Electron Paramagnetic Resonance of Cu^{2+} in $KHCO_3$ Single Crystals

F. Köksal, İ. Kartal, and B. Karabulut

Physics Department, Faculty of Arts and Sciences, Ondokuz Mayıs University, Samsun, Turkey

Reprint requests to Prof. F. Köksal, Fax: +90 362 4576081

Z. Naturforsch. **54 a,** 177–179 (1999); received January 9, 1999

The electron paramagnetic resonance spectra of Cu^{2+} doped $KHCO_3$ single crystals were studied at room temperature. The results indicate a substitutional entrance of the Cu^{2+} ions in place of the magnetically inequivalent K^+ sites. The charge compensation is supposed to be fulfilled by proton vacancies. The hyperfine lines were well resolved and the ^{65}Cu hyperfine coupling tensors were also found. The ground state of Cu^{2+} indicates the dominance of the $d_{x^2-y^2}$ orbital and, therefore, elongation of the polyhedron, similar to a lengthened octahedron.

Key words: EPR; Cu^{2+}; Potassium Bicarbonate; Crystal Field; Substitution; Impurity.

Introduction

The electron paramagnetic resonance (EPR) method can be used for obtaining information about the ground state of a paramagnetic ion and its environmental symmetry of electrical fields produced by the ligands. In particular Cu^{2+} has extensively been used as a probe to obtain information about the crystalline electric fields [1 - 4]. In most of the Cu^{2+} doped compounds, Cu^{2+} replace divalent cations. However, when a divalent Cu^{2+} ion enters the lattice in place of a monovalent cation, an electric charge compensation is supposed to be fulfilled by the vacancy of another monovalent cation, and in some cases it has been found that the magnetic coupling tensors have their principal axes pointing from the divalent ion to the monovalent cation vacancy direction.

Furthermore, in most of the Cu^{2+} doped systems investigated so far, the ion was found to have $d_{x^2-y^2}$ and d_{z^2} mixed ground states and a smaller hyperfine coupling constant. In view of this, we have now studied Cu^{2+} doped $KHCO_3$ single crystal to find the ground state of Cu^{2+}, its site and the ^{65}Cu hyperfine coupling tensor. To our knowledge such a study on this crystal has not been carried out so far.

Experimental

The single crystals were produced by slow evaporation of saturated aqueous solutions of commercially obtained $KHCO_3$ powders. The structure of crystalline $KHCO_3$ at room temperature is monoclinic with space group $P_{2_1/a}$, and unit cell parameters a = 1.51948, b = 0.56307, c = 0.37107 nm, and $\beta = 104°$ 567'. The unit cell contains four molecules [5]. The single crystal study indicates that the K^+ ion is surrounded by eight oxygen atoms with not much different distances to the K^+ ion, and the hydrogen atoms constitute the bridges between the oxygen atoms [5].

The EPR spectra were recorded with a Varian E-109 C model EPR spectrometer using 2 mW microwave power and 100 kHz magnetic field modulation. The single crystals were rotated on a Lucit pillar in three mutually perpendicular planes (c^*a, bc^*, ab), and the spectra were recorded at 10° steps. The g factors were found by comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

Results and Discussions

Two typical EPR spectra of Cu^{2+} doped $KHCO_3$ single crystals are shown in Fig. 1 for two different orientations of the magnetic field. Figure 1a shows the spectrum in the c^*a plane, 30° from the a axis, and Fig. 1b indicates the spectrum in the ab plane, 50° from the b axis. The line positions are shown in Fig. 2 in the c^*a, bc^*, and ab planes. The empty boxes indicate the $^{65}Cu^{2+}$ line positions. The spectra belong obviously to Cu^{2+}, for which $S = 1/2$ and $I = 3/2$. The $^{65}Cu^{2+}$ and $^{63}Cu^{2+}$ lines can be clearly observed nearly along the whole spectra, as in Fig. 1a, with the approximate intensity proportion of 0.44, in accord with the abundancy proportion of the isotopes of the

0932–0784 / 99 / 0300–0177 $ 06.00 © Verlag der Zeitschrift für Naturforschung, Tübingen · www.znaturforsch.com

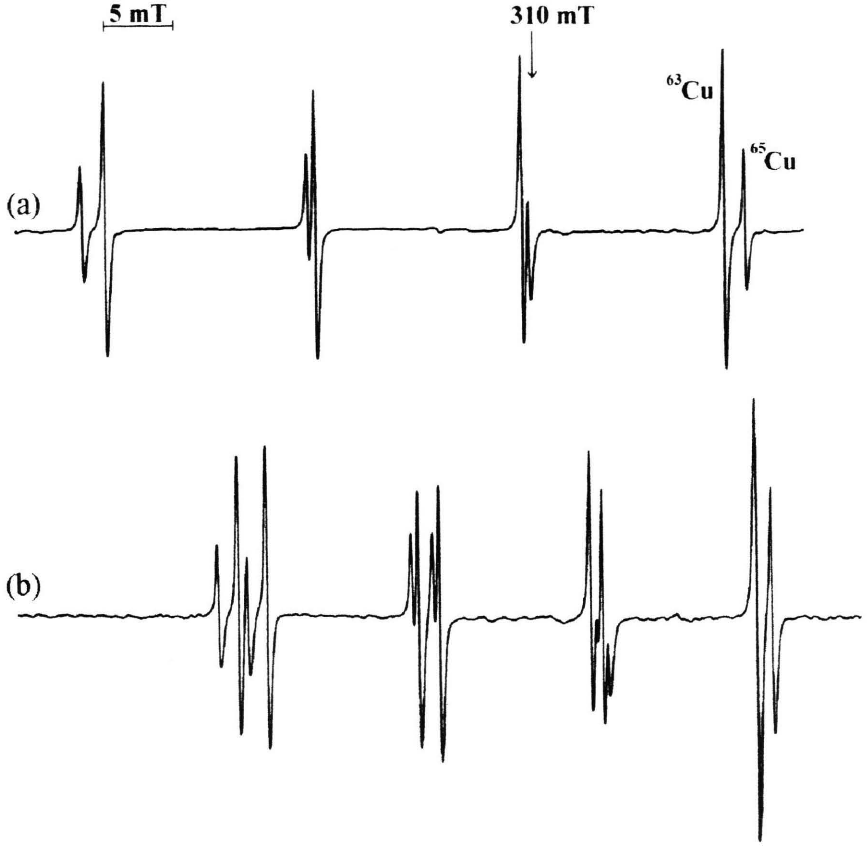

Fig. 1. (a) EPR spectrum of Cu^{2+} in $KHCO_3$. The magnetic field is in the c^*a plane and 30° from the a axis. The weaker lines come from ^{65}Cu. (b) The magnetic field is in the ab plane and 50° from the b axis.

Table 1. Spin Hamiltonian parameters (**g** and **A**) and their direction cosines with respect to the a, b, and c^* axes for $^{63}Cu^{2+}$ in $KHCO_3$ at room temperature ($\Delta g = \pm 0.0005$ and $\Delta A = \pm 0.05$ mT).

Sites	Principal values of **g** and **A** (mT)	a	b	c^*
I	g_{xx} = 2.0513	0.762	±0.514	0.354
II	= 2.0514	0.747	±0.561	0.354
	g_{yy} = 2.0540	–0.303	±0.184	0.934
	= 2.0541	–0.254	±0.251	0.933
	g_{zz} = 2.2346	0.571	±0.820	0.023
	= 2.2349	0.613	±0.788	–0.045
I	A_{xx} = 4.92	–0.246	±0.914	0.322
II	= 4.73	0.064	±0.945	–0.320
	A_{yy} = 6.56	0.083	±0.311	0.946
	= 6.69	0.016	±0.322	0.946
	A_{zz} = 19.64	0.965	±0.260	–0.001
	= 19.76	0.997	±0.055	–0.036

Table 2. The principle values of the spin Hamiltonian parameters (**g** and **A**) for $^{65}Cu^{2+}$ in $KHCO_3$ single crystal at room temperature.

Sites	**g**	**A** (mT)
I	g_{xx} = 2.0522	A_{xx} = 3.37
II	= 2.0504	= 3.44
	g_{yy} = 2.0557	A_{yy} = 5.71
	= 2.0579	= 5.88
	g_{zz} = 2.2335	A_{zz} = 18.65
	= 2.2329	= 18.78

Table 3. K-O distances (in nm) observed by neutron- and X-ray diffraction in $KHCO_3$.

Neutron	X-ray	Neutron	X-ray
0.3008	0.3008	0.2931	0.2929
0.2873	0.2875	0.2696	0.2697
0.2740	0.2742	0.2825	0.2824
0.2784	0.2784	0.2890	0.2885

copper nucleus as indicated. The whole spectra can be fitted to the spin Hamiltonian,

$$\mathcal{H} = \beta B \cdot \mathbf{g} \cdot S + I \cdot \mathbf{A} \cdot S.$$

The principal values of the **g** and **A** tensors and their direction cosines were found by diagonalization [6 - 7]. The results are given in Table 1.

From these experimental results it can be inferred that the Cu^{2+} ions enter the inequivalent K^+ places in

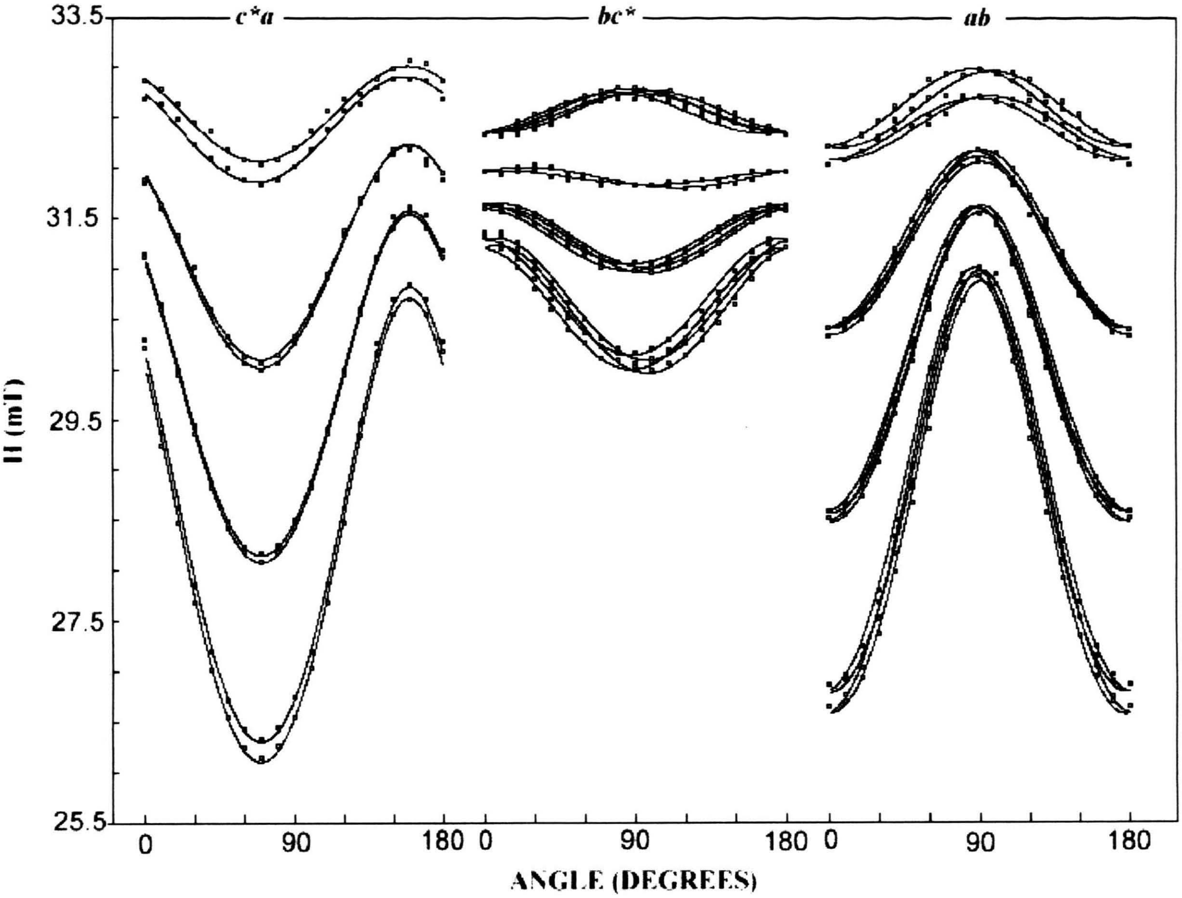

Fig. 2. The line positions of the EPR lines against the magnetic field for Cu^{2+} in $KHCO_3$ at room temperature. The $^{65}Cu^{2+}$ points are indicated by empty boxes.

the $KHCO_3$ single crystal. This agrees with the crystal data, since the crystal is a monoclinic and contains 4 molecules in its unit cell. In a monoclinic crystal, at most two inequivalent sites can be observed, and this was what is observed. The charge compensation seems to be fulfilled by hydrogen vacancies between the oxygen atoms. Since the crystal structure indicates eight oxygens at nearly equal distances to K^+, they seem to constitute a polygon of ligands around the K^+ ion [5], as seen in Table 3. The average K-O distance is 0.2843 nm in this table. The principal values of the **g** and **A** tensors are in agreement with the literature values for the $^{63}Cu^{2+}$, and the principal values of the $^{65}Cu^{2+}$ are smaller than those of the $^{65}Cu^{2+}$ ions. Therefore, this study reports the principal values of the **g** and the **A** tensors for $^{65}Cu^{2+}$. Furthermore, this study also indicates that the disorder in $KHCO_3$ exists only among the hydrogen atoms, and not the other atoms, since otherwise this would destroy the symmetry of the crystal. This conclusion is in accordance with the crystal structure determinations [5].

[1] R. Murugesan, and S. Subramanian, J. Magn. Reson. **36**, 389 (1979).
[2] J. L. Rao, R. M. Krishna, S.V. J. Lakshman, and P. Chand, J. Phys. Chem. Solids **51**, 323 (1990).
[3] S. K. Misra, and L. E. Misiak, Phys. Rev. **B48**, 13579 (1993).
[4] N. M. Green, D. P. Lazar, S. V. Nistor, and M. Stefan, Solid State Commun. **89**, 657 (1994).
[5] J. D. Thomas, R. Tellgren, and I. Olovsson, Acta Cryst. **B30**, 2540 (1974).
[6] H. A. Farach, C. P. Poole, Nuovo Cim. **4**, 51 (1975).
[7] F. Köksal and H. Yüksel, Z. Naturforsch. **30a**, 750 (1975).