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Comments and Addenda

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Mössbauer-Effect Study of Ferroelectric Potassium Ferrocyanide Trihydrate†

M. J. Clauser
Sandia Laboratories, Albuquerque, New Mexico 87115

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The recoilless fraction and thermal shift in the Mössbauer spectra of potassium ferrocyanide trihydrate (KFCT) have been studied around the ferroelectric transition temperature. In contrast to the results of Hazony *et al.*, but in agreement with Gleason and Walker, no anomaly was found. Estimates are presented which show that a 2% or smaller change in the recoilless fraction f may reasonably be expected for a soft-phonon-mode model of KFCT. Since the experiments place an upper limit of about 3% on the change in f, the possibility of a soft-phonon mode cannot be ruled out.

INTRODUCTION

Recently, the ferroelectric transition in potassium ferrocyanide trihydrate (KFCT) has been the object of Mössbauer-effect studies in several laboratories. Hazony[1] and co-workers reported an anomaly in the recoilless fraction f at the ferroelectric transition temperature (≈ 252 K). Two aspects of this anomaly were surprising: First and most remarkable, f appeared to have a maximum at the transition temperature instead of the minimum observed in other ferroelectric materials. Second, the size of the anomaly was quite large ($\approx 50\%$ increase).

In an attempt to verify the results of Hazony *et al.*, we measured the temperature dependence of f in the region of the transition temperature. During the course of these measurements, it came to our attention that Gleason and Walker[2] had just completed measurements of f in KFCT. Our results essentially confirm those of Gleason and Walker; if there is any anomaly, it is smaller than about 3%. In contrast to Gleason and Walker, we feel that this result does not rule out the participation of the iron sublattice in a soft-phonon mode near the transition temperature.

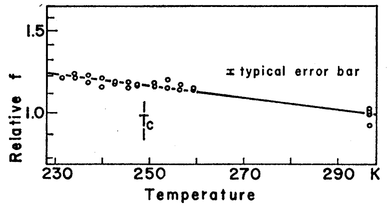

FIG. 1. Relative recoilless fraction observed in potassium ferrocyanide trihydrate as a function of temperature. The data have been arbitrarily normalized to $f=1$ at room temperature.

EXPERIMENTAL ARRANGEMENT

The absorber for this experiment was made from powdered $K_4Fe(CN)_6 \cdot 3H_2O$. The powder was mixed with a small amount of silicone grease and pressed into a disc between two pieces of aluminized Mylar film. The films were used as electrodes for dielectric-constant measurements. The source consisted of 10 mCi of Co^{57} in Pd foil obtained commercially. The drive system is essentially similar to the system described by Kankeleit.[3] The cryostat was of the dipstick variety. A heater and copper-wire thermometer were used in conjunction with an electronic temperature controller in order to maintain the temperature constant to within about 50 mdeg during a run. A copper-constantan thermocouple was used to monitor the actual temperature of the absorber. All the data were computer analyzed with a least-squares fitting program in order to obtain the area of the absorption dip in each run. Taking into account electronic drift of various sorts, the relative error in measuring the recoilless fraction is estimated to be about 1.5%.

RESULTS

The experimental results are shown in Figs. 1 and 2. As can be seen, both the recoilless fraction and the

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† Work supported by the U. S. Atomic Energy Commission.

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

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

[3] E. Kankeleit, Rev. Sci. Instr. **35**, 194 (1964); E. Kankeleit, in *Mössbauer Effect Methodology*, edited by I. J. Gruverman (Plenum Publishing Corp., New York, 1965), Vol. 1, p. 47.

second-order Doppler shift show no evidence of an anomaly. The shape of the absorption dip (i.e., the linewidth) showed no discernible change in the range 230–300 K. The sequence of temperatures started with a run at room temperature 296 K then dropped to 231 K for the first low-temperature run. The temperature was raised in successive steps to 259 K and then lowered back through the same steps. Finally, the temperature was raised again to room temperature. During the sequence of runs, the capacitance of the absorber was measured. No attempt was made to obtain accurate dielectric-constant measurements; however, the behavior of the dielectric constant was observed to agree qualitatively with published dielectric constants for KFCT.

The data in Fig. 1 were fitted with a straight line of the form

$$\ln f = a_0 + a_1 T. \tag{1}$$

The value of a_0 is meaningless since only relative measurements of f were made. The slope of the line a_1 is of some importance, however, because it is a measure of the stiffness of the binding forces acting on the iron ion. Our data yield the value $a_1 = -0.0029\ \mathrm{K}^{-1}$ for the slope. If straight lines are drawn through the data of Hazony *et al.*, the slopes of the lines are about the same as for our data. On the other hand the data of Gleason and Walker have a slope about $\frac{1}{3}$ of ours.

The line shift data in Fig. 2 were fitted with a straight line of the form

$$v_c = v_0 + b(k/mc)T, \tag{2}$$

where k is the Boltzmann constant, m is the mass of the iron atom, and c is the velocity of light. For a classical harmonic model, b should be $\frac{3}{2}$. Our data yield a value of $b = 1.1$, while the data of Gleason and Walker give $b \approx 0.6$. Our value of v_0 gives an isomer shift at room temperature which is in good agreement with commonly accepted values.

DISCUSSION

The recoilless fraction is given approximately by

$$f = \exp[-\langle(\mathbf{k}\cdot\mathbf{r})^2\rangle], \tag{3}$$

where $\mathbf{k}$ is the γ wave vector and $\mathbf{r}$ is the nuclear-displacement vector. For a displacive ferroelectric with a soft-phonon mode, this may be rewritten as

$$f = f_0(T)\exp(-k_z^2 \Delta\langle z^2\rangle), \tag{4}$$

where k_z is the component of $\mathbf{k}$ in the direction of the displacement instability, $\Delta\langle z^2\rangle$ is the change in vibrational amplitude caused by the soft mode, and $f_0(T)$ is the recoilless fraction in the absence of the soft-phonon mode. For a powdered sample such as we used, the average k_z^2 is simply[4]

$$k_z^2 = \tfrac{1}{3}k^2. \tag{5}$$

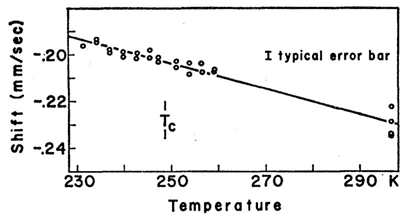

FIG. 2. Line shift observed in potassium ferrocyanide trihydrate as a function of temperature. The shift was observed relative to a Co^{57} in Pd source at room temperature.

The change in f at the ferroelectric transition temperature T_c is then

$$\Delta f / f_0(T_c) \approx \Delta \ln f = -(\tfrac{1}{3})k^2 \Delta\langle z_c^2\rangle, \tag{6}$$

where $\Delta\langle z_c^2\rangle$ is the maximum of $\Delta\langle z^2\rangle$, presumably at T_c. For $|\Delta f/f_0| < 3\%$ and $k = 7.3\ \text{Å}^{-1}$ (14.4 keV), $\Delta\langle z_c^2\rangle$ must be less than $1.7\times10^{-3}\ \text{Å}^2$.

For puposes of comparison with other measurements, we will assume that $\Delta\langle z_c^2\rangle$ is related to $(\Delta z)^2$ where Δz is the ferroelectric displacement of the iron ion. In particular, if Δz is the displacement for $T \ll T_c$, then for a first-order ferroelectric transition $(\Delta z)^2$ and $\Delta\langle z_c^2\rangle$ should be approximately equal, whereas for a second-order transition as in KFCT, we should have $\Delta\langle z_c^2\rangle < (\Delta z)^2$ or even $\Delta\langle z_c^2\rangle \ll (\Delta z)^2$. Both of these relations can easily be understood using the phenomenological double- and triple-well models. Unfortunately, no direct measurement of Δz has been made; however, there are several ways of estimating Δz. The relationship between Δz and the transition temperature T_c which Abrahams *et al.*[5] have proposed, would imply that $\Delta z = 0.1$ Å for $T_c = 250$ K.

On the other hand, Abrahams *et al.* also proposed a relation between Δz and the spontaneous polarization. The spontaneous polarization reported by Waku *et al.*,[6] $P_s = 1.4\ \mu\mathrm{C/cm}^2$ for $T \ll T_c$, would imply $\Delta z < 0.005$ Å. The large discrepancy between these two values of Δz is not surprising, since the relationships proposed by Abrahams *et al.* applied to complex oxide ferroelectrics. Equation (5) of Ref. 5 may also be written as

$$P_s = (n^* e/V)\Delta z, \tag{7}$$

where V is the volume occupied by one molecule, or formula unit, and n^* is the effective number of charges per molecule contributing to the polarization. For $\mathrm{LiNbO_3}$ (to which Abrahams's relations apply), $n^* \approx 8\frac{1}{2}$. For KFCT the molecular volume V is considerably larger, so that $e/V = 4.3\ \mu\mathrm{C/Å\ cm}^2$. Somewhat arbitrarily taking $n^* = 10$ gives $\Delta z = 0.03$ Å or $(\Delta z)^2 = 10^{-3}$

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[4] For the geometry used in Ref. 1, our Eq. (5) would be replaced by $k_z^2 = \frac{1}{2}k^2$.

[5] S. C. Abrahams, S. K. Kurtz, and P. B. Jamieson, Phys. Rev. **172**, 551 (1968).

[6] S. Waku, K. Masuno, T. Tanaka, and H. Iwasaki, J. Phys. Soc. Japan **15**, 1185 (1960). The units for P_s should be $\mu\mathrm{C/cm}^2$.

Å^2. This, in turn, implies $\Delta\langle z_c^2\rangle < 10^{-3}$ Å^2, which is in agreement with our experimental results.

In summary, we find no evidence of the large recoilless fraction anomaly reported by Hazony and co-workers in KFCT. Our results, in agreement with those of Gleason and Walker, place an upper limit of about 3% on the size of the anomaly near the ferroelectric transition temperature. Gleason and Walker interpret these results as excluding the possibility that the iron sublattice participates in a soft-phonon mode. We feel that these results do not rule out this participation since the estimates presented above indicate a soft-phonon mode in KFCT should produce changes in the vibrational amplitude smaller than we are able to detect with the Mössbauer effect.

ACKNOWLEDGMENT

The author would like to thank J. Thomas for assistance in the construction and operation of the experimental apparatus.

Erratum

Stopping Powers and Ranges of 5–90-MeV S^{32}, Cl^{35}, Br^{79}, and I^{127} Ions in H_2, He, N_2, Ar, and Kr: A Semiempirical Stopping Power Theory for Heavy Ions in Gases and Solids, T. E. PIERCE AND M. BLANN [Phys. Rev. **173**, 390 (1968)]. The constant for the exponent in the effective proton charge expression of Eq. (6) (also given in the abstract) is in error. The value given, -2.5, should be changed to -5.0. We are grateful to Dr. M. J. Fluss for bringing this error to our attention.