EPR Spectra of Some Cu^{2+}-Doped Metal Carbonates and Disorder Phase Transition in $K_3H(CO_3)_2$

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Cu^{2+}-doped $K_3H(CO_3)_2$, Rb_2CO_3, and $Rb_2KH(CO_3)_2$ single crystals were investigated by electron paramagnetic resonance (EPR) spectroscopy. The EPR spectrum of $K_3H(CO_3)_2$ indicates two different sites for Cu^{2+} at room and at low temperatures. But the signals for the two sites overlap at 318 K which is attributed to a disorder phase transition. Each of the other compounds exhibits one site. The Cu^{2+} ion seems to substitute the K^+ and Rb^+ ions and the charge compensations are fulfilled by the proton vacancies in $K_3H(CO_3)_2$, and another K^+ and Rb^+ in the other compounds. The spin Hamiltonian parameters **g** and **A** for each compound are determined and discussed.

Key words: Electron Paramagnetic Resonance; Carbonates; Disorder Phase Transition; Cu^{2+} Doping.

1. Introduction

The electron paramagnetic resonance (EPR) technique has been used to study diamagnetic materials with paramagnetic ions as probes [1 – 9]. These types of studies yield valuable information about the local environmental effects on the paramagnetic ions and show if phase transitions occur in the substances. Especially, the $3d^9$ electron configuration is of interest in a transition metal complex, because it represents a simple one magnetic-hole system by which one can hope to obtain information about the electronic wave function even in a ligand field of low symmetry. In most of the Cu^{2+}-doped compounds Cu^{2+} replaces divalent cations. However, when a divalent Cu^{2+} 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. In some cases the magnetic couplings have their principal axes pointing from the divalent ion to the monovalent cation vacancy [1].

Furthermore, in most of the Cu^{2+}-doped systems investigated so far, Cu^{2+} was found to have a $d_{x^2-y^2}$ and d_{z^2} mixed ground state and a smaller hyperfine coupling constant. In view of these findings we have studied the temperature dependence of the EPR spectra of Cu^{2+}-doped $K_3H(CO_3)_2$, Rb_2CO_3, and $Rb_2KH(CO_3)_2$ single crystals. We could not observe any temperature dependence in these substances except for $K_3H(CO_3)_2$. The spin Hamiltonian parameters of all the substances are reported and the temperature dependence of the signals of $K_3H(CO_3)_2$ is attributed to a disorder phase transition.

2. Experimental

The single crystals studied in this work were grown at room temperature by slow evaporation of saturated aqueous solutions in doubly distilled water in about three weeks. Rb_2CO_3 was obtained from Merck. To obtain $K_3H(CO_3)_2$ the stoichiometric proportions of $KHCO_3$ and K_2CO_3 were used. For $Rb_2KH(CO_3)_2$ the stoichiometric proportions of Rb_2CO_3 and $KHCO_3$ were mixed in doubly distilled water. All batches were mixed with $CuSO_4 \cdot 5H_2O$ (5 wt%) as dopant.

The single crystal parameters of $K_3H(CO_3)_2$ were obtained using a Stoe-IPDS-2 X-ray diffractometer equipped with a graphite monochromator (Mo-K_α, $\lambda = 0.71073$ Å) at the Physics Department. The unit cell parameters of $K_3H(CO_3)_2$ were $a = 15.849$ Å, $b = 5.693$ Å, $c = 7.927$ Å, $\beta = 103.7°$, space group $P2_1/c$ and $Z = 2$. The other single crystals were monoclinic [10].

The EPR spectra were recorded using a Varian E-109C model X-band EPR spectrometer. The magnetic field modulation frequency was 100 kHz. The

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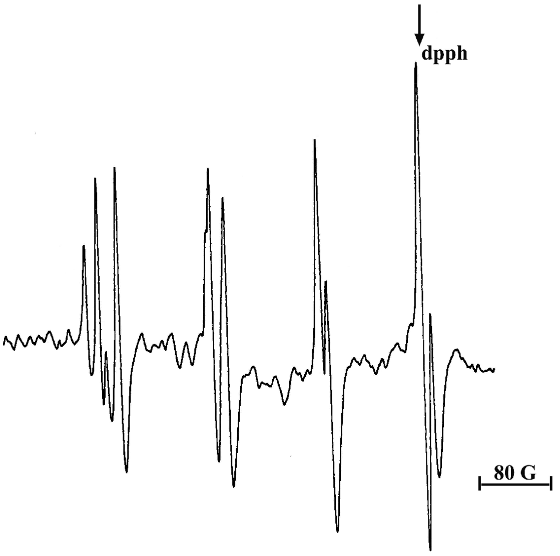

Fig. 1. The EPR spectrum of Cu^{2+}-doped $K_3H(CO_3)_2$ at room temperature at an arbitrary orientation.

single crystals were mounted on a goniometer and the spectra were recorded in three mutually perpendicular planes at 10° steps. The sample temperatures were controlled by a Varian temperature controller. g Values were found by comparison with a diphenylpicrylhydrazyl sample of $g = 2.0036$.

3. Results and Discussion

The EPR spectra of $K_3H(CO_3)_2$ are depicted in Figure 1. The signals obviously belong to the Cu^{2+} ions with $S = 1/2$ and the nuclear spin $I = 3/2$. The signals due to the $^{65}Cu^{2+}$ (abundancy 30%) isotope are clearly observable. When the signals are examined at ambient temperature, two sites for Cu^{2+} were observed which can clearly be seen from the first line of the low-field side of the signals in Figure 1. The temperature dependence of the two sites at the low-field side is depicted in Figure 2. As it is seen from this figure, when the temperature is increased from 143 K to 318 K, the signals approach one another and at 318 K they overlap giving only one site. The temperature dependence of the difference between the fields, $(H_1 - H_2)$/mT, of two sites is shown in Figure 3. This figure indicates that at low temperatures the difference between the two sites seems to be constant, between 273 – 318 K it decreases, and at 318 K the two sites become equal. This can be attributed to the disorder of the holes of protons, since we think that Cu^{2+} replaces K^+ and the charge compensation is fulfilled by the proton vacancies [8]. $K_3H(CO_3)_2$ seems to behave like $KHCO_3$ and is a proton conductor [9 – 11]. Therefore, it appears that at low temperatures the proton vacancies are ordered, but when the temperature rises above 273 K, they become disordered to maintain the proton conduction. When the proton vacancies are disordered, the charge compensating atoms of Cu^{2+} also become disordered and, therefore, the signals of the two sites of Cu^{2+} overlap.

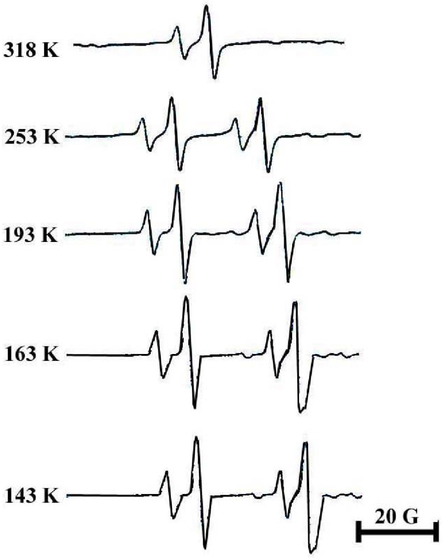

Fig. 2. The temperature dependence of the two sites at the low-field side of Cu^{2+}-doped $K_3H(CO_3)_2$.

All spectra at ambient temperature of Cu^{2+}-doped $K_3H(CO_3)_2$ can be fitted to the spin Hamiltonian

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

The principal values of the **g** and **A** tensors and their direction cosines were found by diagonalization. The results are given in Table 1. The EPR line positions of $K_3H(CO_3)_2$ in the three mutually perpendicular planes are depicted in Figure 4. The figures are consistent with the monoclinic symmetry. There is only one site at the b-axis orientation and in the c^*a-plane. In the other planes two sites are observed. Cu^{2+}-doped Rb_2CO_3 and $Rb_2KH(CO_3)_2$ exhibit only one site in the three planes. For the sake of brevity the corresponding figures are not given for these crystals. The principal values of the **g** and **A** tensors of these crystals are reported in Table 2. The results seem to be reasonable and are in agreement with the literature data [12 – 15].

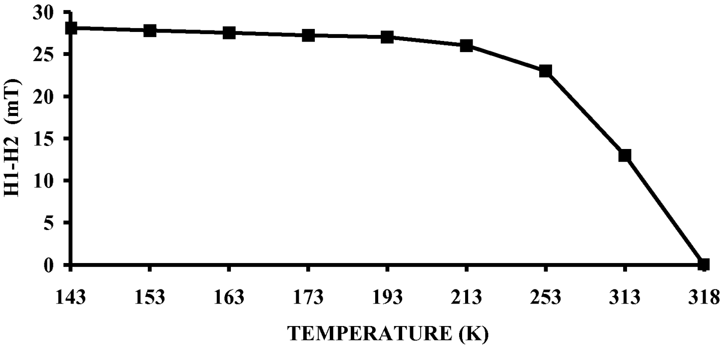

Fig. 3. The temperature dependence of the difference $(H_1 - H_2)$/mT between the fields of the two sites.

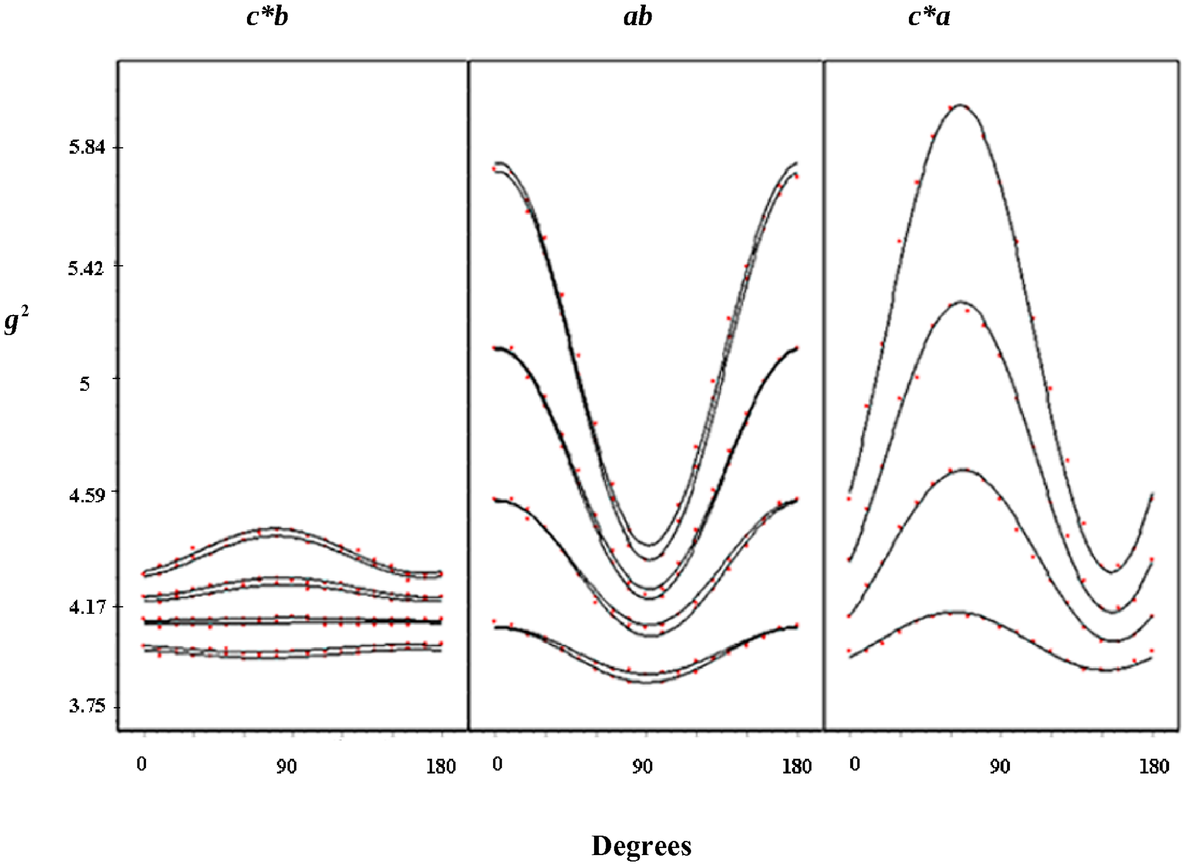

Fig. 4. Experimental g^2 values versus the orientation of the magnetic field in the *ab*-, *bc**- and *c***a*-planes for Cu^{2+}-doped $K_3H(CO_3)_2$ single crystals at room temperature.

The spin Hamiltonian parameters g_{xx}, g_{yy}, and g_{zz} in Tables 1 and 2 are mutually different. Therefore, the local symmetry around the Cu^{2+} ion is rhombic and the ground state for the ion is a mixture of $d_{x^2-y^2}$ and d_{z^2} orbitals. Furthermore it can be seen from Tables 1 and 2 that these values are ordered: $g_{zz} > g_{xx} > g_{yy}$.

It is known that, when $R = (g_{xx} - g_{yy})/(g_{zz} - g_{xx})$ is greater than unity, a predominantly d_{z^2} and, when R is less than unity, a predominantly $d_{x^2-y^2}$ ground state, respectively, is expected [16, 17]. Since $R < 1$ for these three crystals, a predominantly $d_{x^2-y^2}$ ground state should exist for each of them. The components

Table 1. The principal values of the **g** and **A** tensors and their direction cosines with respect to the *a*-, *b*-, and c^*-axes for Cu^{2+}-doped single crystals of $K_3H(CO_3)_2$ at room temperature.

Site	Principal value of **g**	Direction cosine		
I	g_{xx} = 2.015	0.991	−0.124	0.025
	g_{yy} = 2.039	0.124	0.910	−0.395
	g_{zz} = 2.227	0.026	0.395	0.918
II	g_{xx} = 2.013	0.993	−0.114	0.032
	g_{yy} = 2.034	0.117	0.913	−0.389
	g_{zz} = 2.226	0.014	0.390	0.920
	Principal value of **A** (mT)	Direction cosine		
I	A_{xx} = 2.95	0.885	0.421	−0.197
	A_{yy} = 4.95	−0.465	0.819	−0.336
	A_{zz} = 18.70	0.019	0.390	0.920
II	A_{xx} = 3.2	0.979	0.161	−0.125
	A_{yy} = 4.2	−0.197	0.902	−0.383
	A_{zz} = 18.50	0.052	0.399	0.915

Table 2. The principal values of the **g** and **A** tensors and their direction cosines with respect to the *a*-, *b*-, and c^*-axes for Cu^{2+}-doped Rb_2CO_3 and $Rb_2KH(CO_3)_2$ single crystals at room temperature.

Compound	Principal value of **g**	Direction cosine		
Rb_2CO_3	g_{xx} = 2.031	0.895	−0.009	0.445
	g_{yy} = 2.042	−0.086	0.976	0.194
	g_{zz} = 2.221	0.437	0.213	−0.873
$Rb_2KH(CO_3)_2$	g_{xx} = 2.101	0.628	0.763	0.154
	g_{yy} = 2.001	−0.600	0.601	−0.527
	g_{zz} = 2.262	−0.494	0.238	0.836
	Principal value of **A** (mT)	Direction cosine		
Rb_2CO_3	A_{xx} = 1.7	0.813	0.177	−0.553
	A_{yy} = 6.0	−0.065	0.974	0.216
	A_{zz} = 18.7	0.577	−0.139	0.804
$Rb_2KH(CO_3)_2$	A_{xx} = 11.6	0.954	0.279	0.110
	A_{yy} = 1.8	−0.210	0.884	−0.417
	A_{zz} = 17.1	−0.214	0.375	0.902

of the hyperfine tensor, A_{xx}, A_{yy} and A_{zz}, are mutually different for the crystals in Tables 1 and 2. Furthermore the direction cosines of the **g** and **A** tensors of Rb_2CO_3 seem to be similar. The same statement can be made for $Rb_2KH(CO_3)_2$. This indicates that the principal directions seem to be not too far from each other, and the tensors can be said to be coalescent within 20°.

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