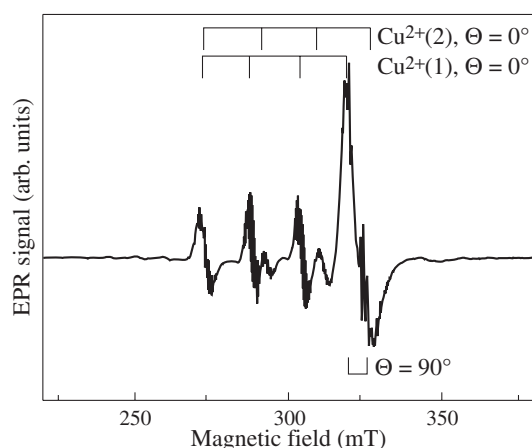


Figure 1. EPR spectrum of Cu^{2+} single-ion centres in KTaO_3 single crystal (microwave frequency $\nu = 9.3$ GHz, $T = 300$ K, $\mathbf{B} \parallel [100]$).

of the octahedral environment along the tetragonal axis. This deformation may be created by, e.g., one or two oxygen vacancies in the Cu^{2+} environment. Each centre shows a well-resolved SHF structure with varying parameters, as listed for $\mathbf{B} \parallel [100]$ in table 1. In the Cu^{2+} environment, potassium and tantalum nuclei have magnetic and quadrupole moments. The isotropic HF interaction constant for potassium atoms (for the 4s electron) is 228 MHz, whereas the corresponding constant for the tantalum ion (6s electron) is 15020 MHz, and the anisotropic HF interaction constant (5d electron), 445.4 MHz (without the angular coefficient) [9]. The isotropic and anisotropic HF interaction constants for the inner s and p electrons of the K^+ (3s, 3p) and Ta^{5+} (5s, 5p) ions were calculated with the use of the wave functions given in [10]; it is important that the constants for tantalum exceed those for potassium by more than a factor of 50. Thus, even if the electron spin density is transferred equally to the potassium and tantalum nuclei (which is actually not the case, because the spin-density is transferred to the tantalum ion to a much greater extent owing both to the covalence effects and to the wavefunction overlap), the SHF interaction constant for potassium is negligible, compared with that for tantalum. Figure 2(a) shows a SHF structure for a $\text{Cu}^{2+}(1)$ centre at $\mathbf{B} \parallel [100]$. The SHF structure originates from the interaction of the unpaired electron of Cu^{2+} with four tantalum nuclei on the next-nearest-neighbour sites in the directions perpendicular to the tetragonal axis of the centres. Tantalum has high magnetic moment of nuclei (nuclear spin $I = 7/2$). As seen at different angles with respect to the tetragonal axis, the structural pattern of SHF is very complicated, being a result of superposition of allowed and forbidden transitions because of the interaction with the large quadrupole moment of tantalum.

Table 1. Spin-Hamiltonian parameters of single Cu^{2+} centres and Cu^{2+} – Cu^{2+} exchange-coupled pair.

Centre	g_{\parallel}	g_{\perp}	D (10^{-4} cm $^{-1}$)	A_{\parallel} (10^{-4} cm $^{-1}$)	A_{\perp} (10^{-4} cm $^{-1}$)	a_i (mT)
$\text{Cu}^{2+}(1)$	2.24	2.04	—	173	30	0.28
$\text{Cu}^{2+}(2)$	2.20	2.04	—	193	33	0.32
Cu^{2+} – Cu^{2+}	2.22	2.04	420–455 ^a	91	15	0.15

^a See text.

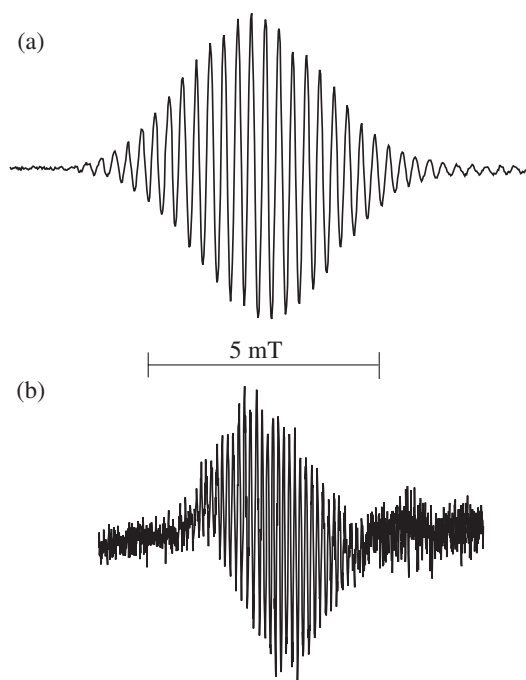


Figure 2. (a) Superhyperfine structure of Cu^{2+} single ion and (b) Cu^{2+} – Cu^{2+} pair. (a) Detailed acquisition of the third Cu^{2+} (1) centre hyperfine line; (b) detailed acquisition of the third hyperfine line of the low-field fine structure group ($\nu = 9.3$ GHz, $T = 100$ K).

3.2. Exchange-coupled Cu^{2+} – Cu^{2+} pairs

A quite different copper centre was also found in the $\text{KTaO}_3:\text{Cu}$ crystal. The Q-band EPR spectrum of this centre is shown in figure 3. When the direction of magnetic field \mathbf{B} is parallel to the $[100]$ axis, this spectrum consists of two groups of seven hyperfine (HF) structure lines with intensities in the ratio 1:2:3:4:3:2:1, according to the presence of identical interactions with two equivalent nuclear spins $I = 3/2$. Two broad lines ($\Theta = 90^\circ$), partially resolved and also showing a structure of seven components, are symmetrically arranged around the g_\perp positions of the single- Cu^{2+} ion centres.

The spectrum shown in figure 3 is typical of a triplet spin state with $S = 1$. Indeed, the two groups of lines have the same structure and can be attributed to $\Delta M_S = \pm 1$ transitions between $M_S = 0 \leftrightarrow M_S = 1$, $M_S = -1 \leftrightarrow M_S = 0$ energy levels for \mathbf{B} parallel to the centre axis, and between $M_S = -1 \leftrightarrow M_S = 0$, $M_S = 0 \leftrightarrow M_S = 1$ energy levels for \mathbf{B} perpendicular to the same axis. We attribute this spectrum to a centre formed by two exchange-coupled Cu^{2+} ions. The X-band EPR spectra are shown in figure 4. The forbidden transitions $\Delta M_S = +2$ are described in the inserts. A well-resolved group of seven lines for $\Theta = 45^\circ$ between the centre axis and \mathbf{B} direction (figure 4(a)) and an unresolved line for $\Theta = 90^\circ$ (figure 4(b)) appear at low magnetic fields. The angular dependence of the fine and HF transitions (and also of the forbidden transition) in this Cu^{2+} – Cu^{2+} pair in the (110) plane is shown in figure 5, with points representing the experimental results. The angular dependence was computed (lines in figure 5) using software developed by Grachev [11]. The rotation in the (110) plane reflects the axial symmetry of the spectrum and the angular behaviour confirms that the symmetry axes of the centres are parallel to one of the three equivalent $\langle 100 \rangle$ directions.

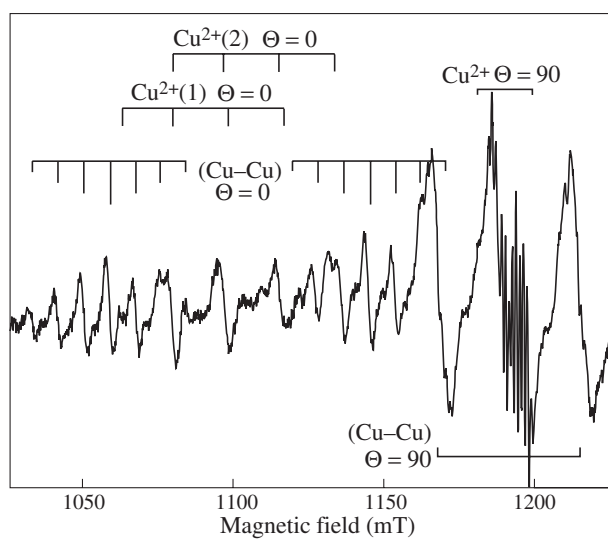


Figure 3. EPR spectrum of single Cu^{2+} centres and exchange-coupled pair $\text{Cu}^{2+}\text{-Cu}^{2+}$ centres in KTaO_3 single crystal in the Q band ($\nu = 34.5$ GHz, $T = 300$ K, $B \parallel [100]$).

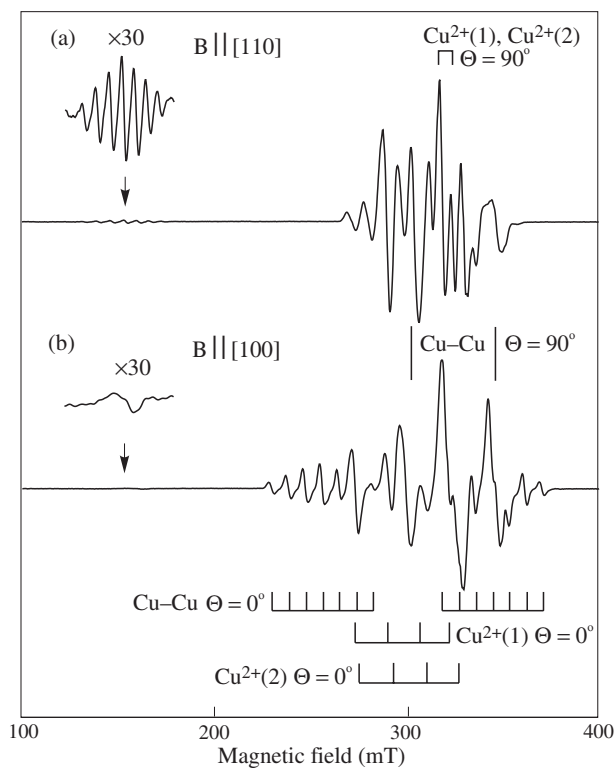


Figure 4. EPR spectra of copper centres in the X band ($T = 300$ K, $\nu = 9.3$ GHz) for two different magnetic field orientations (a) $B \parallel [110]$, and (b) $B \parallel [100]$. Forbidden transitions are also shown in the insert.

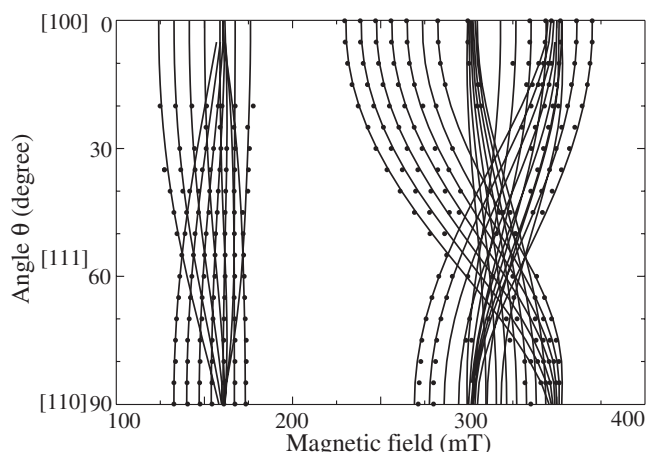


Figure 5. Angular dependence of $\text{Cu}^{2+}\text{-Cu}^{2+}$ pair with sample rotating about the $\langle 110 \rangle$ axis. Dots, experimental data; lines, calculation.

The coupling of the two ions in the pair, with spin $S_i = S_j = 1/2$, giving rise to a purely triplet state ($S = 1$), suggests that the term corresponding to the exchange interaction between the two Cu^{2+} ions is large as compared with the Zeeman term.

The spin Hamiltonian of an exchange-coupled pair for electron spin $S = 1/2$ of separate ions, which includes the exchange and Zeeman interaction, has the form [12]]:

$$H = -J\mathbf{S}_1\mathbf{S}_2 + \mu_B\mathbf{B}\mathbf{g}(S_1 + S_2) \quad (2)$$

where J is the exchange constant, μ_B is the Bohr magneton, and \mathbf{g} is the g tensor of copper pair centre.

For $J \gg g\mu_B B$, two states may arise, with spin $S = 0$ and $S = 1$. For an axial system with spin $S = 1$, the spin Hamiltonian is given by

$$H = \mu_B\mathbf{B}\mathbf{g}\mathbf{S} + D\left(S_z^2 - \frac{1}{3}S(S+1)\right) + S\frac{\mathbf{A}}{2}(\mathbf{I}_1 + \mathbf{I}_2) + \sum_{i=1}^N S\frac{\mathbf{a}_i}{2}\mathbf{I}_i \quad (3)$$

where the first term is the Zeeman interaction, the second describes the fine structure and all the possible effects due to anisotropy, and the third and fourth describe the HF interaction with both the nuclear spins and the SHF interaction, respectively.

The parameters of the spin Hamiltonian of the observed $\text{Cu}^{2+}\text{-Cu}^{2+}$ centre in KTaO_3 at 300 K are listed in table 1. It should be noted that in $\text{KTaO}_3\text{:Cu}$ the parameter D is $420 \times 10^{-4} \text{ cm}^{-1}$ while in $\text{K}_{1-x}\text{Li}_x\text{TaO}_3\text{:Cu}$ and $\text{K}_{1-x}\text{Li}_x\text{Ta}_{1-y}\text{Nb}_y\text{O}_3\text{:Cu}$ the D value is $455 \times 10^{-4} \text{ cm}^{-1}$, indicating a very large sensitivity of the D value to minor crystal field variations.

It should be emphasized that pair centres of only a single type are observed in the crystals, whereas there are two kinds of single- Cu^{2+} centres. It is easy to see from the spin Hamiltonian parameters of the single- Cu^{2+} centres that the g -values and hyperfine constants for $\text{Cu}^{2+}\text{-Cu}^{2+}$ centre can be expressed as

$$g_{\parallel} = \frac{g_{\parallel}^1 + g_{\parallel}^2}{2}, \quad g_{\perp} = \frac{g_{\perp}^1 + g_{\perp}^2}{2}, \quad A_{\parallel} = \frac{A_{\parallel}^1 + A_{\parallel}^2}{4}, \quad A_{\perp} = \frac{A_{\perp}^1 + A_{\perp}^2}{4}$$

where indices 1 and 2 refer to $\text{Cu}^{2+}(1)$ and $\text{Cu}^{2+}(2)$, respectively.

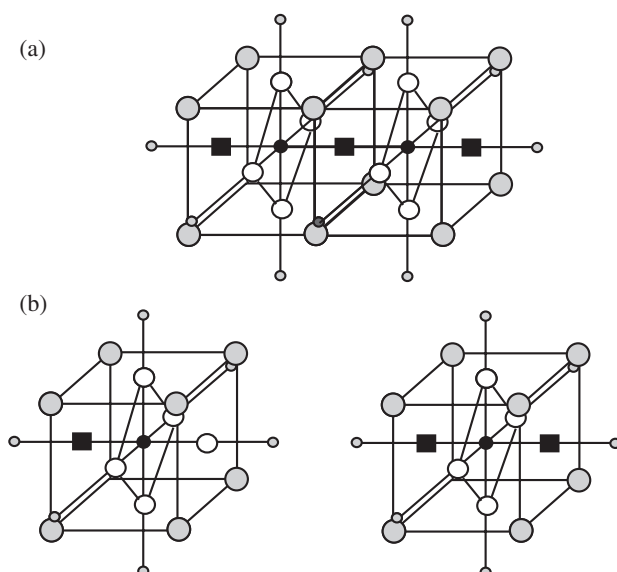


Figure 6. (a) Model of copper centres in KTaO_3 single crystal for $\text{Cu}^{2+}\text{-Cu}^{2+}$ pairs and (b) $\text{Cu}^{2+(1)}$ and $\text{Cu}^{2+(2)}$ centres. ●, copper; ○, oxygen; small grey circles, tantalum; big grey circles, potassium; ■, oxygen vacancy.

The SHF structure of an exchange-coupled pair is shown in figure 2(b) for $\mathbf{B} \parallel [100]$. a_i is anisotropic and equal to 0.15 mT at $\mathbf{B} \parallel [100]$. As for the HF constants, those values are the average of the SHF constants (divided by two) of $\text{Cu}^{2+(1)}$ and $\text{Cu}^{2+(2)}$ centres. We suggest that this structure originates from the interaction with surrounding tantalum ions, but the low signal-to-noise ratio gives no way of analysing this structure in detail.

The EPR signal intensity increases when the temperature is lowered to 3.5 K. This behaviour indicates that the isotropic part of the exchange interaction is positive, i.e., the triplet state ($S = 1$) has lower energy as compared with the singlet state ($S = 0$) and the coupling between the Cu^{2+} ions in this centre is ferromagnetic.

Since the Cu^{2+} ions are in the $|x^2 - y^2\rangle$ state, the superexchange interaction cannot occur via the p_z orbital of the apical oxygen ion along the pair axis. However, direct exchange must prevail in this direction, because of the observed ferromagnetic $\text{Cu}^{2+}\text{-Cu}^{2+}$ coupling. Indeed, an oxygen vacancy lying between two adjacent Cu^{2+} ions along one of the equivalent $\langle 100 \rangle$ directions in the crystal would favour a ferromagnetic interaction between copper ions via direct exchange. Moreover, the presence of a single vacancy near the Cu^{2+} ions is insufficient for complete neutralization of the extra charge. Complete neutralization can be effected in the $\text{Cu}^{2+}\text{-Cu}^{2+}$ centre by three oxygen vacancies, probably located along the tetragonal z -axis, as shown in figure 6(a). Such a model of the pair centre agrees with the axial symmetry, with the ferromagnetic exchange and with the fact that only a single kind of pair centre has been observed in all of our investigations on several samples prepared by different methods. In addition, the g -factor, A and \hat{a} constants, which agree with the average values for $\text{Cu}^{2+(1)}$ and $\text{Cu}^{2+(2)}$ centres, suggest that the $\text{Cu}^{2+}\text{-Cu}^{2+}$ centre may arise from association of $\text{Cu}^{2+(1)}$ and $\text{Cu}^{2+(2)}$ centres, according to the models of single $\text{Cu}^{2+(1)}$ and $\text{Cu}^{2+(2)}$ centres (figure 6(b)) with one or two oxygen vacancies along one of the $\langle 100 \rangle$ directions. Mention should be made of the fact that no pair centres formed by $\text{Cu}^{2+(1)}$ and $\text{Cu}^{2+(1)}$, or by $\text{Cu}^{2+(2)}$ and $\text{Cu}^{2+(2)}$, have ever been observed.

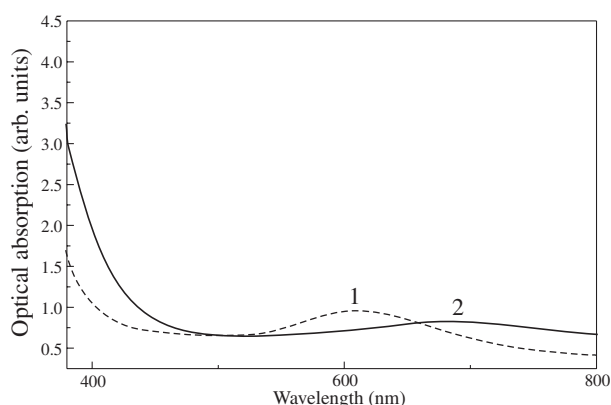


Figure 7. Optical absorption spectra at room temperature of KTaO_3 samples with predominant Cu^{2+} single ions (1) and $\text{Cu}^{2+}\text{-Cu}^{2+}$ pairs (2).

The number of $\text{Cu}^{2+}\text{-Cu}^{2+}$ centres seems to increase upon addition of copper, but we did not find any simple correlation between the relative intensities of $\text{Cu}^{2+}\text{-Cu}^{2+}$ and single Cu^{2+} centres with nominal copper concentration.

We also made an attempt to estimate the optical absorption of copper pair centres in KTaO_3 . Significant differences can be revealed in the optical absorption spectra of different samples, as shown in figure 7. The spectrum with an absorption band peaked at 600 nm (1) belongs to a sample with mainly single Cu^{2+} ions (its EPR spectrum is shown in figure 1). The optical absorption spectrum with a peak at about 750 nm (2) belongs to a sample with a large amount of pair centres whose EPR spectrum is shown in figure 4. We suggest that line (2), much broader than line (1), originates from copper pairs.

4. Conclusion

The nature of copper centres in KTaO_3 , $\text{K}_{1-x}\text{Li}_x\text{TaO}_3$ and $\text{K}_{1-x}\text{Li}_x\text{Ta}_{1-y}\text{Nb}_y\text{O}_3$ single crystals has been studied in detail by EPR spectroscopy. Exchange-coupled pairs $\text{Cu}^{2+}\text{-Cu}^{2+}$ are present together with $\text{Cu}^{2+}(1)$ and $\text{Cu}^{2+}(2)$ single centres. These pair centres, showing tetragonal symmetry with the z -axis oriented along one of the $\langle 100 \rangle$ axes, originate from the association of two different $\text{Cu}^{2+}(1)$ and $\text{Cu}^{2+}(2)$ centres, but Cu^{2+} ions are equivalent in the pair. The temperature dependence of the EPR signal intensity indicates the presence of ferromagnetic coupling between the Cu^{2+} ions of the pairs. The SHF structure arising from the interaction with Ta^{5+} ions is also described. The presence of $\text{Cu}^{2+}\text{-Cu}^{2+}$ exchange-coupled pairs gives rise to a broad absorption band in the 600–800 nm spectral region.

Acknowledgments

We gratefully acknowledge Dr P P Syrnkov (Ioffe Institute) and Professor A J Agranat (Department of Applied Physics of the Hebrew University) for the provision of single-crystal specimens. This work was supported in part by the Russian Foundation for Basic Research (grants 00-02-16950, 99-02-18074), NATO Linkage Grant SA (PST.CLG. 977348) 5941, Czech Grant 202/00/1425 and LN 00A0 15 Grant of MSM.

References

- [1] Mueller K A 1981 *J. Phys.* **42** 551
- [2] Abraham M M, Boatner L A, Olson D N and Hoehli U T 1984 *J. Chem. Phys.* **81** 2528
- [3] Laguta V V, Glinchuk M D, Karmazin A A and Bykov I P 1985 *Sov. Phys. Solid State* **27** 94
- [4] Azamat D V, Badalyan A G, Baranov P G, Symikov P P, Trepakov V A, Rosa J and Jastrabik L 1999 *JETP Letters* **69** 943
- [5] Pesach B, Refaeli E and Agranat A J 1998 *Opt. Lett.* **23** 642
- [6] Pesach B, Bartal G, Refaeli E and Agranat A J 2000 *Appl. Opt.* **39** 746
- [7] Baranov P G, Badalyan A G and Azamat D V 2001 *Phys. Solid State* **43** 98
- [8] Tsuel C C and Kirtley J R 2000 *Rev. Mod. Phys.* **72** 969
- [9] Morton J R and Preston K F 1978 *J. Magn. Reson.* **30** 577
- [10] Clementi E and Roetti C 1974 *At. Data Nucl. Data Tables* **14** 177
- [11] <http://www.physik.uni-osnabrueck.de/resonanz/Grachev>
- [12] Owen J and Harris E A 1972 *Electron Paramagnetic Resonance* ed S Geschwind (New York: Plenum Press) p 427