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JAHN-TELLER EFFECTS IN 10% ZINC DOPED COPPER FLUOSILICATE HEXAHYDRATE (CZFH): AN X–BAND EPR STUDY

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Stable crystals of copper fluosilicate hexahydrate (CZFH) have been successfully grown. X-band (9 GHz) EPR spectral studies carried out at room and liquid nitrogen temperatures have revealed some new features of Jahn-Teller effect in CZFH.

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1. *Introduction*

Jahn-Teller (J-T) effect [1] pertains to the inherent instability associated with an orbitally degenerate electronic state of a non-linear molecule. The first unambiguous evidence of J-T effects was obtained from the observation of isotropic EPR spectrum of Cu^{2+} ions in sites of trigonal symmetry (Cu^{2+} ions doped in $ZnSiF_6{\cdot}6H_2O$) at room temperature (RT) [2]. The first theoretical discussion of this phenomenon was initiated by Abragam and Pryce [3]. They suggested that an averaging process was occurring as a result of rapid orientation of $[Cu{\cdot}6H_2O]$ complex between its different possible static distortions at room temperature and isotropic Cu^{2+} EPR spectrum was observed. Their explanation was subsequently verified by the observation of anisotropic EPR spectrum characteristic of the ground state of a tetragonally distorted octahedral Cu^{2+} complex at 50 K and below [4, 5]. This phenomenon is often described as the 'so-called' dynamic → static J-T transition. EPR, optical and other manifestations of J-T effects in many other systems have since then been discovered and theoretical interpretations of various degrees

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of sophistication have been put forward. Exhaustive reviews on the subject are available [6a-g].

In not too distant past, Cu^{2+}: $ZnSiF_6{\cdot}6H_2O$ J-T system was again investigated at high microwave frequencies of 74 GHz and 148 GHz at liquid oxygen temperature under uniaxial compression [7] and at 4.2 K under hydrostatic pressures in the range 0 – 13 Kbar [8] to study the effects of applied pressures on J-T parameters as well as spin Hamiltonian parameters. Surprisingly, not much attention was given to the concentrated J-T system, $CuSiF_6{\cdot}6H_2O$ (CFH), the structure of which [9], contrary to the earlier belief, is not isomorphous with that of $ZnSiF_6{\cdot}6H_2O$ (ZFH) [10]. Although the structure is still rhombohedral (space group R $\overline{3}$), the unit cell, which has dimensions $a = b = 1.818$ nm and $c = 0.9857$ nm, is four times as large and contains three magnetically non-equivalent tetragonally distorted elongated [Cu(1)$\cdot 6H_2O$] octahedra and one regular [Cu(2)$.6H_2O$] octahedron. Cu(1) and Cu(2) correspond to two types of Cu^{2+} ions. De et al. [11] carried out EPR measurements on CFH at K-band ($\simeq$ 24 GHz). They observed resolved signals due to two types of Cu^{2+} ions - one having tetragonally distorted octahedral coordination and the other having regular octahedral coordination consistent with X-ray findings [9]. An anomalously low g-value (2.093) for the Cu^{2+} ion having regular octahedral coordination was observed which could not be reconciled with the usual ligand field theory. CFH is not a very stable crystal and so utmost caution is required to carry out any measurement on it. Sukharevskii et al. [12] have described a method to grow solid solutions of CFH and ZFH having the composition $Cu_{0.9}Zn_{0.1}SiF_6{\cdot}6H_2O$ (CZFH) which is quite stable like ZFH. They have shown that the physical properties such as latent heat and specific heat of CFH and CZFH are similar in the temperature range 77 K – 310 K. They have also observed that both CFH and CZFH exist in three phases [12–14] of which phase I and phase II were studied by X-ray diffraction method. For CZFH, phase I has been observed to occur between temperatures 296 K – 302 K with cell parameters $a = 0.9344$ nm, $c = 0.9695$ nm, $Z = 3$ and space group R$\overline{3}$. For CFH, phase I could not be accurately determined because of its intensive tetrahydrate formation stimulated by the II $\leftrightarrow$ I phase transition. Phase II is observed between temperatures 280 K – 290 K for both compounds CFH and CZFH, unit cell dimensions of the latter being $a = 1.8138$ nm, $c = 0.9787$ nm, and the space group remaining the same as in phase I [12]. A third low-temperature phase (phase III) has been detected from calorimetric study under slow cooling. However, for phase III, the X-ray single-crystal diffraction data are not available. Phase transition II $\leftrightarrow$ III has considerable thermal hysteresis of 18 K (275 K – 256 K). When the samples are cooled quickly (50 K/min) to liquid nitrogen temperature (LNT), the phase III does not form; rather, the phase II is quenched. EPR studies on CZFH have not so far been reported. The present X-band (9 GHz) EPR investigation on freshly prepared single crystals of CZFH is carried out at RT and at LNT. Single crystals of CZFH, prepared essentially following the method of Sukharevskii et al. [15] and having a quite significant magnetic dilution (Cu:Zn $\approx$ 9:1) are expected to show resolved EPR signals due to two types of Cu(II) octahedra. It is also of interest to verify whether the anomalous low g-value assigned to the regular octahedral Cu(2) ions of CFH (observed at 24 GHz) [11] is also observed in the case of CZFH at 9 GHz.

2. Experimental

Single crystals of solid-solution CZFH are grown by slow evaporation from an aqueous solution of CFH and ZFH mixed in proportion 4:1 and kept in a polythene beaker inside a desiccator. CaO is used as dehydrating agent. The 10 cm diam. desiccator is kept inside a specially designed small refrigerator. The refrigerator is made vibration free by keeping its compressor outside it. The heater wire, made of canthal and wound over a hollow ebonite pipe is kept inside the desiccator surrounding the polythene beaker. The current through the heater is controlled by an electronic temperature controller (kept outside the refrigerator) in conjunction with a Si diode temperature sensor which is kept very close to the beaker so as to maintain the temperature stable within the desiccator at a pre-selected temperature, the stabilization being within ±0.1 °C. The temperature can be controlled in the temperature range 0 °C – 15 °C. The crystallization temperature was fixed at ≈ 9 °C to avoid the growth of tetrahydrated form of CFH (monoclinic). Transparent, blue coloured, moderately large single crystals (suitable for EPR studies) having well-developed rhombohedral faces are successfully grown in the time span of 25 – 30 days. The crystals, unlike CFH, are quite stable in open air.

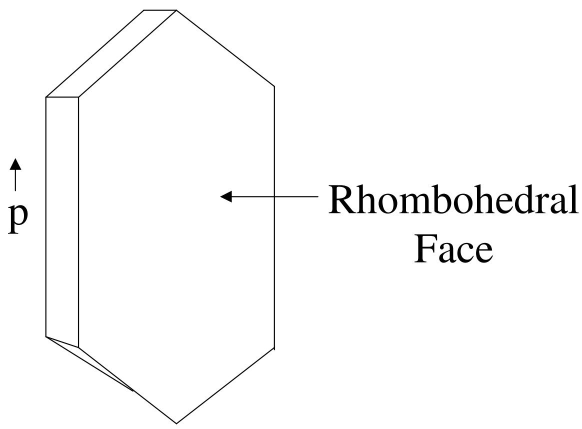

Fig. 1. Rhombohedral face of the $Cu_{0.9}Zn_{0.1}SiF_6{\cdot}6H_2O$ *single crystal.*

A Varian X-band E-109 Century Series EPR spectrometer is employed to record the spectra in the rhombohedral plane at the regular intervals of 10°, measured from the reference axis ‘p’ (0°) (Fig. 1) of a given crystal at RT (287 K) as well as at LNT. This is performed by rotating the crystal mounted on a quartz rod and fixed to a goniometer, through different angles within the X-band rectangular cavity working in the TE_{102} mode. The low temperature measurements are carried out in conjunction with a narrow tailed quartz dewar containing liquid nitrogen and inserted into the cavity. For EPR measurements at LNT, temperature is lowered very slowly. The single crystals used for EPR studies are then analysed by an atomic absorption spectrometer for their Cu and Zn contents. Their relative composition is found to be very close to the ratio Cu:Zn = 9:1. Optical absorption spectra of the crystal are recorded with the help of JASCO UV/VIS/NIR - spektrophotometer V-530 at RT (Fig. 2).

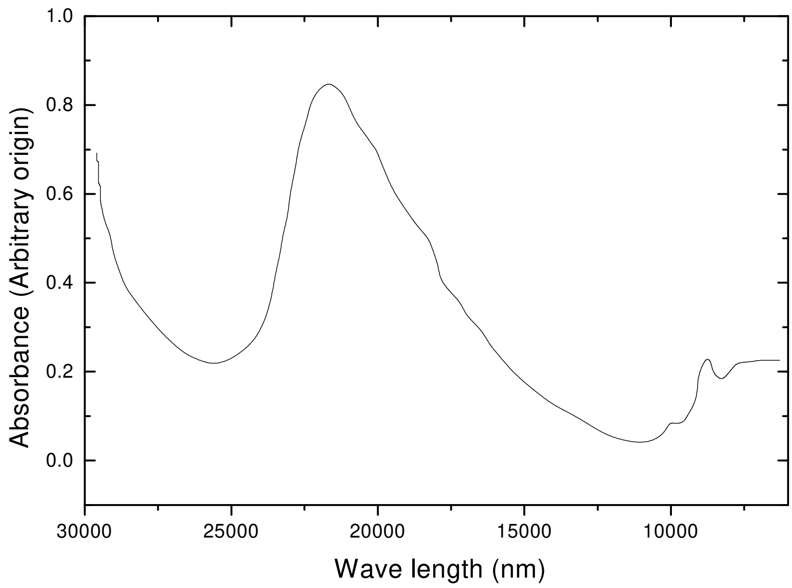

Fig. 2. Optical absorption spectra of $Cu_{0.9}Zn_{0.1}SiF_6{\cdot}6H_2O$.

3. Results and discussion

Single and nearly symmetric EPR derivative spectra are observed in most directions of the rhombohedral plane at both RT and LNT. However, a shoulder on the high-field side of the main spectrum indicating the presence of a second resonance line is also visible in several directions. The dominant spectrum shows little anisotropy in g-values: $g_{\rm mean} \simeq 2.22$. No noticeable change in the LNT spectra has been observed, which indicates that no phase transformation has occurred, i.e., phase II remains quenched. Optical spectrum depicts a strong absorption peak at 13,300 cm^{-1} having a weak shoulder at 10,800 cm^{-1} (Fig. 2). Following observations of Billing and Hathaway [16], who studied a great number of tetragonally distorted elongated octahedral Cu(II) – oxygen systems, the above bands may be assigned to the $^2B_{1g} \rightarrow {}^2E_g$ and $^2B_{1g} \rightarrow {}^2B_{2g}$ ligand field transitions, respectively.

These bands are nearly identical with those obtained in case of $CuSiF_6{\cdot}6H_2O$ and Cu(II): $ZnSiF_6{\cdot}6H_2O$ [17].

3.1. Computer simulation of EPR spectra and information obtained about J-T effects in CZFH

For a quantitative analysis, computer simulation studies of the spectra are carried out. Lorentzian line shape is assumed for the EPR lines. The Lorentzian derivative line shape has the normalized form [18]

$$I(H) = A\frac{\dfrac{H-H_0}{\Delta H_{p-p}/2}}{\left[3+\left(\dfrac{H-H_0}{\Delta H_{p-p}/2}\right)^2\right]^2}\,, \tag{1}$$

where A is the derivative amplitude (considered here as a constant term), $H_0 = \frac{h\nu}{g\beta}$, H is the applied magnetic field and ΔH_{p-p} the peak-to-peak derivative linewidth. The hyperfine interaction is not considered since we are dealing with a nearly concentrated Cu(II) paramagnetic system and, moreover, no hyperfine structure is observed. A similar expression as (1) is considered for the derivative of the second line having different ΔH_{p-p} (say, $\Delta H'_{p-p}$), g (say, g') and intensity (say, I'). The principle of superposition of the two lines is applied to construct the observed composite line. Table 1 shows fitted g-values and derivative linewidths obtained by computer simulation. It is found that the observed EPR line in one orientation, i.e., at an angle $\theta = 50°$, measured from the reference direction 'p' in

TABLE 1. Computer-fitted derivative linewidths (ΔH_{p-p}) and g-values in some orientations in the rhombohedral plane of $Cu_{0.9}Zn_{0.1}SiF_6{\cdot}6H_2O$ *at room temperature (RT) and liquid nitrogen temperature (LNT).* $g(1)$ *and* $g(2)$ *correspond to* Cu(1) *and* Cu(2) *ions, respectively.*

Temp.	Orientation with respect to p-axis (θ) (Ref. Fig 1.)	g-values			
		$g(1)$	$\Delta H_{p-p}(1)$ (mT)	$g(2)$	$\Delta H_{p-p}(2)$ (mT)
RT	50°	2.230±0.005	15	2.120±0.005	5
	100°	2.220±0.005	22	2.140±0.005	5
	140°	2.220±0.005	26	2.140±0.005	5
LNT	50°	2.220±0.005	12	2.123±0.005	5
	100°	2.215±0.005	13	2.120±0.005	5
	140°	2.210±0.005	16	2.123±0.005	5

the rhombohedral plane (Fig. 1), at RT as well as at LNT, is constituted of two lines having different g-values and intensities (Figs. 3a and c). Our analysis further reveals that the lines observed at the orientations 100° (50° off from $\theta = 50°$ orientation) and 140° (90° off from $\theta = 50°$ orientation) (Figs 3b and d) are also composed of two lines as above (Table 1). The fitting is quite good, i.e., the theoretically computed first derivative spectra agree quite well with the experimental spectra. It is thus seen that the EPR spectra observed in different directions are composed of two nearly isotropic lines at both RT and LNT. So, instead of the expected three anisotropic lines corresponding to three tetragonally distorted octahedral Cu(1)·$6H_2O$ complexes and an isotropic line corresponding to the regular octahedral Cu(2)·$6H_2O$ complex, two nearly isotropic lines have been observed. This is not in conformity with what was observed in CFH at K-band [11] (the corresponding microwave frequency is about 2.5 times higher than that at X-band) where three anisotropic lines and one isotropic line had been identified in a gen-

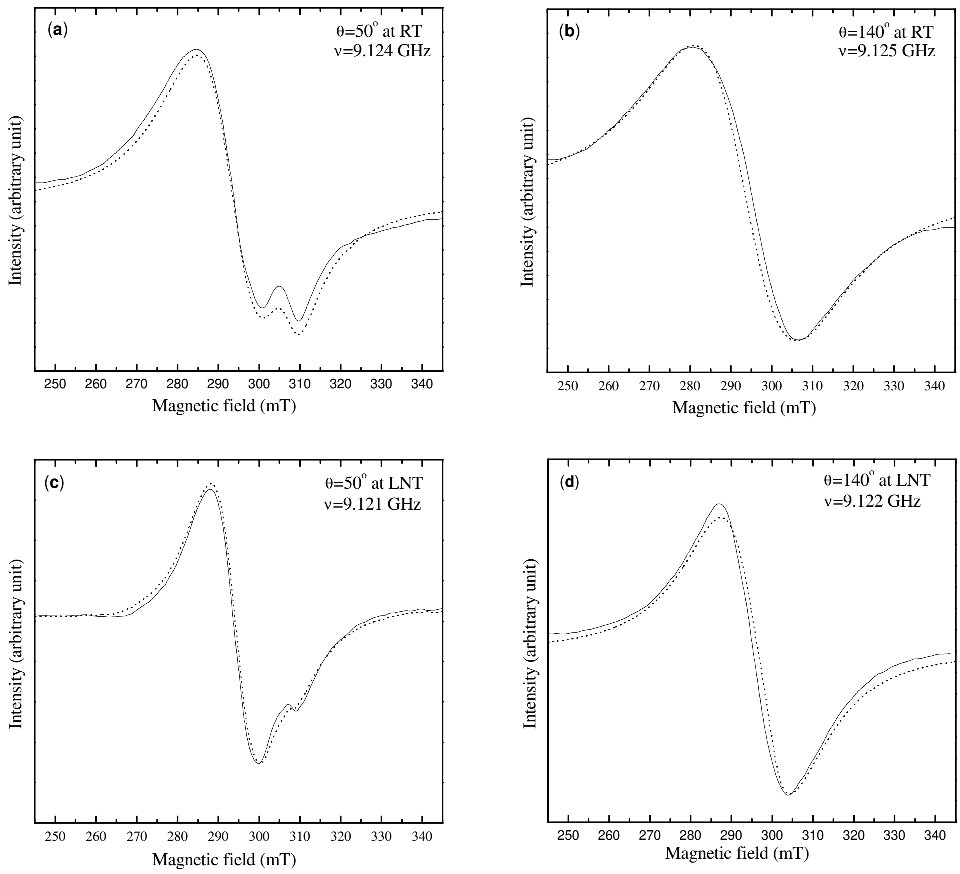

Fig. 3. Computer simulated derivative EPR spectra (- - - - - - - -) and experimental derivative EPR spectra (———).

eral direction in the rhombohedral plane, in agreement with the X-ray structure [9]. It is also significant to note that the observed isotropic g-value (2.23) is close to the average of the anisotropic g-values ($g_{\|} = 2.390$, $g_{\perp} = 2.093$), obtained at K-band [11]. The low g-value line ($g = 2.12$) obviously corresponds to regular octahedral Cu(2) sites. It is noted that this low g-value is slightly larger than that obtained at K-band ($g = 2.093$) [11]. So, it may be inferred that anisotropy in g-values associated with Cu(1) sites observed at higher microwave frequency (24 GHz) in CFH is averaged out at lower microwave frequency (9 GHz) in CZFH to yield an isotropic g-value ($g = 2.23$). Phonons induce thermal transitions between the vibronic states of J-T sites [19], and if the frequency of such relaxation process for Cu(1) sites is greater than the microwave frequency (9 GHz) employed in the present EPR experiment, it may lead to averaging of the anisotropic contributions to the spin Hamiltonian and the isotropic spectrum will be observed. It is thus seen that, besides Cu(2) ions, Cu(1) ions also behave as dynamic J-T ions so far as EPR measurements at X-band in the LNT range are concerned.

Observed optical spectra in CFH and CZFH are nearly identical and so do not provide any clue regarding different behaviour of copper(II) sites observed in the mixed crystal CZFH at X-band from that in CFH at K-band [12].

In this connection, it is worthwhile to mention that EPR of CFH at Ku ($\nu =$ 16.16 GHz) band [11] have also confirmed the existence of the low g-value line corresponding to Cu(2) sites which remains isotropic even at 4.2 K. Thus, it is seen that the low isotropic g-value lines observed in CFH and CZFH corresponding to regular Cu(2) octahedral sites are quite distinct from the isotropic g-value lines ($g \approx$ 2.22) observed in several other trigonally distorted water octahedron coordinated Cu(II) systems, like copper bismuth nitrate hexahydrate, copper lanthanum nitrate hexahydrate and copper bromate hexahydrate [20, 21]. To our knowledge, we are not aware of any adequate theory which could explain the origin of low g-values associated with the regular octahedral Cu(2) sites in CFH and CZFH observed at K-band and X-band, respectively.

3.2. EPR linewidth behaviour of Cu(1) and Cu(2) ions

It is noted from Table 1 that derivative linewidths of Cu(1) spectra (high g-value lines), obtained particularly at 100° and 140° orientation at LNT are significantly less compared to those obtained at RT. On the other hand, derivative linewidth of Cu(2) spectrum is much less (5 mT) and is practically constant in the LNT range. From the X-ray data [9], it can be shown that both Cu(1) and Cu(2) sites have similar magnetic environments. Each Cu(1) ion has 18 neighbouring Cu^{2+} ions, i.e., 8 Cu(1) ions and 6 Cu(2) ions are 0.909 nm and 4 Cu(1) ions are 0.985 nm away from each Cu(1) ion, while each Cu(2) ion has 22 Cu^{2+} neighbours, i.e., 10 Cu(1) ions are 0.909 nm and 12 Cu(2) ions are 0.985 nm away from each Cu(2) ion. So, the dipolar broadening and magnetic exchange effects on their EPR linewidth ought to be similar for both Cu^{2+} sites. Another source of broadening is random strain. This may result from inhomogeneities, dislocations or nearby point defects [22]. But the random strain should have equally affected the linewidths of both isotropic lines due to Cu(1) and Cu(2) ions. So, larger linewidth and its temperature dependence observed in the case of Cu(1) ions most likely arise from higher spin-lattice relaxation rate ($1/T_1$) of Cu(1) ions compared to that of Cu(2) ions. Temperature-independent linewidth in the latter case suggests that $1/T_1$ has negligible contribution to the linewidth. The minimum magnetic exchange required for the merger of two Cu(II) signals having g values 2.22 (g_1) and 2.12 (g_2) is estimated from the difference of their Zeeman energies [$\approx (g_1 - g_2)\beta H$] and is found to be 0.013 cm^{-1}. So, it may be concluded that magnetic exchange present in CZFH is much less than 0.013 cm^{-1}.

3.3. Relative intensity of Cu(1) *and* Cu(2) *spectra*

In ZFH [10], Zn(II) ion has regular octahedral coordination of H_2O ligands. It is likely that in mixed CZFH, Zn(II) ions enter into Cu(2) sites. In that case, the relative population of Cu(1) and Cu(2) ions will become 5:1. So, their EPR intensities should have the same proportion. However, computer simulation reveals that Cu(2) EPR spectrum is much less intense than the Cu(1) spectrum (intensity ratio $\sim$ 1:100). This is most surprising. The only plausible explanation, which could be put forward, is the following:

Spin-lattice relaxation of Cu(1) ions is much faster (see Sect. 3.2) and overlap of spectra due to Cu(1) and Cu(2) ions is quite extensive. Thus, it seems likely that profound intensity transfer from Cu(2) spectrum to Cu(1) spectrum takes place, resulting in the observed weak intensity of the Cu(2) spectrum.

4. Concluding remarks

i. Like the Cu(2) ions, Cu(1) ions also behave as dynamic J-T ions at X-band. For further elucidation of the J-T behaviour of the two kinds of Cu(II) ions present in CZFH, EPR measurements at higher microwave frequencies and at lower temperatures, preferably in the liquid helium temperature range, are preferred.

ii. The g-value assigned to the Cu(2) ions and obtained at 9 GHz in CZFH has a positive shift with respect to that obtained in CFH at 24 GHz.

iii. Different EPR linewidth behaviour of Cu(1) and Cu(2) ions have originated from different spin-lattice relaxation rates in the two cases.

iv. Magnetic exchange between the two types of neighbouring Cu^{2+} sites is very feeble ($\ll 0.013$ cm^{-1}).

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References

[1] H. Jahn and E. Teller, Phys. Rev. **49** (1936) 874.

[2] B. Bleaney and D. J. E. Ingram, Proc. Phys. Soc. A **63** (1950) 408.

[3] A. Abragam and M. H. L. Pryce, Proc. Phys. Soc. A **63** (1950) 409.

[4] B. Bleaney, K. D. Bowers and R. S. Trenam, Proc. Royal. Soc. A **228** (1955) 157.

[5] L. S. Dang, R. Buisson and F. T. B. Williams, J. Phys. (Paris) **34** (1974) 49.

[6] (a) F. S. Ham, Phys. Rev. **166** (1968) 307; (b) M. D. Sturge, *Solid State Physics*, eds. F. Seitz, D. Turnbull and H. Ehrenreich: Vol. 20, pp. 91-211, Academic Press, New York (1967); (c) F. S. Ham, *Electron Paramagnetic Resonance*, ed. S. Geschwind, Plenum, New york (1972) pp. 1-119; (d) R. Englman, *The Jahn-Teller Effect in Molecules and Crystals*, Wiley-Interscience, London (1972); (e) L. J. Challis and A. M. de Goer, *The Dynamical Jahn-Teller effect in Localized Systems*, ed. Yu. E. Perlin and M. Wagner, North-Holand, Amsterdam (1984) pp. 533-708; (f) I. B. Bersuker and V. Z. Polinger, *Vibronic Interactions in Molecules and Crystals*, Springer-Verlag, Berlin (1989); (g) M. C. O'Brien and C. C. Chancey, Am. J. Phys. **61** (1993) 688.

[7] S. N. Lukin, Sov. Phys. Solid State **33** (1991) 25.

[8] S. N. Lukin, Sov. Phys. Solid State **34** (1992) 1012.

[9] S. Ray, A. Zalkin and D. H. Templeton, Acta Crystallogr. B **29** (1973) 2748.

[10] S. Ray, A. Zalkin and D. H. Templeton, Acta Crystallogr. B **29** (1973) 2741.

[11] D. K. De, J. Sthanapati, A. K. Ghosal and A. K. Pal, J. Magn. Reson. **47** (1982) 181.

[12] B. Ya. Sukharevskii, F. A. Boiko, A. M. Bykov, V. E. Ganenko, E. O. Tsybul'skii and G. E. Shatalova, Sov. Phys. Dokl. **26** (1981) 131.

[13] B. Ya. Sukharevskii, E. O. Tsybul'skii, G. E. Shatalova and I. M. Vitebskii, Sov. Phys. Crystallogr. **28** (1983) 288.

[14] G. E. Shatalova, B. Ya. Sukharevskii, E. O. Tsybul'skii, N. E. Pis'menova, Preprint No. 10 (1985) [in Russian], Physics Technical Institute, Donetsk (1984).

[15] B. Ya. Sukharevskii, V. L. Kovarskii, E. O. Tsybul'skii, G. E. Shatalova, Sov. Phys. Solid State **28** (1986) 293.

[16] D. E. Billing and B. J. Hathaway, J. Chem. Soc. (1968) 1516.

[17] R. Pappalardo, J. Mol. Spectrosc. **6** (1961) 554.

[18] C. P. Poole, Jr., *Electron Spin Resonance: A Comprehensive Treatise on Experimental Techniques*, (Second Edition), Wiley-Interscience, New York (1983) p. 476.

[19] F. S. Ham, *Electron Paramagnetic Resonance*, ed. S. Geschwind, Plenum Press, New York (1972) Ch. 1, p. 53.

[20] D. Bijl and A. C. Rose-Innes, Proc. Phys. Soc. A **66** (1953) 954.

[21] B. Bleaney, K. D. Bowers and R. S. Trenam, Proc. Roy. Soc. A **228** (1955) 157.

[22] F. S. Ham, Phys. Rev. **166** (1968) 307.

JAHN-TELLEROVI EFEKTI U BAKARNOM FLUOR-SILICIJ HEKSAHIDRATU S 10% CINKA: EPR MJERENJA U X-POJASU

Uspješno smo pripremili stabilne kristale bakarnog fluor-silicij heksahidrata (CZFH). Načinili smo mjerenja EPR spektara u X-pojasu (9 GHz) na sobnoj temperaturi i temperaturi tekućeg dušika koja pokazuju neke nove odlike Jahn-Tellerovog efekta u CZFH.