FIZIKA, 1 (1969) 159–170

EPR AND OPTICAL ABSORPTION SPECTRA OF Cu^{2+} DOPED ROCHELLE SALT

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Received 28 October 1968; revised manuscript received 11 December 1968

Abstract: The electron paramagnetic resonance and optical absorption spectra of Rochelle salt doped with $CuCl_2$ and $Cu(CH_3COO)_2$ have been measured in the paraelectric, ferroelectric and antiferroelectric states. Both ways of doping lead to similar EPR spectra consistent with the assumption that the Cu^{2+} replaces the Na^+ ion. From the optical absorption data the bonding parameters of copper to the ligand oxygens and the theoretical g_{xx} and g_{yy} values were calculated.

On passing the lower Curie point, the EPR lines of the A Cu^{2+}— ions site show a significant shift with regard to the slight shift of the B site lines, while on passing the upper Curie point the lines of the B site are more shifted than those of A site.

1. *Introduction*

The ferroelectric crystals are studied by electron paramagnetic resonance (EPR) when doping with paramagnetic ions[1–7] or introduction of irradiation damages[8–12] is possible.

The data derived from the spin Hamiltonian describing the introduced centers are sensitive for structural changes of the surrounding. Thus an insight into the high and low temperature phases can be obtained.

Rochelle salt as a well known ferroelectric crystal easy to grow could serve as a prototype for an investigation of hydrogen bonded ferroelectric crystals. Though its properties have been intensively studied for the last forty years, little is known about the nature of its ferroelectricity on the molecular level. Even its crystal structure at low temperature phase is not known acuratelly. Recently interesting electric field effects on the EPR spectra of Cu^{2+} doped Rochelle salt have been observed[13, 14] but there are differences in the g and hiperfine tensors components determined by different authors[1, 2]. To resolve these discrepances and to see if different ways of doping would results in different properties of the paramagnetic centers copper ligand bonds and the nature of the ferroelectric phase transitions, we measured the EPR and optical absorption spectra again.

2. *Experimental*

Rochelle salt ($KNaC_4H_4O_6 \cdot 4H_2O$) is ferroelectric between the two Curie points —18° C and 24° C. The crystal structure of the paraelectric phase is orthorhombic $P2_12_12$ with four molecules per unit cell[15]. In the ferroelectric phase the monoclinic space group $P2_1$ is a good approximation. The crystal structure at the low temperature, probably antiferroelectric phase, is not known exactly, but can be approximated by $P2_12_12$[16, 17].

The crystals were grown by cooling the thermostat at a rate of 1° C/day, starting from 38° C downwards. In addition to a 50% KOH–NaOH mixture 10% $CuCl_2$ and $Cu(CH_3COO)_2$ respectively, were included in the Rochelle salt solution, to prevent the precipitation of the copper complexes. Crystals obtained by this method are bluecolored, with (210) and the (001) as the best developed faces. The concentration of Cu^{2+} in the Rochelle salt crystals was 0,05% (weight percent). The dielectric measurements show for the crystals grown from solution including $CuCl_2$* a Curie temperature shifts to 19° C and —16° C and for those grown from a solution including Cu-acetate* to 13° C and —13° C (Fig. 1).

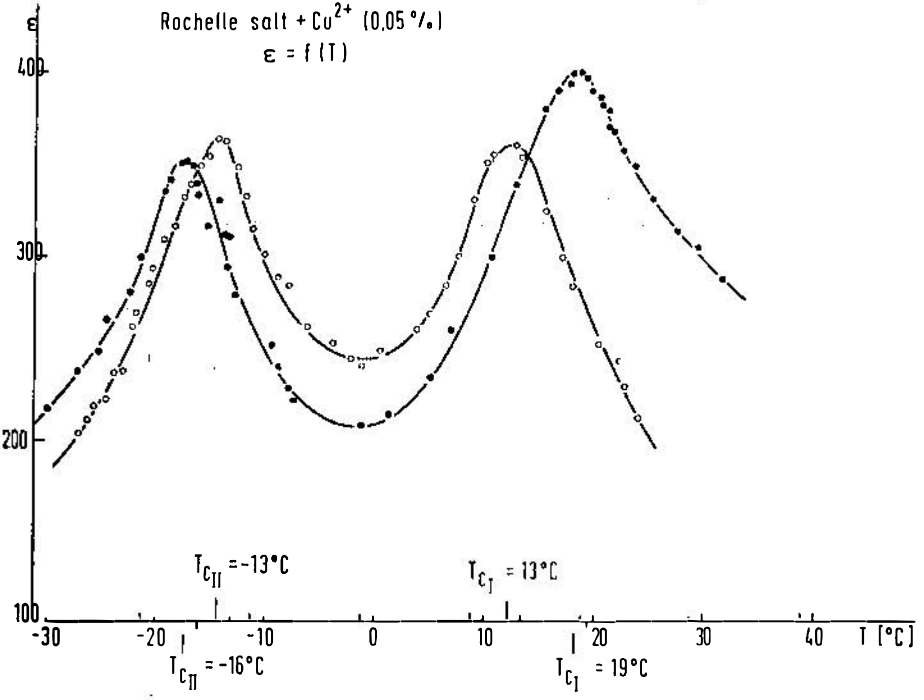

Fig. 1: Temperature dependence of the dielectric constant of Cu^{2+} doped Rochelle salt single crystals, ... $CuCl_2$ doped crystal, ° ° ° Cu-acetat doped crystal.

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* In the following text reported as $CuCl_2$ or Cu acetate doped crystals.

The EPR spectra were measured on a home built spectrometar (9375 Mc/s). The magnetic field was varied from zero to 4 k gauss. DPPH, Mn^{2+} doped ZnS and ruby were used as field markers. The angular dependence of the spectra was measured at 10^0 intervals for rotations about three crystallographic axes. A typical EPR spectrum of Cu^{2+} doped Rochelle salt is given in Fig. 2., where the EPR lines of two out of the four physically different Cu^{2+} ions related by the orthorhombic symmetry are presented. As a result of the hyperfine interaction with ^{63}Cu nuclei each component is split into four lines. The less intense lines belong to the centers with ^{65}Cu nuclei.

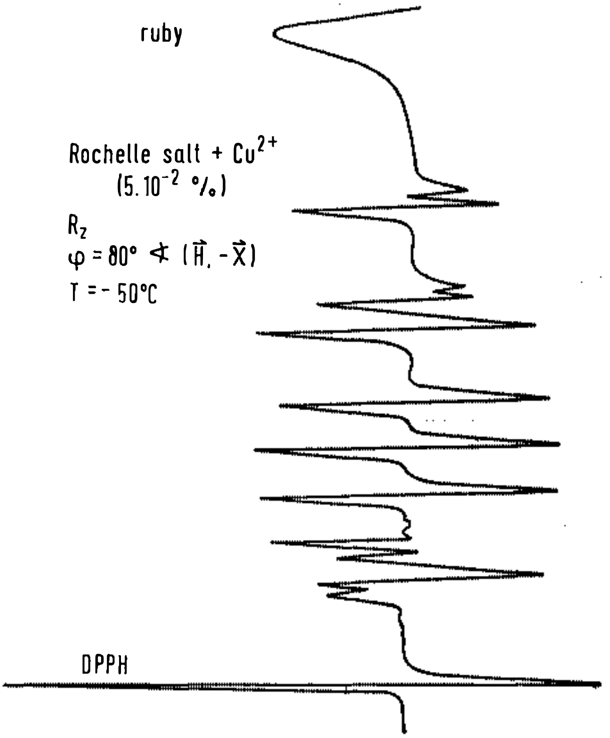

Fig. 2: A typical EPR spectrum of Cu^{2+} doped Rochelle salt. Ruby and DPPH are field markers.

The EPR spectra can be described by the simple spin Hamiltonian:

$$H_2 = \beta \vec{H} g \vec{S} + \vec{S} A \vec{I} + \vec{I} Q \vec{I} \ , \qquad (1)$$

where the electron spin $S = \frac{1}{2}$ and the nuclear spin $I = \frac{3}{2}$. The principal values and direction cosines of the g and A tensors were calculated from the angular dependences of the spectra measured at -50^0 C and are presented in Table 1 for a sample doped with $CuCl_2$, and in Table 2 for a sample doped with $Cu(CH_3COO)_2$.

Table 1

	cos α	cos β	cos γ
$g_x = 2{,}046 \pm 0{,}005$	(+ + + +) 0,87	(— + — +) 0,32	(— + + +) 0,26
$g_y = 2{,}055 \pm 0{,}005$	(— + + +) 0,26	(— — — —) 0,66	(+ + — —) 0,65
$g_z = 2{,}325$	(— — + +) 0,34	(+ — — +) 0,62	(+ + + +) 0,70
$A_x = -(16 \pm 5) \cdot 10^{-4}$ cm^{-1}	(+ — + +) 0,80	(— + + +) 0,49	(— — + +) 0,24
$A_y = -(35 \pm 5) \cdot 10^{-4}$ cm^{-1}	(— + + +) 0,46	(— + — —) 0,55	(+ + — +) 0,66
$A_z = -(153 \pm 5) \cdot 10^{-4}$ cm^{-1}	(— — + +) 0,33	(+ — — +) 0,61	(+ + + +) 0,71

Table 2

	cos α	cos β	cos γ
$g_x = 2{,}056 \pm 0{,}005$	(— + — —) 0,83	(+ + + —) 0,54	(+ + — —) 0,11
$g_y = 2{,}062 \pm 0{,}005$	(+ + + —) 0,47	(+ — + +) 0,47	(+ — — —) 0,67
$g_z = 2{,}297 \pm 0{,}005$	(— + — +) 0,30	(— — + +) 0,61	(+ + + +) 0,74
$A_x = -(7 \pm 5) \cdot 10^{-4}$ cm^{-1}	(— + — —) 0,93	(+ + — +) 0,33	(— — — +) 0,16
$A_y = -(34 \pm 5) \cdot 10^{-4}$ cm^{-1}	(— — + —) 0,14	(+ — + +) 0,74	(+ — — —) 0,66
$A_z = (128 \pm 5) \cdot 10^{-4}$ cm^{-1}	(— + — +) 0,34	(— — + +) 0,58	(+ + + +) 0,74
$Q = 2{,}10^{-4}$ cm^{-1}			

Here α, β, γ are the angles between the principal tensor axes and the crystal axes (a, b, c). The signs before the direction cosines are related to four physically nonequivalent Cu^{2+} sites.

The results obtained with $CuCl_2$ doped samples agree rather well with the data of Windsch[2] who used a $CuSO_4$ doped crystal, whereas the Cu-acetate doped sample showed some differences in the g and A tensors components, perserving the same directions of the mean values g_{zz} and A_{zz} as in the $CuCl_2$ doped sample. Cu doping can change the physical properties of the Rochelle salt crystal (T_c measurement Fig. 1) as by different conditions of the procedure the surrounding of the Cu ion can be changed significantly, explaining the disagreement of the published data on the crystal.

In agreement with the assumption of the $P2_12_12$ symmetry in the low temperature phase we find four physically nonequivalent Cu^{2+} sites in the unit cell which are related by operations of the 222 point group.

The directions of the principal axes of the largest eigenvalues of the g and A tensors form an angle of 15^0 with the normal to the (1, 7, 5, 10) oxygen plane, whereas in ref.[1], it is stated that this angle is close to zero. In spite of this 15^0 deviation, the present data support the conclusion[1, 2] that the Cu^{2+} ion is located in the center of the (1, 3, 5, 7, 10) oxygen octahedron thus replacing the Na^+ ion (Fig. 3).

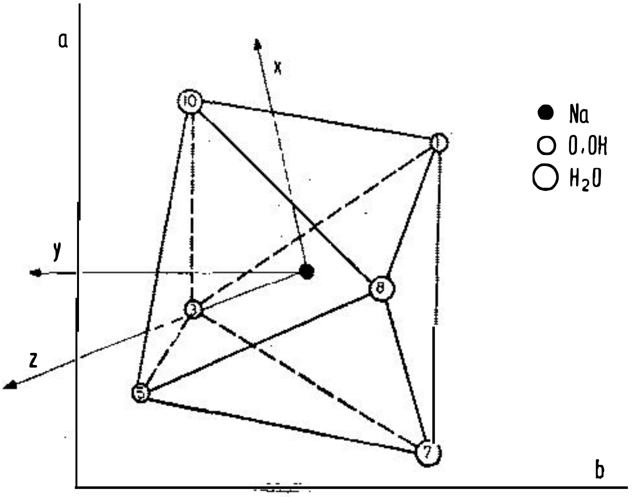

Fig. 3: The Cu complex bond coordinate system, determined from the g and hyperfine tensors mean value directions, relative to the octahedron from Breevers and Hughes structure[15]).

3. *Effect of the ferroelectric phase transitions on the EPR spectra*

The changes in the EPR spectra on going through the two Curie points are so small that they can be studied only at such orientations where the lines of all four physically nonequivalent Cu^{2+} sites are well resolved. The differences in the principal values of the g and A tensors in the various phases are namely extremely small. The observed shifts of the EPR lines are similiar to those obtained with an electric field applied in a »soft« direction. By the present theories of the ferroelectric phase transitions in Rochelle salt[18, 19] two position dipoles in the (1, 3, 5, 8, 7, 10) oxygen octahedron are responsible for the dielectric anomalies. According to Fraser[7] these dipoles might be the O(5) — H groups, but as far as this work is concerned they might be H_2O molecules as well.

There are two sublattices in the unit cell of the Rochelle salt (A and B, by the notation of ref.[18]), the dipole moments of which cancel each other in the low temperature phase. On going from the low temperature phase to the ferroelectric phase the two position dipoles at the A sublattice become disordered so that the still ordered B sublattice dipoles produce a spontaneous polarization. This disordering influences the energy levels of A_1 and A_4 Cu^{2+} ions more than the B_2 and B_3 Cu^{2+} ions and can be detected as a shift of the EPR lines, which is at $\varphi = 95^0$ and $\vartheta = 85^0$ (φ is the angle between H and the a axis, and ϑ is the angle between H and the b axis), for the A–site spectrum about 7 gauss and only about 1 gauss for the B site spectrum. On passing the upper Curie point the B sublattice becomes as well disordered and the spontaneous polarization reduces to zero. In agreement with these expectations and contrary to the observed behaviour at the lower Curie point, one finds that on going through the upper Curie point the B–sites are more affected than the A–sites; the lines in the B spectrum are shifted for about 4 gauss and that of A spectrum about one gauss only. With an electric field applied in the »soft« direction (parallel to a axes) these displacements change back to the position which they have in the low temperature phase, indicating an ordering of the dipoles. If an electric field is applied in the opposite direction the displacements are enlarged.

4. *The optical absorption spectra and electron structure*

The optical spectra were measured on a Zeiss spectrophotometer SMI with the doped crystal in one and the undoped crystal in the other beam. The difference spectra in the range from 2 000–10 000 Å were recorded. The spectra thus obtained are characteristic of the Cu^{2+} ion in the Rochelle salt (Fig. 4). The structure of the peaks depends on the crystal orientation and the direction of polarization of the light beam. Splittings of the order of 200 Å were detected.

Combining the optical and EPR results we tried to calculate by the molecular orbit theory the parameters characterising the Cu–ligand bonds.

From the symmetry of the g and A tensors we assume that the approximate symmetry of the paramagnetic center is D_{2h}. Combining the oxygen 2s and 2p orbitals with Cu^{2+} 3d orbitals and following Gersman and Swallen[20] we obtain for the wave function of Cu^{2+} energy levels the following results:

$$\Psi_{B_{1g}} = \alpha d_{xy} - \frac{1}{2}\alpha' \left[-\overset{(1)}{\sigma}_{xy} + \overset{(2)}{\sigma}_{xy} + \overset{(3)}{\sigma}_{xy} - \overset{(4)}{\sigma}_{xy} \right], \tag{2a}$$

$$\Psi_{A_{2g}} = \beta d_{x^2-y^2} - \frac{1}{2}(1-\beta^2)^{1/2} \left[-\overset{(1)}{p}_{xy} - \overset{(2)}{p}_{xy} + \overset{(3)}{p}_{xy} + \overset{(4)}{p}_{xy} \right], \tag{2b}$$

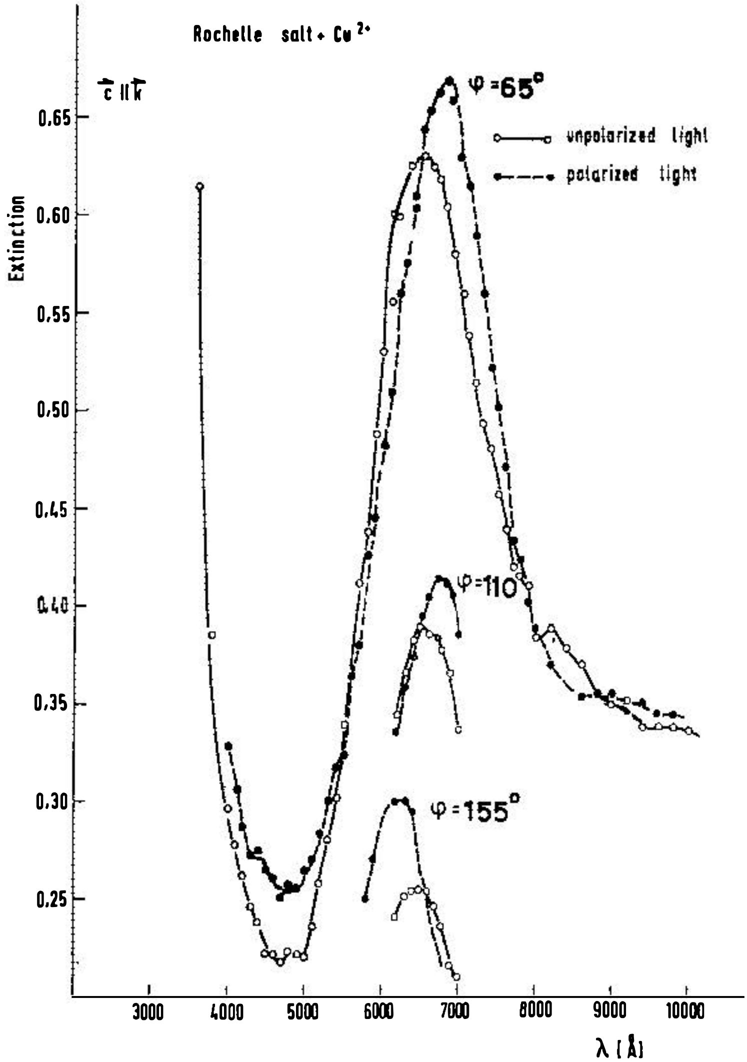

Fig. 4: Optical absorption spectra of Cu^{2+} doped Rochelle salt single crystal with the incident beam parallel to the *c* axis ($c \parallel k$): *full line* – unpolarized light *dotted line* – polarized light. φ is the angle between the direction of polarization counted in the *b* to *a* direction of the (001) plane.

$$\text{(2c)} \qquad \Psi_{A_{3_g}} = \gamma d_{3z^2-r^2} - \frac{1}{2}\left(1-\gamma^2\right)^{1/2}\left[\sigma_{xy}^{(1)} + \sigma_{xy}^{(2)} - \sigma_{xy}^{(3)} - \sigma_{xy}^{(4)}\right],$$

$$\text{(2d)} \qquad \Psi_{B_{3g}} = \delta' d_{yz} - \frac{1}{2}\left(1-\delta'^2\right)^{1/2}\left[p_z^{(1)} + p_z^{(2)} - p_z^{(3)} - p_z^{(4)}\right],$$

(2e) $$\Psi_{B_{2g}} = d_{xz} \ ,$$

where:

$$\sigma = np \mp (1 - n^2)^{1/2} s \qquad 0 < n < 1 .$$

The normalization of the B_{1_g} orbital yields: $\alpha^2 + \alpha'^2 - \alpha\alpha' S = 1$ where S is the oxygen overlap integral $S = \langle d_{xy} | -\sigma_x^{(1)} + \sigma_y^{(2)} + \sigma_x^{(3)} - \sigma_y^{(4)} \rangle \frac{1}{2}$, and is according to Maki and Mc Garvey[21] $S = 0.094$. Similar relations hold between the other coefficients but the overlap integrals are small and can be neglected. These wave functions were used to solve a crystal field Hamiltonian using second order perturbation theory and assuming that B_{1_g} is the ground state. The resulting spin Hamiltonian is:

$$H = \beta\,(g_x H_x S_x + g_y H_y S_y + g_z H_z S_z) + A_x I_x S_x + A_y I_y S_y + A_z I_z S_z \ ,$$

where the magnetic parametra g_i and A_i are given by the terms:

(3a) $$g_z = 2{,}0023 - (8\lambda/\Delta E_{x2-y2}) \left[\alpha^2 \beta^2 - f(\beta)\right],$$

(3b) $$g_x = 2{,}0023 - (2\lambda/\Delta E_{xz})(\alpha^2 - \alpha\alpha' S) \ ,$$

(3c) $$g_y = 2{,}0023 - (2\lambda/\Delta E_{yz})\ (\alpha^2 \delta'^2 - \alpha\alpha' S\, \delta'^2)$$

(3d) $$A_z = P\left[-\alpha^2 \left(\frac{4}{7} + k\right) - 2\lambda\alpha^2 \left(\frac{4\beta^2}{\Delta E_{x^2-y^2}} + \frac{3}{14} \frac{\delta'^2}{\Delta E_{yz}} + \frac{3}{14} \frac{1}{\Delta E_{xz}} \right)\right],$$

(3e) $$A_x = P\left[\alpha^2 \left(\frac{2}{7} - k\right) - \frac{22}{14} \frac{\lambda\, \alpha^2}{\Delta E_{xz}} \right],$$

(3f) $$A_y = P\left[\alpha^2 \left(\frac{2}{7} - k\right) - \frac{22\ \lambda\, \alpha^2\, \delta'^2}{14\ \ \Delta E_{yz}} \right],$$

$$f(\beta) = \alpha\alpha'\beta^2 S + \alpha\alpha' (1 - \beta^2)^{1/2}\, T(n)/2 .$$

λ is the spin orbit coupling, constant for the free Cu^{2+} ion, $\lambda = -828\ cm^{-1}$

$$P = 2\gamma_{Cu}\beta\beta_N \langle d_{xy} \left| \frac{1}{r^3} \right| d_{xy} \rangle \sim 0{,}036\ cm^{-1} ,$$

γ_{Cu} = gyromagnetic ratio of the copper nucleus, k is Fermi contact term. $T(n) = n - (1 - n^2)^{1/2} R\, 8\, (z_p z_s)^{5/2} (z_s - z_p) / (z_s + z_p)^5 a_0$, and is by Maki and Mc Garvey[21)] 0.220 for the z axis, R = metal-ligand distance, z_s and z_p represent the effective nuclear charges on the s and p orbitals, respectively, and a_0 is the Bohr radius. For the x and y axes $T(n)$ can be neglected. From the optical data the following orbital excitation energies measured relative to the ground state B_{1g} have been evaluated in Table 3 for a) $CuCl_2$ doped Rochelle salt and b) Cu acetate doped Rochelle salt:

Table 3

a)	b)
$E_{3z^2-r^2}$ = 14 300 cm^{-1}	$E_{3z^2-r^2}$ = 14 500 cm^{-1}
$E_{x^2-y^2}$ = 15 000 cm^{-1}	$E_{x^2-y^2}$ = 15 200 cm^{-1}
E_{yz} = 16 000 cm^{-1}	E_{yz} = 16 100 cm^{-1}
E_{xz} = 26 700 cm^{-1}	E_{xz} = 26 700 cm^{-1}

From equations (3) and the above experimental data the bonding parameters α, α', β, δ' as well as the Fermi contact term k and theoretical values of g_{xx}, g_{yy} and A_{yy} could be calculated. The obtained results are presented on Table 4:

Table 4

	α	α'	β	δ'	k	g_{xx}	g_{yy}	A_{yy}cm^{-1}
$CuCl_2$ doped crystal	0,90	0,53	0,97	0,78	0,40	2,49	2,49	26.10^{-4}
Cu-acetate doped crystal	0,88	0,58	0,97	0,78	0,37	2,47	2,47	25.10^{-4}

The parameters in Table 4 are comparable to the other published data on Cu complexes[20, 21, 22)]. Complex formation can be observed already in the $CuCl_2$ Rochelle salt solution where hyperfine splittings of 58,3 cm^{-1} have been observed in the EPR spectrum. The values in the D symetry model indicate out of plane π bonding. In agreement with Gersman and Swallen[20)] we took tke B_{1g} state as the ground one. The polarization measurements were helpful, but the detailed assignement is based on the EPR data.

The differences in the $CuCl_2$ and Cu–acetate dopped sample are significant as the Cu^{2+} is deposited on the same place in the lattice and the anions Cl^- and acetate are not included. Dielectric measurements (Fig. 1) give strong indication that there are changes all over the crystal lattice, may be as a small distortion observable in the Cu^{2+} EPR spectra and much less pronounced in the optical absorption spectra. From Table 4 a stronger d_{xy} participation in covalent bonding for the $CuCl_2$ doped sample could be expected, and hydrogen bonds participating in the phase transition mechanism are directly influenced.

The changes in the EPR spectra on passing the two Curie points are similar to the ones found by quadrupole perturbed magnetic resonance of ^{23}Na (ref. [18]) and can serve as an additional argument in favour of the two sublattice model of ferroelectricity in Rochelle salt[18, 19].

Aknowledgement

We wish to thank Professor R. Blinc for a number of useful suggestions throughout the course of this work and for a helpful discussion of the manuscript.

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EPR I SPEKTRI OPTIČKE ABSORPCIJE Cu^{2+} U ROŠELSKOJ SOLI

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Sadržaj

Izmerili smo optičke i EPR spektre rošelske soli dopirane sa $CuCl_2$ i Cu-acetatom u paraelektričkoj, feroelektričkoj i antiferoelektričkoj fazi. Oba načina daju slične EPR spektre a rezultati merenja slažu se sa pretpostavkom da Cu^{2+} u kristalnoj rešetci rošelske soli zamjenjuje Na^+ ion. Pomoću rezultata optičkih absorpcija merenja izračunali smo parametre vezivanja bakra sa ligandima, kao i teoretske vrednosti g_{xx} i g_{yy}.

Kod prelaza kroz nižu Curiejevu tačku, primetili smo znatan pomak EPR linija Cu^{2+} iona subrešetke A, a kod linija Cu^{+2} iona u subrešetci B pomak je manji. Iznad gornje Curiejeve tačke veličina pomaka je veća za subrešetku B.