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Mössbauer Test for a Lattice-Dynamical Model for the Ferroelectric Phase Transition in Potassium Ferrocyanide*

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A lattice-dynamical model is proposed for the ferroelectricity in potassium ferrocyanide, in contrast to the previously accepted order-disorder model. This proposed model associates the dielectric anomaly with a mode instability where $\omega_{\mathrm{TO}}\to 0$ at $q\to 0$ in the $[10\bar{1}]$ crystallographic direction. Measurements of the Mössbauer fraction as well as the dielectric constant were carried out simultaneously on a single crystal, as a function of temperature, to provide identification of the phase transition and as a test for the dynamics of the iron framework through the transition. The results show large changes in the Mössbauer fraction in the vicinity of the transition temperature perpendicular to the [010] direction only. This is compatible with our lattice-dynamical treatment. This model is further supported by a structural discussion, analysis of acoustic data, and the shifts of the transition temperature on deuteration and atomic substitution. The Mössbauer and substitutional data presented are incompatible with the order-disorder theory.

INTRODUCTION

FERROELECTRIC transitions have been broadly classified into two categories[1]: (i) An order-disorder transition of a system of permanent dipoles; (ii) a solid system in which the polarization is produced by a displacive modification of the lattice.

Order-disorder models have been proposed for the ferroelectric transition in $K_4Fe(CN)_6\cdot 3H_2O$ (KFCT).[2–6] Extensive efforts failed to provide direct experimental evidence for these models.[7] In the second category the transition is believed to be associated with a mode instability, where the frequency of a low-lying TO mode approaches zero at $q\to 0$ and $T\to T_c$.[8–11] We propose that this is the mechanism for the ferroelectricity in KFCT and that the mode instability occurs due to a particular balance of forces between the three interpenetrating lattices of K^+ ions, $Fe(CN)_6{}^{4-}$ complexes, and water molecules. Mössbauer results are presented that support this model followed by a discussion of other available experimental evidence.

According to the present model, a mode instability should occur in the $[10\bar{1}]$ direction along which the major dielectric anomaly and spontaneous polarization are found.[12–14] Since one of the interpenetrating lattices is Mössbauer active, such an instability might be detected by measuring the temperature dependence of the relative Mössbauer fraction along the $[10\bar{1}]$ direction. The Mössbauer fraction is given by

$$f=\exp(-k^2\langle x^2\rangle)\,, \tag{1}$$

where $\langle x^2\rangle$ is the mean-square displacement of the Mössbauer atom along the direction of the measurement.

The contribution of the high intramolecular vibrations to the temperature dependence of $\langle x^2\rangle$, in the temperature range of interest, is rather small.[15] On the other hand the intermolecular frequencies are rather low and their contributions may be described by their high temperature limit

$$(d/dT)\ln f(\theta_l<T<\theta_h)=-(kE^2/Mc^2)\sum_l (A_l{}^2/\hbar^2\omega_l{}^2)\,, \tag{2}$$

where l and h denote the inter- and intramolecular vibrations, respectively. The normalized weight factors $A_l{}^2$ are directionally dependent and describe the relative contributions of the intermolecular normal

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[7] The order-disorder model was first suggested by Blinc *et al.* (see Ref. 2) on the basis of the temperature dependence of NMR line shapes and on an assumption of no structural variations at T_c. Kiryama *et al.* (see Ref. 3) have shown that these line-shape anomalies do not occur at the transition temperature. However, they assume on the basis of "some experimental evidence of no significant change in the atomic arrangements of the heavier atoms at the Curie point" that this is an order-disorder transition. O'Reilly, Schacher, and Tsang (see Ref. 4–6) propose their model of an order-disorder transition on the basis of the same assumption referring to this statement by Kiryama *et al.* However, no direct experimental verification of this assumption has been reported. Using inelastic neutron scattering, Rush *et al.* failed to find any evidence for changes in the dynamics of the water molecules in the vicinity of the transition temperature [J. J. Rush, P. S. Leung, and T. I. Taylor, J. Chem. Phys. **45**, 1312 (1966)].

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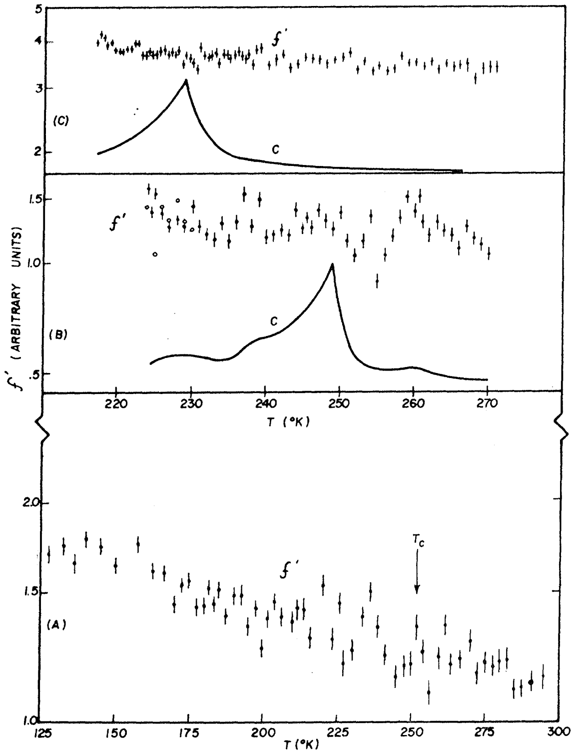

FIG. 1. Mössbauer fraction as a function of temperature. (A) The [010] axis of the KFCT crystal at 45° to the γ-ray beam. (B) Same sample geometry as (A) but using 1°C temperature increments and shown with the simultaneously measured capacitance (arbitrary units). After the run was completed, having taken three days, a new temperature cycle was started to check reproducibility. These extra data points are shown by open circles. (C) The Mössbauer beam was parallel to the [010] crystal axis. One-half deg C temperature increments were used in the transition temperature region. The same f' scale is used for both (B) and (C). The error bars represent ±1 standard deviation.

frequencies to the dynamics of the iron atoms.[15] A lattice-dynamical instability will be associated with the temperature dependence of some ω_l^2 and/or A_l^2 and should result in deviations from a straight line in the $\ln f$ curve.

EXPERIMENTAL

A Mössbauer experiment to test the lattice-dynamical model has been performed using a 50-mCi Co^{57} source diffused in palladium and a thin single crystal of KFCT oriented at 45° to its [010] direction as an absorber. This direction was chosen as an experimental compromise between the solid angle and the [10$\bar{1}$] direction (crystal habit is platy with the [010] axis perpendicular to the plane surface). Silver electrodes were painted on the opposite edges of the crystal and the capacity of the sample was measured and recorded at the same time as the Mössbauer data were accumulated. In order to avoid the loss of water of crystallization due to the vacuum in the cryostat, the sample was hermetically sealed in a lucite sample holder. The experimental apparatus consisted of a modified Elron constant velocity spectrometer, a Janis cryostat, and an automatic temperature controller. Both velocities and temperatures were programmed, automatically changed, and recorded together with the Mössbauer data on IBM cards which were then analyzed by nonlinear least mean square, on an IBM 7094 computer. With an 0.5-mm NaI(Tl) detector and a Hamner NC-20 Spectrum Stabilizer, the baseline stability was of the order of 1% at a counting rate of 10^4 cps within the 14.4-keV channel. A detailed description of the experimental arrangement will be given elsewhere.[16]

RESULTS

The twin habit of KFCT and the existence of a metastable nonferroelectric tetragonal phase may result in clamping of substantial portions of the sample giving rise to multiple transitions as well as large thermal hysteresis,[12,17,18] as demonstrated by the experimental results.

The results shown in Fig. 1(a) were obtained on increasing the temperature of the sample from 78°K ($\Delta T \cong 3$°C) over a period of about 70 h. The relative intensity f' (area of the resonance line) is shown on arbitrary logarithmic scale as a function of temperature. The error bars were determined by the computer curve

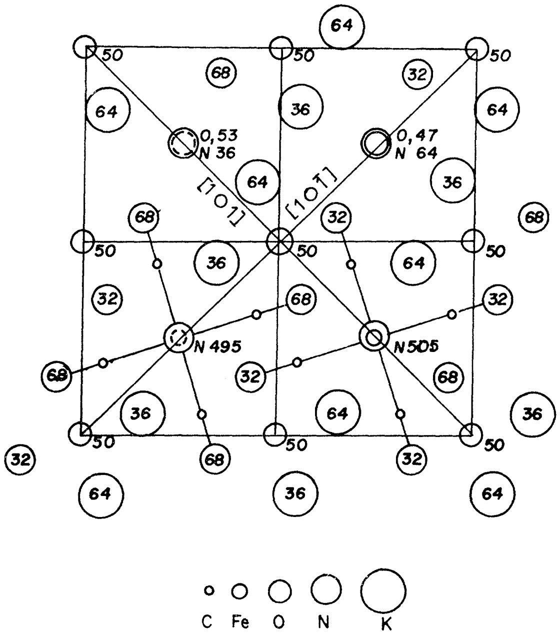

FIG. 2. Projection of the crystal structure of KFCT on the [010] plane. The numbers indicate the y parameters. The numbers indicate the y parameters. The water molecules are represented by the oxygen atoms only. The water (II) molecules are located at the intersections of the solid lines.

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TABLE I. The effect of substitution and deuteration on the transition temperature.

	T_c(°C) (H_2O)	T_c(°C) (D_2O)	ΔT_c(°C) due to substitution of H_2O	Fe	K or Ba
a					
$K_4Fe(CN)_6 \cdot 3H_2O$	−24.5	−18.0	6.5		
$K_4Os(CN)_6 \cdot 3H_2O$	−2.4	+1.8	4.2	22.1	
$K_4Ru(CN)_6 \cdot 3H_2O$	−14.5	−7.3	7.2	10.0	
$K_4Mn(CN)_6 \cdot 3H_2O$	−40.0			15.5	
b					
$(K, Ru_{45}\%)_4Fe(CN)_6 \cdot 3H_2O$	−100				75.5
$(K, Tl_{2.3}\%)_4Fe(CN)_6 \cdot 3H_2O$	−105				80.
$(K, NH_{4\ 21.4}\%)_4Fe(CN)_6 \cdot 3H_2O$	−120				95.5
c					
KH_2PO_4	−150	−60	90		
d					
$BaTiO_3$	120				90
$(Ba, Pb_{20}\%)TiO_3$	210				

[a] See Ref. 12. [b] See Ref. 13. [c] See Ref. 1, p. 389. [d] See Ref. 1, p. 241.

fitting program and correspond to ±1 standard deviation. The temperature at which the maximum of the dielectric constant occurred is indicated at $T_c \sim 252$°K. In the second run a much finer temperature scale ($\Delta T \sim 1$°C) was used. The results are shown in Fig. 1(b) together with the simultaneously measured capacitance of the sample. The two runs show reproducible anomalous variations of the Mossbauer intensity with temperature. The largest f' anomaly shows an increase of about 50% in intensity over a temperature range of 4°K (255–259°K). The maxima in f' are associated with the maxima in the dielectric constant. In contrast, the results of a measurement along the [010] direction are shown in Fig. 1(c). The dielectric anomaly in this run occured at $T_c \sim$ 229°K, and no appreciable change in the lnf' was observed when the sample was in this orientation.

DISCUSSION

It is evident from these results that the $Fe(CN)_6^{4-}$ complex participates in lattice-dynamical instabilities which occur in a direction perpendicular to the [010] direction at about the same temperatures as the dielectric anomalies.

However, the nature of these Mössbauer anomalies is unexpected. At first glance one would expect $\langle x^2 \rangle$, along with [10$\bar{1}$] direction, to approach a maximum when $\omega_{TO} \to 0$. Apparently, $\langle x^2 \rangle$ of the Fe atoms go through a minimum rather than a maximum at the transition temperature. This indicates that on approaching T_c, the balance of forces between the three interpenetrating lattices changes with temperature in such a way that the thermal energy of the TO mode is taken up to a larger extent by the K^+ ions and/or the water molecules at the expense of the $Fe(CN)_6^{4-}$ complexes.

The crystal structure proposed by Kiriyama *et al.*,[3] and recently confirmed by Taylor and Mueller by neutron-diffraction methods,[6,19] is shown in Fig. 2 with the protons omitted. If one visualizes the three interpenetrating lattices independently, no preference exists for the [101] versus the [10$\bar{1}$] direction. It is only when the three lattices are recombined that this difference becomes apparent; this is confirmed by inspection of the local environment of the water molecules. It should be emphasized that the proton positions are not essential to illustrate the differences in the [101] and [10$\bar{1}$] directions. Such a directional anisotropy of forces acting between the three interpenetrating lattices will result in a lattice-dynamical anisotropy which is compatible with the observed dielectric properties of the structure, namely, that the dielectric anomaly and spontaneous polarization occur mainly along the [10$\bar{1}$] direction.

When $\omega_{TO} \to 0$ and $q \to 0$ one might expect interaction between the TO and TA modes which will give rise to an anomaly in the shear component of the elastic properties of the crystal at the ferroelectric transition. In a recent measurement of the sound velocity, Schacher reports anomalies in the temperature dependence of the sound velocity in the [101] and [10$\bar{1}$] directions at the transition temperature. This he associates with anomalous behavior of the elastic constants C_{15} and/or C_{35} which relate the longitudinal stress to the shear strain.[6] This situation is typical of many displacive ferroelectrics,[1] and is further evidence for the existence of a mode instability at the transition temperature.

Further support for this model is obtained from the shifts of T_c caused by deuteration, substitution of the iron atom, and partial substitutions of K atoms (Table

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I). If one assumes the ferroelectric transition in KFCT to be associated with the reorientation of the water molecules, T_c should depend on the rotational inertia of the water molecules, which is linearly dependent on the mass of the protons; therefore, it should be comparable with that of KH_2PO_4 (Table I). In fact it is one order of magnitude smaller. The effect of deuteration on the translational inertia of the water molecules is much smaller and is comparable with the effect of the substitution of the iron atom on the translational inertia of the $Fe(CN)_6{}^{4-}$ complex; the corresponding shifts of T_c are also small and comparable. However, the effects of the partial substitutions of the potassium atoms on T_c are large and comparable with those found in displacive transitions like $BaTiO_3$ and $PbTiO_3$ (Table I).

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Magnetic Properties of $La_{0.5}Sr_{0.5}CoO_3$ near Its Curie Temperature

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Samples of $La_{0.5}Sr_{0.5}CoO_3$ were prepared, and a study was made of their electrical and magnetic properties. Investigation of the initial susceptibility immediately above the Curie point T_c determined that the critical exponent $\gamma=1.27\pm0.02$, where γ is defined by the equation $\chi_0{}^{-1}=A(T-T_c)^\gamma$. In addition, we found that $\delta=3.05\pm0.06$ at $T=T_c$, where the magnetic moment σ and the magnetic field H_i are related by the equation $H_i=A'\sigma^\delta$. The difference between these results and those previously reported for other ferromagnetic materials is discussed. However, despite this difference, the interrelationship of magnetic field, magnetic moment, and temperature is found to obey the magnetic equation of state recently proposed by Kouvel and Rodbell.

INTRODUCTION

SEVERAL studies have recently been made of the magnetic susceptibility in ferromagnetic metals immediately above their Curie points. In this region, the inverse of the initial susceptibility can be represented by the relationship

$$\chi_0{}^{-1}\propto(T-T_c)^\gamma, \qquad (1)$$

and it was found that, within experimental error, $\gamma=\frac{4}{3}$ in nickel,[1] iron[2] and its alloys,[3] and gadolinium.[4]

This value of γ was in accord with the value which had then been calculated on the basis of extrapolation of the first six terms of the high-temperature susceptibility series expansion.[5,6] However, more recent calculations have altered this result. For $S=\frac{1}{2}$, extrapolation from the series extended to 10 terms predicted $\gamma=1.43$.[7] In the classical limit $S\rightarrow\infty$, improved extrapolations of extended series led to a predicted value of 1.36,[8] and to values which vary from 1.38 to 1.42 depending on the structure.[9]

All the theoretical results discussed above are limited to consideration of the simple cubic, fcc, and bcc structures. Furthermore, the theoretical calculations of γ assumed a nearest-neighbor Heisenberg model, and therefore are not, strictly speaking, applicable to ferromagnetic metals. However, the agreement between the earlier calculations[5,6] and the experiments cited seemed to indicate that the $\gamma=\frac{4}{3}$ "rule" had a universality which went beyond the model on which it was based. The one notable experimental exception to this "rule" has been fcc cobalt, for which Colven and Arajs[10] found $\gamma=1.21\pm0.04$.[11]

In this paper we present a study of the magnetic properties of $La_{0.5}Sr_{0.5}CoO_3$, with particular emphasis

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