1, 321 (1958).
[41] G. A. Prinz (private communication).
[42] M. F. Sykes, J. L. Martin, and D. L. Hunter, Proc. Phys. Soc. (London) 91, 671 (1967).
[43] P. M. Levy and D. P. Landau, J. Appl. Phys. 39, 1128 (1968).

PHYSICAL REVIEW B VOLUME 3, NUMBER 3 1 FEBRUARY 1971

Mössbauer Study of the Ferroelectric Phase Transition in Potassium Ferrocyanide Trihydrate

P. A. Montano and H. Shechter
Physics, Technion-Israel Institute of Technology, Haifa, Israel
and
U. Shimony
Electrical Engineering, Technion-Israel Institute of Technology, Haifa, Israel

(Received 19 May 1970)

An increase in the area of the Mössbauer spectrum at the ferroelectric transition point has been observed in single crystals of potassium ferrocyanide trihydrate (KFCT), for spectra with the γ beam in a direction near the ferroelectric [10$\bar{1}$] axis. Also an anomalous change in the center shift appears at the transition point. This behavior is related to polarization effects, due to the presence of small quadrupole splitting in KFCT and to changes in the orientation of the electric field gradient caused by the onset of ferroelectricity.

I. INTRODUCTION

Recently, contradictory results have been reported on the behavior of the Mössbauer recoiless fraction in $K_4Fe(CN)_6\cdot 3H_2O$ (KFCT), near the ferroelectric transition. Hazony *et al.*[1] measured the Mössbauer spectral area on single crystals of KFCT and found an anomalous increase related to the f factor near T_c, when the observation direction was close to the ferroelectric axis. Gleason and Walker[2] and Clauser[3] do not observe any changes in the spectral area of powder samples at the transition temperature. We measured the Mössbauer spectral area of KFCT single crystals in a direction close to [10$\bar{1}$] (ferroelectric axis) and [010] directions and results similar to those of Hazony *et al.* were obtained; the anomalies are related to polarization effects that may average in powders.

The KFCT crystallizes from a water solution.[4] The water molecules are located in layers perpendicular to the [010] axis. Between each layer of water there are two layers of $Fe(CN)_6^{-4}$ groups and interspersed potassium ions, with the iron nuclei located at the center of a regular octahedra formed by cyanide ions.[5,6] The basic structure is either tetragonal, which is metastable at room temperature (rt) or monoclinic, which is pseudotetragonal ($\beta = 90 \pm 3$) and stable at rt. Under practical conditions of crystal growth, complex lamellar twin crystals and polytypic structures often appear, in which monoclinic and tetragonal layers alternate in a microscopic scale.[6,7] The tetragonal modification of KFCT is changed irreversibly into the ferroelectric monoclinic at 218 °K. The monoclinic structure of KFCT shows a spontaneous polarization below 248 °K in the [10$\bar{1}$] direction.[8,9] The phase transition at 248 °K is accompanied by a change in the crystal symmetry, $C_{2/c}$ to C_c. Anomalies have been observed in the sound velocity in KFCT in the [10$\bar{1}$] and [101] directions at the transition point.[10] Recently, the ferroelectric transition in KFCT has been investigated under hydrostatic pressure[11] suggesting that the KFCT is a hard ferroelectric with a second-order transition.

It has been suggested that ferroelectricity in KFCT is of the water molecule order-disorder type.[12] A simple order-disorder model of O'Reilly and Schacher[13] explains qualitatively the behavior of the spontaneous polarization in KFCT. However, contribution to the spontaneous polarization and internal field due to displacement and, polarizability of the K^+ and $Fe(CN)_6^{-4}$ have to be considered as well, since there is experimental evidence that the movement of the water molecules shows no anomalies at the ferroelectric transition.[14,15]

II. EXPERIMENTAL PROCEDURE

The samples were selected from grown single crystals of $K_4Fe(CN)_6\cdot 3H_2O$. These yielded a Laue pattern with a twofold symmetry, when observed perpendicular to the [010] plane. The polarization axis was identified through capacity measurements. The crystal was found to have a polytypic structure of a monoclinic crystal with microscopic layers of tetragonal stacks[6,7] and dielectric transitions at 248.5 and 230 °K. These transition points were

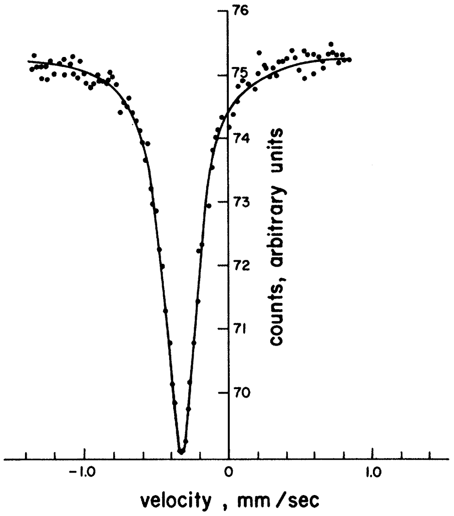

FIG. 1. KFCT Mössbauer line at 244 °K.

measured for the selected Mössbauer sample by conventional dielectric measurements.

The crystal, of thickness $t = 2.7$, was sealed in a Mylar sample holder to prevent dehydration in the evacuated surrounding.

A Pd : Co^{57} (10-mCi) source was used throughout the experiments. The f factor of this source is 0.66; 10^5 counts per velocity channel yielded sufficient statistical accuracy.

Mössbauer spectra were recorded for the [010] direction parallel to the γ beam at various temperatures. It was found difficult to prepare a single crystal with the $[10\bar{1}]$ parallel to the direction of the beam, due to the presence of the cleavage plane. The measurements were therefore taken at an angle of 40° between the γ direction and $[10\bar{1}]$.

The sample was cooled below 218 °K to convert it into monoclinic and then gradually heated between runs, thus avoiding problems of thermal hysteresis. The temperature at each run was kept stabilized within 0.5 °K.

A typical KFCT line is shown in Fig. 1. The background intensity has received special attention since the accuracy of the line area is dependent on it. The spectra were recorded and analyzed by a nonlinear least-square program.

For center shift measurements a reference absorber of sodium nitroprusside, $\mathrm{Na_2Fe(CN)_5NO \cdot 2H_2O}$, was mounted on the cryostat window. This precaution allowed the elimination of any electronic drift.

III. RESULTS AND DISCUSSION

The area of the absorption spectrum versus temperature for γ direction parallel to [010] is shown in Fig. 2. No anomalous changes are apparent at T_c within the experimental error. In Fig. 3 the area of the absorption spectrum versus temperature is plotted for the γ ray along $[10\bar{1}]^{40}$ direction ($[10\bar{1}]^{40}$ direction means that the γ ray is at 40° to the $[10\bar{1}]$ axis). Here, two anomalous changes appear at the ferroelectric transition temperature, one at T_c, and one at a lower temperature due to the polytypic structure of the sample. The shift of the line centroid versus temperature is plotted in Fig. 4; when the γ ray is along $[10\bar{1}]^{40}$ direction, one anomaly appears at T_c and one below the transition temperature. No such "anomaly" is apparent in the [010] direction.

In a recent study on KFCT single crystals,[16] we have found that the single line shows actually a slight quadrupole broadening. By applying an external magnetic field the quadrupole splitting becomes more apparent. If the unresolved component lines are not symmetric, changes in the direction of the electric field gradient (EFG) at the ferroelectric transition cause a shift of the centroid and an anomaly in its temperature dependence. At a finite absorber thickness, polarization effects[17] are followed by changes in the spectral area (the f factor does not necessarily change). Particularly, in the $[10\bar{1}]^{40}$ direction, where the effective thickness was

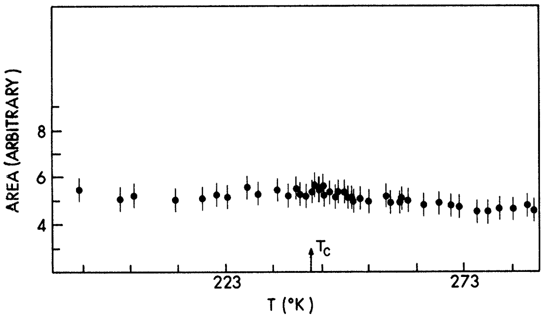

FIG. 2. Experimental area of KFCT versus temperature in the [010] direction.

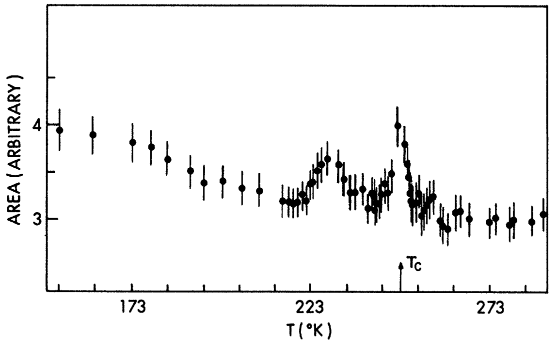

FIG. 3. Experimental area of KFCT versus temperature in the $[10\bar{1}]^{40}$ direction.

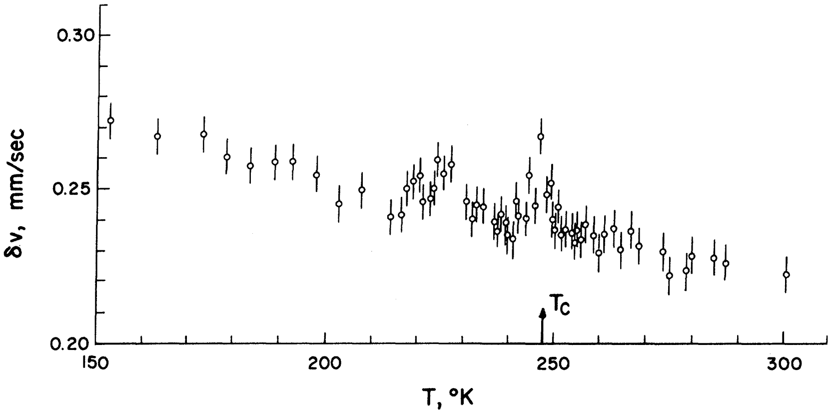

FIG. 4. Center shift of KFCT line at various temperatures, relative to $Na_2Fe(CN)_5NO \cdot 2H_2O$. γ direction near the [10$\bar{1}$] ferroelectric axis.

about 4, such effects are expected.

The rt EFG is attributed to slight displacement of the K^+ ion from cubic symmetry around the $Fe(CN)_6^{-4}$ complex. In the ferroelectric phase the water molecules contribute to the EFG at the iron site by their electric dipole moments. This contribution was calculated using the atomic positions of the water molecules given by Poperov and Zdanov[5] for the monoclinic paraelectric phase and assuming that all water molecules are aligned in the [10$\bar{1}$] direction. (This is far from correct but it gives an order of magnitude for the EFG.) This calculation yielded a maximum quadrupolar broadening of 0.12 of the natural linewidth. This simplified model predicts an axial symmetry for the EFG. From the direction of the apparent center shift relative to zero it can be concluded that the EFG is positive, $V_{zz} > 0$. The Sternheimer factor which was not considered here could increase the quadrupole splitting, and the incomplete alignment of the water dipoles at $T > 0$ may reduce it.

It has been shown that the contribution of the water molecules to the ferroelectricity is noticed at temperatures lower than T_c.[14] Also it is conceivable that small displacements of the K^+ at the transition temperature may contribute to the quadrupole interaction. The net result of the ferroelectric ordering is then a change in the quadrupole splitting, as well as reorientation of the EFG principal axis. Since this is a second-order transition, the reorientation of the EFG may be gradual through the transition range of a few degrees Kelvin. It will be shown that, during the process of reorientation, an increase of the spectral area is expected. At rt a careful study of the variation of the line position with rotation of the crystal shows that the principal axes of the EFG are set so that one axis is parallel to the b-crystallographic axis, and the other two lie on the ac plane. This is also expected from the symmetry of the crystal at rt. Apparently, the z axis lies on the ac plane: the line "shift" is caused by the dependence of the two quadrupole components on the angle between the γ direction and the z axis of the EFG tensor.[16] Since the lines are unresolved, it is impossible to extend this statement further.

Bykov and Xien[18] show that the spectral area, when a quadrupole splitting is involved but polarization is not considered, is given by

$$A = \pi\alpha f\left[K(t_1) + K(t_2) - K(t_1)K(t_2)\left(\frac{K(t_1)\,K(t_2)}{K(t_1) + K(t_2) - K(t_1+t_2)} + \frac{\Delta^2\,[K(t_1) + K(t_2) - K(t_1+t_2)]}{K(t_1)\,K(t_2)}\right)^{-1}\right] , \tag{1}$$

where $K(t) = te^{-t/2}[I_0(t/2) + I_1(t/2)]$ and $I_0(t/2)$ and $I_1(t/2)$ are the zero- and first-order Bessel functions of imaginary argument, respectively. Δ is the quadrupole splitting in units of $\Gamma/2$, t is the effective thickness, $\sigma_0 fn$, of the absorber, α is the relative fraction of resonant γ's in the emission spectrum, f is the source factor.

If the splitting is very small, in the limit $\Delta \to 0$, the area is given as

$$A = \pi\alpha f K(t_1 + t_2), \tag{2}$$

the t_1 and t_2 are the effective thicknesses of the individual transitions.

For a polarized absorber, the area saturates with the effective thickness in a different way. Housley *et al.*[17] have calculated the behavior of the area with polarization for relatively thin absorbers and unpolarized sources, when the quadrupole

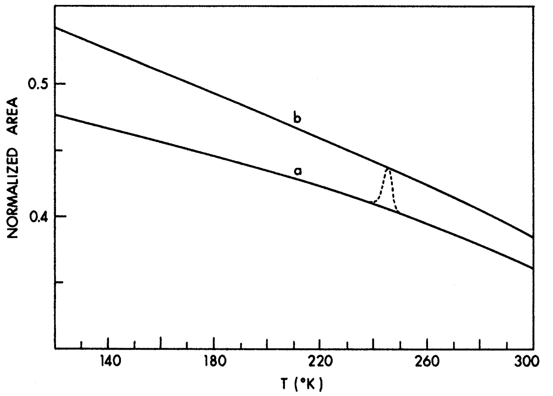

FIG. 5. Normalized area versus temperature calculated from formula (5). (a) for $\vec{k} \parallel x$ principal axis, (b) for $\vec{k} \parallel z$ principal axis.

doublet is well resolved. If there is overlapping of the lines the calculation of Housley *et al.*[17] can be generalized. The effective thickness can be represented by a matrix,[17]

$$\sigma=\sum_{ij}\begin{pmatrix}\rho_{11}^{ij} & \rho_{12}^{ij}\\ \rho_{21}^{ij} & \rho_{22}^{ij}\end{pmatrix}\frac{\sigma_0 n_j f_j}{(2E/\Gamma-2E_{ij}/\Gamma)^2+1}\ . \tag{3}$$

The site is labeled by j and the component by i, the ρ^{ij} are defined in Ref. 17.

If we assume that there is only one resonant site per unit all, then the (complex) index of refraction may be diagonalized for any direction of the γ ray. For an unpolarized source

$$A=\pi\alpha f\{K[\sigma_{11}(t_1)+\sigma_{11}(t_2)]+K[\sigma_{22}(t_1)+\sigma_{22}(t_2)]\}\ , \tag{4}$$

For a relatively thin absorber, with $a=(\sigma_{11}-\sigma_{22})/(\sigma_{11}+\sigma_{22})$ and $p=\frac{1}{2}(\sigma_{11}+\sigma_{22})$:

$$\begin{aligned}A=2\pi\alpha f\{&p(1)+p(2)-\tfrac{1}{4}[1+a^2(1)]p(1)^2\\ &-\tfrac{1}{4}[1+a^2(2)]p^2(2)\\ &-[a(1)a(2)+1]p(1)p(2)+\cdots\}.\end{aligned} \tag{5}$$

The difference between the relation for well-resolved and overlapping lines is the presence of a mixing term.

If the behavior of the f factor is considered, the polarization dependence of the experimental area as well as the anisotropy of the f factor have to be considered. It seems that at rt there is not too much difference in the f factor measured along [010] and $[10\bar{1}]$.

In order to estimate qualitatively the behavior of the area, we assume for simplicity $\eta=0$, and that there is only one resonant site per unit cell. The normalized area versus temperature was calculated from (5) for the γ $\vec{k}$ vector parallel to the x principal axis [Fig. 5(a)], and for $\vec{k}$ parallel to the z axis [Fig. 5(b)].

Due to the establishment of the electric ordering at a certain temperature, the principal axes of the EFG change orientation. During this process, the direction of the z principal axis passes through the direction parallel to k and an increase in the spectral area is expected (Fig. 5). Associated with this anomaly, a change in the intensity ratio of the "doublet" will cause an apparent "line shift." If the EFG axis rotates by 180°, the net result will be an increase and a reduction of the area, accompanied by a similar behavior of the line shift. This is an oversimplified model, but it reproduces qualitatively the experimental results in KFCT single crystals in the $[10\bar{1}]$ direction.

The behavior of the spectral area in the [010] direction suggests that the EFG principal axes rotate in the *ac* plane without causing changes in the fractional polarization in this direction. The experimental linewidth in the [010] direction changes at T_c from 0.27 ± 0.01 mm/sec to 0.29 ± 0.01 mm/sec below T_c. In the $[10\bar{1}]$[40] direction the linewidth is 0.37 ± 0.01 mm/sec at T_c and 0.34 ± 0.01 mm/sec above T_c. This change is associated with the onset of ferroelectricity.

The two transitions (Fig. 3) are related to the polytypic structure of the sample,[19] and they were considered equivalent for the discussion.

The behavior of the f factor with temperature, for powdered samples where polarization effects can be ignored, is rather interesting. Housley and Hess[20] found that for an harmonic solid, the mean-square displacement versus temperature must lie between two straight lines which intersect at a particular temperature T. One of these lines passes through the origin, the other intercepts $T=0$ at $\langle x_\alpha^2\rangle_0=\frac{1}{2}\hbar(\langle x_\alpha^2\rangle_T/mkT)^{1/2}$. α is the direction of the displacement.

An f factor of 0.45 for powdered KFCT at rt was found, in agreement with Kerler.[21] For this f factor the msd of the Fe^{2+} exceeds any harmonic limit.[20] The behavior of the f factor indicates therefore some low-temperature anharmonicity. It was shown[22,23] that a model based on the relative sizes of the ions in the crystal gives rough information on the dimensions of the effective potential well ("rattle space"). In the particular case discussed here, ionic sizes and crystal dimensions exclude possible rattle space for an ion iron. However, the entire $Fe(CN)_6^{-4}$ complex is allowed a rattle space of some 1.4 Å in the direction of polarization, $[10\bar{1}]$. This space is mainly restricted by the potassium ions. The rattle space calculated from the simple model of ionic sizes is larger in the [010] direction (perpendicular to the cleavage plane) than it is in the $[10\bar{1}]$ direction. These large rattle spaces predict a low f factor, in agreement with the powdered KFCT measurements.

[1] Y. Hazony, D. E. Earls, and I. Lefkowitz, Phys. Rev. 166, N2, 507 (1968).

[2] T. J. Gleason and J. C. Walker, Phys. Rev. 188, 893 (1969).

[3] M. J. Clauser, Phys. Rev. B 1, 357 (1970).

[4] L. N. Matusevich and K. N. Schabalin, Zh. Prikl. Khim., 25, 1157 (1952).

[5] V. A. Poperov and G. S. Zdanov, Z. Fiz. Khiar. SSSR, 21, 405 (1947); 21, 521 (1947); 21, 879 (1947); Structure Report XI, pp. 421–424 (unpublished).

[6] H. Toyoda, N. Niizeki, and S. Waku, J. Phys. Soc. Japan 15, 10 (1960).

[7] A. Ya. Krasnikova, V. A. Koptsik, B. A. Strukov, and Wang Wing, Fiz. Tverd. Tela, 9, 116 (1967) [Soviet Phys. Solid State 9, 85 (1967)].

[8] S. Waku, H. Hirabayashi, H. Toyoda, H. Iwasaki, and R. Kiriyama, J. Phys. Soc. Japan 14, 973 (1959).

[9] S. Waku, K. Masuno, T. Tanaka, and H. Iwasaki, J. Phys. Soc. Japan 15, 1185 (1960).

[10] G. E. Schacher, J. Chem. Phys. 46, 3565 (1967).

[11] A. Ya. Krasnikova and I. N. Polandov, Fiz. Tverd. Tela, 11, 1753 (1969) [Soviet Phys. Solid State 11, 1421 (1970)].

[12] R. Blinc, M. Brenman, and J. S. Waugh, J. Chem. Phys. 35, (1961).

[13] D. E. O'Reilly and G. E. Schacher, J. Chem. Phys. 43, 4222 (1965).

[14] R. Kiriyama, H. Kiriyama, T. Wada, N. Niizeki, and H. Hirabayashi, J. Phys. Soc. Japan 19, 4 (1964).

[15] J. J. Rush, P. S. Leung, and T. I. Taylor, J. Chem. Phys. 45, (1966).

[16] P. A. Montano, H. Shechter, A. Biran, and U. Shimony (unpublished).

[17] R. M. Housley, R. W. Grant and U. Gonser, Phys. Rev. 178, 514 (1969).

[18] G. A. Bykov and Pham Zuy Xien, Joint Institute for Nuclear Research Report No. P-1231, 1962 (unpublished) [transl.: *Working Conference on the Mössbauer Effect, Proceedings of the Dubna Conference*, 1962 (New York Consultants Bureau Enterprises, Inc. New York, 1963)].

[19] A. Ya. Krasnikova and V. A. Koptsir, Fiz. Tverd. Tela, 10, 905 (1968) [Soviet Phys. Solid State 10, 709 (1968)].

[20] R. M. Housley and F. Hess, Phys. Rev. 146, 517 (1966).

[21] W. Kerler, Z. Physik 167, 194 (1962).

[22] J. G. Dash, D. P. Johnson, and W. M. Visscher, Phys. Rev. 168, 1087 (1968).

[23] D. P. Johnson and J. G. Dash, Phys. Rev. 172, 983 (1968).

PHYSICAL REVIEW B VOLUME 3, NUMBER 3 1 FEBRUARY 1971

Contribution of Some 4*d* and 5*d* Transition-Metal Ions on Octahedral Sites to the Anisotropy of Ferrites and Garnets*

P. Hansen

Philips Forschungslaboratorium Hamburg GmbH, 2000 *Hamburg* 54, *Germany*

(Received 8 September 1970)

The contribution to the magnetocrystalline anisotropy of transition-metal ions in ferrites on octahedral sites is calculated for the strong crystalline-field case for d^1, d^2, d^4, and d^5 configurations. The single-ion model is used which requires small concentrations of such ions. Good agreement with experiment was found for trivalent ruthenium. For this case, anisotropy measurements of Ru^{3+} ($4d^5$)-doped yttrium-iron garnet of the composition $Y_{3-y}Ca_yFe_{5-x}Ru_xO_{12}$ were carried out in the temperature range of 4.2–500 °K. By fitting the theory to the measured anisotropy data, one finds for the product of the g factor times the exchange field, $gH_e = 1.1\times10^7$ Oe and the ratio of the trigonal field to the spin-orbit energy $v/\xi = -1$.

I. INTRODUCTION

The anisotropy of ferrites can be considerably influenced by very low concentrations of transition-metal ions[1-6] and rare-earth ions.[7,8] In these cases, the spin-orbit coupling is an important parameter, since it measures the coupling energy of the spin in a certain direction. Thus, such ions contribute to the free energy due to the directional dependence of the magnetization. For the metal ions of the second- and third-transition series, the spin-orbit coupling is much higher than for the first transition-metal ions, so that especially for these elements a large contribution to the anisotropy may be expected. Since only very little experimental or theoretical work is available in this field, the influence on the anisotropy will be calculated here for some of these ions with an md^n configuration for $n = 1,\ 2,\ 4,\ 5$.

The phenomenological energy expression for the magnetocrystalline anisotropy F is given in the case of cubic symmetry by

$$F = K_0 + K_1 s + K_2 p + K_3 s^2 + \cdots , \qquad (1)$$

where

$$s = \alpha_1^2\alpha_2^2 + \alpha_2^2\alpha_3^2 + \alpha_1^2\alpha_3^2, \quad p = \alpha_1^2\alpha_2^2\alpha_3^2 .$$

The α_i are the direction cosines of the magnetization with respect to the cubic axes. The contribu-