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EPR study of the ferroelectric transition in $K_4Fe(CN)_6 \cdot 3H_2O$

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Electron-parmagnetic-resonance studies in $K_4Fe(CN)_6 \cdot 3H_2O$(KFCT) single crystals have been conducted over a range of temperatures covering the ferroelectric transition T_c around -26°C using Co II and Fe I ions, stabilized by γ irradiation at room temperature, as probes. No anomalies in the temperature dependence of g and A tensors have been observed around T_c. However, the hyperfine octet of Co II has shown a m_I-dependent linewidth of the type $a + b\, m_I + cm_I^2$ in the temperature range -40 to -140°C by which temperature the lines started to split. These results clearly indicate that the inequivalence of Fe II sites which is expected to be brought about by the phase transition seems to average out, presumably due to rapid motion of H_2O molecules down to -140°C, suggesting that H_2O molecules probably do not play a significant role at the phase transition.

I. INTRODUCTION

Potassium ferrocyanide trihydrate, $K_4Fe(CN)_6 \cdot 3H_2O$ (KFCT), has a paraelectric to ferroelectric phase transition around -26 °C, accompanied by a change in the crystal symmetry from $C_{2/c}$ to C_c. This phase transition has been the subject of a number of magnetic-resonance[1–4] and Mössbauer-effect (ME) studies[5–8] in an attempt to understand the microscopic nature of the onset of ferroelectricity. The order-disorder model in which the permanent electric dipoles present above T_c become ordered at and below T_c was first proposed by Blinc, Brenman, and Waugh[1] on the basis of the temperature dependence of NMR line shapes and the assumption of no structural variation at T_c. Kiriyama, Kiriyama, Wada, Niizeki, and Hirabayashi[2] have shown that these line-shape anomalies do not occur at the transition temperature. However, they also assumed an order-disorder model for the phase transition on the basis of some indirect experimental evidence of no significant change in the atomic arrangements of the heavier atoms at the Curie point. Based on the same assumption, O'Reilly and Schacher[3] explained their EPR results of V^{2+} in KFCT on an order-disorder model. However, no direct experimental verification of this has been reported. Using inelastic neutron scattering, Rush, Laung, and Taylor[9] have failed to find any evidence for changes in the dynamics of water molecules in the vicinity of the transition temperature. Hazony, Earls, and Lefkowitz[5] in their ME study of KFCT single crystals found an anomaly in the temperature dependence of the recoil-free fraction (for γ-rays perpendicular to the $\langle 010 \rangle$ direction only) and explained the results on a model in which the polarization is produced by a displacive modification of the lattice. In this model the transition is believed to be associated with the distortion of the crystal for a particular mode of vibration at T_c. The process leading to such a distortion of the crystal can be described in terms of a cancellation of long-range Coulomb forces by short-range forces between the ions.[10] The cancellation of these forces leads to an anomaly in the frequency of a TO vibrational mode of the crystal. This particular mode, called soft mode, has wave vector $\vec{q}$ equal to zero, which corresponds to entire Bravais sublattices moving as rigid units relative to each other. The effects of this mode instability are expected to be seen in ME if the Fe sublattice takes part in that mode. Gleason and Walker[6] and Clauser[7] observed no anomalies with powder absorbers and the validity of the displacive mechanism was questioned. Montano, Shechter, and Shimony[8] in a recent ME study of KFCT single crystals rationalized the conflicting reports of earlier workers by relating the ME results with polarization effects and explained their results by proposing a model in which the electric field gradient (EFG) tensor rotates through 180° around the Y axis in the vicinity of T_c. In the present paper we report the EPR of Co II ions (in the low-spin configuration they will have $S = \frac{1}{2}$) in KFCT. In KFCT what is of interest at the moment is not the detection of spontaneous polarization below T_c, as its presence and other characteristics have been already established, but the microscopic structural changes which cause the onset of such an electrical ordering at and below T_c. The interaction of the polarizing electric field with the magnetic ion will contribute predominantly to the D tensor (i.e. for ions with $S \geq 1$); the gyromagnetic factor and hyperfine structure will be unaffected in first order for orbital singlets. Therefore, the EPR of ions with $S = \frac{1}{2}$ will be unaffected by the internal electric fields in first order, and Co II, having anisotropic g and A tensors, is a "good candidate" for separately studying the structural modifications affecting the EFG tensor. Our results suggest that the EFG tensor is unaffected at T_c owing to factors other than spontaneous polarization. Furthermore, fairly direct evidence is obtained to suggest that the order-disorder model is not valid, which indirectly supports some sort of a lattice-dynamical model for the mechanism of ferroelectricity in KFCT. The present EPR results are discussed in conjunction with the earlier Mössbauer work and an attempt is made to understand the mechanism of the onset of ferroelectricity in KFCT.

II. EXPERIMENTAL

Single crystals of KFCT were grown by slow evaporation of water solutions containing (1-2%) by weight of $K_3Co(CN)_6$. The crystals grew in their usual habit with a well-developed (010) plane. These crystals were γ (or x) irradiated up to dose of 2 MR. The EPR spectra were taken on a Varian V-4502 X-band spectrometer. The Varian variable-temperature accessory was used to study the temperature dependence of the spectra. 1, 1-diphenyl-2-pycryl hydrazyl (DPPH) ($g = 2.0036$) was used as a field marker.

III. RESULTS AND DISCUSSION

A. Spectra of Co (II) and Fe (I) in KFCT

KFCT single crystal doped with Co III did not show any EPR as expected, since low-spin Co III is diamagnetic. However, after γ irradiation a fairly intense octet was detected at room temperature, and its angular variation, studied in the crystallographic (010) plane and two other planes mutually perpendicular to (010), has shown that Co II complexes have axial symmetry with Z axis along the crystallographic ⟨010⟩ axis. The cyano complex of Co II has low-spin configuration $t_{2g}^6\, e_g^1$ and gives one EPR absorption line which further is split into eight lines due to hyperfine interaction with the nucleus having $I = \frac{7}{2}$ resulting in the observed octet. The spectrum can be described by the usual spin Hamiltonian appropriate for the axial symmetry:

$$\mathcal{H} = \beta\, [g_\parallel H_z S_z + g_\perp (H_x S_x + H_y S_y)] + A I_z S_z + B\, (I_x S_x + I_y S_y)\ . \qquad (1)$$

The spin-Hamiltonian constants obtained are $g_\parallel = 2.020 \pm 0.005$, $g_\perp = 2.251 \pm 0.005$, $A = (80.0 \pm 2) \times 10^{-4}\ \text{cm}^{-1}$, and $B = (27.0 \pm 2) \times 10^{-4}\ \text{cm}^{-1}$. Here, it is assumed, on considerations of size and charge, that $[Co(CN)_6]^{3-}$ enters KFCT substitutionally at $[Fe(CN)_6]^{4-}$. However, as the dopant $K_3Co(CN)_6$ and the host KFCT are not isostructural and due to the charge difference, the accommodation of the impurity in the host lattice may not be simple substitution and it is probably associated with a charge-compensating defect such as an anion vacancy. The association of such a defect, however, was not reflected in the EPR spectrum. Co III substitutionally at the Fe II site is a good electron trap and one expects the formation of $[\text{Co II}(CN)_6]^{4-}$ on γ irradiation. The spin-Hamiltonian parameters obtained in the present case compare quite favorably ($g_\perp$ in the present case is slightly higher) with those reported by Lin, McDowell, and Ward[11] for a Co II complex which could be either an axially elongated $[\text{Co II}(CN)_6]^{4-}$ or an axial $[\text{Co II}(CN)_5]^{3-}$. In a recent study on $K_3Co(^{13}CN)_6$, Booth and Lin[12] have shown that the complex is indeed $[\text{Co II}(CN)_5]^{3-}$ rather than $[\text{Co II}(CN)_6]^{4-}$. The present axial spectrum with a preferential distortion in the ⟨010⟩ direction is probably due to the removal of a $(CN)^-$ ion, following the formation of Co II, which seems to take place preferentially in a direction perpendicular to the layer structure of KFCT as the bonding is weakest in that direction. For the magnetic field parallel to the Z axis, apart from the strong parallel spectrum, a weak perpendicular spectrum appeared. It is most probably due to 90° stacking in the layer structure of KFCT. Similarly, a weak parallel spectrum appeared when the magnetic field was in the XY plane. The EPR spectrum obtained with the magnetic field in the XY plane is shown in Fig. 1. An extra intense line other that the octet of Co II was observed, as shown in Fig. 1, and its angular variation followed closely that of the Co II spectrum, and the g tensors of both centers have the same principal axis system. Its g values are $g_\parallel = 2.003 \pm 0.005$ and $g_\perp = 2.113 \pm 0.005$. The type of g anisotropy of this line and its faithful following of the Co II spectrum strongly suggests that it is probably due to the isoelectronic ($3d^7$) Fe I species. Furthermore, this remarkable similarity in the EPR of Fe and Co species supports the assumption of a substitutional position for the cobalt complex in KFCT. The g values of the Fe I complex further suggest[13] that it is most probably a hexacyano complex in contrast to the possible pentacyano complex of Co II. The Fe I species could not be observed in pure KFCT after γ irradiation. This suggests that the presence of Co III is probably necessary to stabilize the Fe I species. Fe I was found to decay in about a year's time in contrast to the stable Co II. This is shown in Fig. 1.

B. Temperature variation and study of the phase transition

KFCT is known to crystallize in two types of modifications, one monoclinic and the other tetragonal. However, because of the pseudotetragonality of the former structure and also of the layer structure of both of them, samples of single crystals grown from solution show complicated varieties due to twinning and oriented overgrowth. This problem has been solved by subjecting the sample

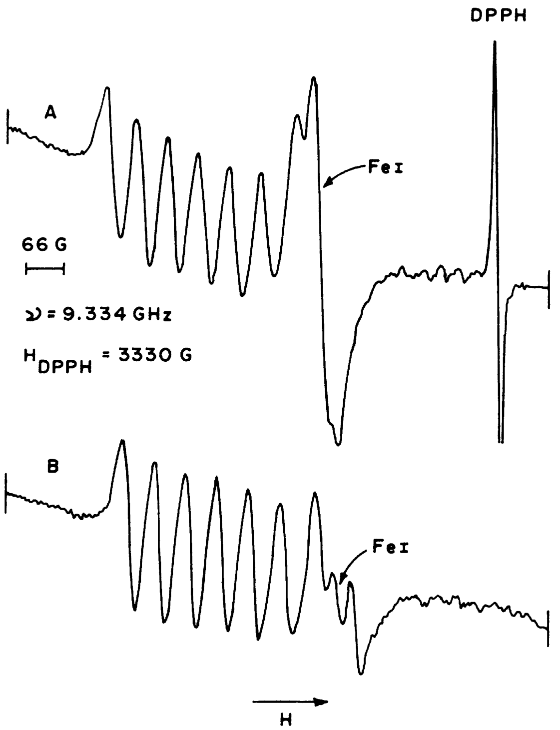

FIG. 1. The EPR spectrum of Fe I and KFCT : Co II with magnetic field along the X axis. (A) Spectrum recorded about 1 h after γ irradiation. (B) Spectrum recorded after about 1 y after γ irradiation. The near absence of Fe I can be seen in case B. The weak lines around $g = 2$ are parallel components due to 90° stacking.

to a thermal cycle of cooling it below $-60\,^\circ$C and warming it up to room temperature, before conducting the variable temperature work, to convert all the layers into monoclinic phase.[14]

The temperature dependence of the spectra of Co II and Fe I has been studied by keeping the Z axis and the X axis parallel to the direction of the magnetic field. The spectra have been recorded at very close temperature intervals around T_c, and at relatively larger temperature intervals down to $-170\,^\circ$C. The spectrometer was operated at fairly low microwave power levels to avoid microwave heating of the sample. No visible changes in the spectrum were observed both for Co II and Fe I as the sample was cooled through T_c, and the g and A values remained essentially constant in this temperature range. However, the intensity of the spectra increased considerably with the lowering of temperature. From about $-40\,^\circ$C, the spectrum of Co II started showing a rather interesting behavior. The linewidths of the octet ceased to be equal and there was a pronounced m_I dependence of the type $a + b\, m_I + \mathrm{c} m_I^2$, where a, b, and c are constants. X-ray-diffraction work of Kiriyama *et al.*[2] has shown that there are two inequivalent kinds of oxygen atoms in KFCT above T_d, the 4(e) type located at (0, 0.47, 0.75) and the 8(f) type at (0.25, 0.50, 0).[19] There are two inequivalent water molecules in 4(e) sites and another two in 8(f) sites. At temperature above T_c, 4(e) and 8(f) molecules interchange orientations within a set. Thus two crystallographically inequivalent sites at temperatures below T_c are expected which become equivalent above T_c. Therefore, one would expect the EPR spectrum to split around T_c, showing the onset of inequivalence brought on by the phase change, apart from any other effects due to polarizing electric fields. The absence of splitting of lines both for Co II and Fe I just below T_c implies that the equivalence of Fe II sites has not been destroyed with ferroelectric ordering. This means that the 4(e) and 8(f) molecules continue to interchange their position in the ferroelectric phase at a rate at which it creates a dynamic situation such that the splittings cannot be resolved, and this indeed is responsible for the observed m_I dependence of the linewidths. It is well known that such a m_I dependence of linewidths in a hyperfine set is expected whenever the anisotropies in g and A tensors are averaged out owing to random fluctuations at the site of the magnetic ion with a correlation frequency shorter than the difference in hyperfine constants (in frequency units) that is getting averaged out. The random fluctuations in the present case presumably come from the rapid intercharge of water molecules in 4(e) and 8(f) positions. This water-molecule motion seems to continue down to $-140\,^\circ$C, the temperature at which the high-field lines started to split. The spectrum recorded with $\vec{H} \parallel \vec{Z}$ at $-100\,^\circ$C is shown in Fig. 2 along with the spectrum in the paraelectric phase around $-20\,^\circ$C. The m_I dependence of the linewidths can be clearly seen in the spectrum at $-100\,^\circ$C. The higher field lines are slightly asymmetric, probably owing to incomplete averaging. The constants a, b, and c are calculated from the spectrum at $-100\,^\circ$C. These constants are functions of the correlation time τ_c and the g and A tensors of the static spectrum. The order of magnitude of the correlation time at $-100\,^\circ$C has been estimated using the hyperfine constants of spectra below $-140\,^\circ$C, and this is given in Table I together with the values of a, b, and c and other linewidth data.

The evidence of fast water-molecule motion below T_c, down to $-140\,^\circ$C, is consistent with NMR results of Kiriyama *et al.*[2] and also with the inelastic-neutron-scattering results of Rush *et al.*[9] This suggests that the phase transition is probably not associated with any anomaly in the motion of water molecules and, furthermore, the crystallographic equivalence of Fe sites in the ferroelectric phase is preserved down to $-140\,^\circ$C.

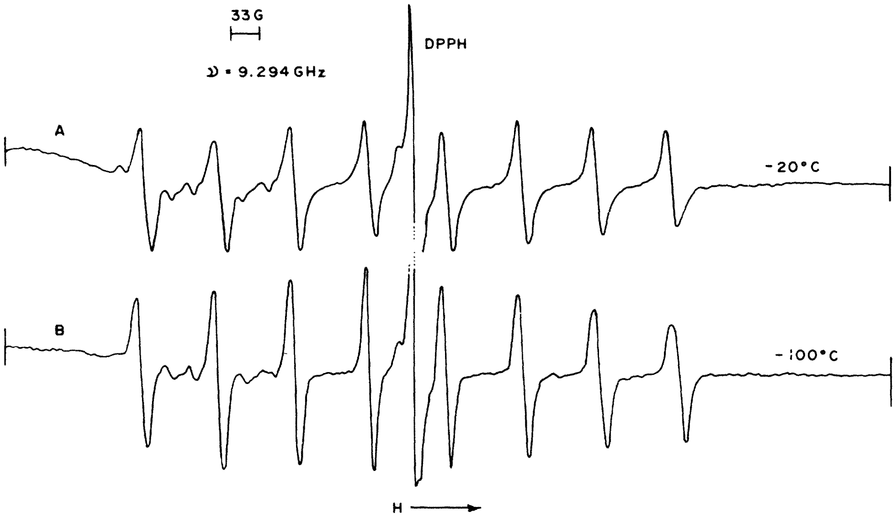

FIG. 2. EPR spectrum of KFCT : Co II with magnetic field along the Z axis. (A) Spectrum recorded just above T_c in paraelectric phase (−20 °C). (B) Spectrum recorded well below T_c in the ferroelectric phase (−100 °C). Well-defined m_I dependence of the linewidths can be seen in the latter case B.

C. Conclusions and general comments

The temperature dependence of the EPR spectra of Co II and Fe I has been found to be similar; more interesting features, however, have been reflected in the Co II spectrum owing to the presence of hyperfine structure. The important conclusions that can be drawn from the present study are the following: (i) The principal-axis system of the EFG tensor probably does not rotate in the vicinity of T_c. (ii) Direct EPR evidence of water-molecule motion down to −140 °C is observed which makes all the Fe sites equivalent down to temperature. A comparison of the present results with those of previous measurements, EPR and ME, has to be qualified, as those measurements were either on pure KFCT or on KFCT doped with isostructural compounds. In this case a simple substitution of the impurity ion is assured in contrast to an "assumption" to that effect in the present case. The evidence of water-molecule motion down to −140 °C as obtained in the present study, is consistent with the neutron-diffraction results. This suggests that water molecules probably do not play a very significant role in the mechanism of ferroelectric ordering in KFCT. Furthermore, the present observation that the principal axis system of the EFG tensor is unaffected in close vicinity of T_c does not "support" the model suggested by Montano *et al.*[8] to explain the ME results. Therefore, the actual mechanisms that are operative during the ferroelectric transition still seem to be far from clear. The ME studies reported so far lead only to one definite conclusion—that the Fe sublattice does not take part in the soft mode, as seen by the absence of any anomalies in the temperature dependence of the recoilless fraction f ($f = \exp[-\langle(\vec{k}\vec{X})\rangle^2]$, $\vec{k}$ is the wave vector of the Mössbauer γ ray) with the powder absorbers.[15] The interest in the ME results essentially revolves around the observed[5,8] maximum in the recoilless fraction in the vicinity of T_c, with single-crystal absorbers, in contrast to the theoretically expected minimum as observed in other ferroelectrics. Recent experiments of Champeney and Woodhams,[16] and Champeney and Sedgwick[17,18] on the Mössbauer scattering by systems containing no Mössbauer nuclei bring out a very important point which probably will explain the reported ME results in KFCT. Consider KFCT as a system having interpenetrating Bravais lattices in which the Fe sublattice does not take part in any mode of vibration of consequence to the ferroelectricity around T_c. The Mössbauer γ ray undergoes, apart from the resonant absorption by ^{57}Fe nuclei, scattering by the rest of the lattice, particularly by those atoms taking part in the soft mode, whose cross section becomes temperature dependent through the tem-

TABLE I. Linewidth data of the EPR spectrum of KFCT : Co at −100 °C.

Constants obtained	m_I	Calculated linewidths (G)	Experimentally observed linewidths
$a = 7.90$ G $b = 0.21$ G $c = 0.34$ G $\tau_0 \sim 2\times10^{-7}$ sec	$-\frac{7}{2}$	11.2	11.3
	$-\frac{5}{2}$	9.5	9.6
	$-\frac{3}{2}$	8.3	8.4
	$-\frac{1}{2}$	7.8	6.8
	$+\frac{1}{2}$	8.1	9.0
	$+\frac{3}{2}$	9.0	9.0
	$+\frac{5}{2}$	10.5	10.0
	$+\frac{7}{2}$	12.7	12.8

perature dependence of $\langle x^2 \rangle$ and should show a minimum around T_c. This would manifest itself as an increased absorption by ^{57}Fe consistent with what has been experimentally observed. This effect is expected to be most pronounced for γ rays parallel to the direction of maximum $\langle x^2 \rangle$, i.e., the polar axis, and in powders, therefore, it is expected to be small. This model can be put to experimental test by conducting Mössbauer scattering experiments similar to those of Champeney and co-workers,[16–18] using $K_4Ru(CN)_6 \cdot 3H_2O$ single crystals, as they exhibit the same behavior as KFCT.

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[19] e and f refer to the symmetry positions of molecules in a crystal of the space group $C2/c$ as defined in *International Tables for X-ray Crystallography* (Kynoch, Birmingham, 1952), Vol. I.