(1968).

[30] P. G. de Gennes, *Superconductivity* (Benjamin, New York, 1966), p. 270.

[31] S. Foner, E. J. McNiff, Jr., B. T. Matthias, T. H. Geballe, R. H. Willens, and E. Corenzwit, Phys. Letters 31A, 349 (1970).

[32] M. Weger, Solid State Commun. 9, 107 (1971).

[33] M. Weger (private communication).

PHYSICAL REVIEW B VOLUME 4, NUMBER 9 1 NOVEMBER 1971

Characteristic Temperatures of the Mössbauer Fraction and Thermal-Shift Measurements in Iron and Iron Salts*†

L. Dwynn Lafleur‡ and Clark Goodman
Department of Physics, University of Houston, Houston, Texas 77004

(Received 21 June 1971)

Mössbauer spectra have been measured in metallic iron, sodium nitroprusside, sodium ferrocyanide, and potassium ferrocyanide absorbers between 78 and 293 °K. The temperature dependences of the Mössbauer fraction f_a and the resonant velocity V_0 were fitted to Einstein and Debye lattice-vibration models. The characteristic temperatures of the models fitted to f_a are consistently lower than those fitted to V_0, showing the sensitivity of f_a to low-frequency modes of vibration. The characteristic temperatures obtained from V_0 are higher for the salts than for the metal, indicating the presence of higher-frequency modes in the salts. This interpretation is verified semiquantitatively by comparing the thermal-shift Debye temperatures of the salts to their infrared absorption frequencies. The Mössbauer fraction of potassium ferrocyanide shows a weaker temperature dependence than expected for a harmonic solid which suggests potassium ferrocyanide is anharmonic in the temperature range studied.

I. INTRODUCTION

The Mössbauer effect has been used by several investigators to study thermal-vibration properties of solids. Specifically, measurements of the Mössbauer (recoilless) fraction and the thermal shift in resonant γ energy are directly related, respectively, to the mean-square displacement and mean-square velocity of the Mössbauer nucleus in the solid. These studies fall into two general categories—source measurements and absorber measurements. In the former, the Mössbauer nucleus is usually present as a dilute impurity in the host lattice, so that information is obtained regarding the lattice-dynamical properties of an impurity atom in a solid. In the case of absorber studies, the Mössbauer nucleus is most often a major constituent of the solid, and measured properties are more directly dependent on the vibrational modes of the entire lattice.

Because the 14.4-keV γ-ray transition of Fe^{57} exhibits a strong Mössbauer effect in most materials even at room temperature, most of these studies have used that isotope. For example, Steyert and Taylor[1] studied sources consisting of the parent isotope Co^{57} diffused into several metal lattices. They were able to fit Mössbauer fraction measurements with Debye models for the lattice except at high temperatures ($\gtrsim 600$ °K) where diffusion and anharmonicity were significant. Thermal-shift measurements were also fitted with Debye models and showed consistently lower Debye temperatures than those obtained from the Mössbauer-fraction measurements. Better agreement was obtained when Einstein models were used, indicating perhaps the presence of a localized mode of vibration of the source nucleus.

Very few Mössbauer-fraction measurements in absorbers have been fitted to lattice-dynamical models. Herber and Wertheim[2] have measured relative Mössbauer fractions in powdered ferrocine absorbers at temperatures from 20 to 295 °K. The results are interpreted as indicating contributions to the Mössbauer fraction from both optic and acoustic modes of vibration, but no fits to models are given. Kerler[3] measured Mössbauer fractions in metallic iron and several iron compounds at temperatures from 153 to 353 °K. Within the accuracy of his data, all temperature dependences were linear, indicating a temperature range near the classical Dulong-Petit limit. Debye temperatures were calculated for the iron metal and the salts.

Preston *et al.*[4] studied the Mössbauer spectrum of metallic iron absorbers from 4 to 1300 °K. Measurements of the thermal shift were fitted to a Debye model in the low-temperature region. At high temperatures, there was a definite deviation from the Dulong-Petit limit which they interpreted as a temperature-dependent isomer shift. (Their thermal-shift data have recently been reexamined by Housley and Hess.[5])

More recently, Johnson and Dash[6] measured Mössbauer fractions and thermal shifts in powdered absorbers of anhydrous ferrous chloride at temperatures between 10 and 300 °K. By applying a general harmonic model[7] to the thermal-shift data, they calculated the average component of the force constant on an iron ion due to its own displacement. Both the Mössbauer-fraction and thermal-shift measurements at high temperatures were fitted to Einstein models. The experimental values of the Mössbauer fraction at low temperatures were larger than those predicted by the Einstein fit, leading the authors to postulate a low-temperature anharmonicity.

The present paper described measurements of the Mössbauer fraction and thermal shift in the spectra of a metallic iron absorber and three powdered absorbers (sodium nitroprusside, sodium ferrocyanide, and potassium ferrocyanide) over the temperature range 78–293 °K. A comparison to the predictions of the general harmonic theory[7] is made, and the data are fitted numerically to Einstein and Debye models.

Several factors were considered in the choice of the absorbers used in this study. Mössbauer spectra of the iron salts had been measured previously, showing them to be quite efficient—Mössbauer absorbers even with a natural abundance of Fe^{57}. It is believed, however, that no detailed comparative Mössbauer study of the lattice dynamics of the salts exist. Furthermore, infrared absorption spectra of these salts in powdered form have been measured in the frequency range 300–4000 cm^{-1} for the ferrocyanides and 300–880 cm^{-1} for sodium nitroprusside.[8,9] These spectra show absorption lines interpreted as interatomic vibrations involving the iron ions.[10] It seems desirable to compare the temperature dependence of the Mössbauer fraction and resonant energy in these salts displaying optical modes of vibration to that in metallic iron which has no optical modes.

II. THEORY

In the harmonic theory of lattice dynamics, the Mössbauer fraction (f) is given by[11]

$$f = e^{-k^2\langle x^2\rangle} \quad . \tag{1}$$

Here, k is the magnitude of the wave vector $\vec{k}$ of the photon emitted or absorbed by the Mössbauer nucleus, and $\langle x^2\rangle$ is the mean-square nuclear displacement along k. The value of f_a in a Mössbauer absorber can be determined by measuring the area under the absorption lines in the spectrum, provided that these lines are resolved and not broadened by inhomogeneous nuclear environments. We define the effective thickness parameter of the ith line in a hyperfine spectrum as

$$t_i = n_M \sigma_i f_a ,$$

where n_M is the area density of Mössbauer nuclei in the absorber, σ_i is the absorption cross section at resonance for the ith line, and f_a is the Mössbauer fraction of the absorber. It can be shown[12] that the area under the ith line, after correction for background, is given by

$$A_i = \frac{\pi}{2}\,\frac{f_s \Gamma_c}{E_0} \sum_{n=1}^{\infty} \frac{(-1)^{m+1}}{n!}\,\frac{(2n-3)!\,!}{(2n-2)!\,!}\, t_i^{\,n} , \tag{2}$$

where f_s is the Mössbauer fraction of the source, c is the speed of light, and Γ is the natural linewidth of the nuclear transition. Thus, from the measured area A_i, one can determine by graphical solution of Eq. (2) the value of t_i for that line. It is also true that

$$\sum_i \sigma_i = \sigma_0 ,$$

where the sum is over all hyperfine lines in the spectrum, and where σ_0 is the resonant cross section for an unsplit nuclear transition. Since the value of σ_0 is dependent only on the nuclear transition studied, the total thickness parameter for the absorber

$$t \equiv \sum t_i = n_M \sigma_0 f_a \tag{3}$$

can be used to determine the Mössbauer fraction for the absorber. (In the absence of a good value for σ_0, relative values of f_a can be obtained for identical Mössbauer nuclei in different environments.) Equation (1) then provides the relation between the measured value f_a and $\langle x^2\rangle$ for the nucleus.

The thermal shift (second-order Doppler shift) in the resonant energy of absorption is given by

$$\delta E = -E_0\langle v^2\rangle / 2c^2 ,$$

where E_0 is the resonant energy of the nuclear transition in the rest frame of the nucleus, and $\langle v^2\rangle$ is the mean square of the total velocity of the Mössbauer nucleus.[13] In most cases, the resonant energy of absorption in a substance is measured relative to a standard absorber, so that the source velocity at resonance is given by

$$V_0 = \delta_0 - \langle v^2\rangle / 2c , \tag{4}$$

where δ_0 is the isomer shift that would exist between the standard absorber and the substance in the absence of lattice vibrations in the latter.

The dependence of $\langle x^2\rangle$ and $\langle v^2\rangle$ on temperature can be approximated in many cases by assuming harmonic interatomic forces in the lattice. In the most general model,[7] we have

$$\langle x^2\rangle = \frac{\hbar}{m} \sum_{i=1}^{3N} \left(\frac{1}{2} + \frac{1}{e^{\hbar w_i / k_B T} - 1} \right) \frac{b_{xi}^{\;2}}{w_i} \tag{5}$$

and

$$\langle v^2\rangle = \frac{\hbar}{m} \sum_{i=1}^{3N} \left(\frac{1}{2} + \frac{1}{e^{\hbar \omega_i / k_B T} - 1} \right) (b_{xi}^{\;2} + b_{yi}^{\;2} + b_{zi}^{\;2})\, w_i \, ; \tag{6}$$

in the above expressions, m is the mass of the Mössbauer nucleus, N is the number of atoms in the solid, w_i is the angular frequency of the ith normal mode of the lattice, k_B is the Boltzmann constant, and the b_{xi}, etc., are the elements of the matrix transforming the normal coordinates of the lattice modes to the Cartesian coordinates of the nucleus.

In studying temperature-dependent properties such as $\langle x^2 \rangle$ and $\langle v^2 \rangle$ which involve summations over the entire lattice-vibration spectrum, it is convenient to use somewhat simpler models than the general harmonic theory discussed above. The two most widely used are the Einstein and Debye models,[14] where the lattice is described in terms of the characteristic temperatures Θ_E and Θ_D, respectively. In the Einstein model,

$$\langle x^2 \rangle = \frac{\hbar^2}{m k_B \Theta_E} \left(\frac{1}{2} + \frac{1}{e^{\Theta_E / T} - 1} \right) \tag{7}$$

and

$$\langle v^2 \rangle = \frac{3 k_B \Theta_E}{m} \left(\frac{1}{2} + \frac{1}{e^{\Theta_E / T} - 1} \right); \tag{8}$$

while in the Debye model,

$$\langle x^2 \rangle = \frac{3\hbar^2}{4 m k_B \Theta_D} \left(1 + \frac{4T^2}{\Theta_D^2} \int_0^{\Theta_D / T} \frac{u\, du}{e^u - 1} \right) \tag{9}$$

and

$$\langle v^2 \rangle = \frac{9 k_B \Theta_D}{8m} \left(1 + \frac{8T^4}{\Theta_D^4} \int_0^{\Theta_D / T} \frac{u^3\, dn}{e^u - 1} \right). \tag{10}$$

III. EXPERIMENTAL PROCEDURE AND RESULTS

The absorbers studied were metallic Fe, sodium nitroprusside $[Na_2Fe(CN)_5NO \cdot 2H_2O]$, sodium ferrocyanide $[Na_4Fe(CN)_6 \cdot 10H_2O]$, and potassium ferrocyanide $[K_4Fe(CN)_6 \cdot 3H_2O]$. The metallic Fe was a 0.0010-in. foil, while the salts were finely powdered and dispersed uniformly in acrylic plastic. All absorbers contained a natural isotopic abundance of Fe^{57} in area densities of 0.46 mg/cm^2 for the foil and 0.10 mg/cm^2 for the salts.

The source used for all spectra was Co^{57} diffused into copper, with a nominal activity of 10 mCi. In addition to having a single emission line, this source has a well-determined Mössbauer fraction f_s and has been suggested as a standard for use in Mössbauer-fraction measurements.[15] In this work, a value $f_s = 0.710 \pm 0.014$ has been used.

Absorption spectra were obtained using an electromechanical constant-acceleration transducer[16] with a 400-channel analyzer operating in the multiscaling mode. The detector was a proportional counter filled to 1 atm with 97% Kr-3% CO_2. The absorber temperature was kept at desired values by means of a gas-flow cryostat using liquid-nitrogen vapors as a coolant.[17] A chrome-constantan thermocouple and microvolt potentiometer were used to measure the absorber temperature. The error signal due to potentiometer unbalance was used in an electromechanical feedback circuit to control the flow rate of the coolant through the cryostat. In this way, absorber temperature variations during experimental runs were less than ± 0.15 °K at any desired temperature between 78 and 293 °K.

Because of the proximity of the source to the absorber cryostat, thermal isolation was provided for the source while the absorber temperature was varied. This was accomplished by placing the source and transducer in a wooden enclosure in which the air temperature was thermostatically maintained at (25.0 ± 0.1) °C.

A computer program was written to fit the spectra to a mathematical model consisting of the sum of a baseline and Lorentzian line(s), all multiplied by a parabola to account for instrumental modulation (e.g., due to systematic source displacement). The program calculated the spectral parameters (baseline, linewidth, line intensities, and line positions) as well as their standard deviations. The velocity scale on each spectrum was calibrated by using statistically weighted averages of the known hyperfine splittings in metallic Fe and in sodium nitroprusside.[18]

After background corrections, the areas under the lines were calculated and Eqs. (2) and (3) were used to determine the thickness parameter t for each absorber as a function of temperature. Because several different experimental values for the internal conversion coefficient for Fe^{57} have been obtained in the past few years,[19] there is no well-accepted value for σ_0. To prevent the uncertainty in this constant from affecting the lattice-dynamical calculations, absolute Mössbauer fractions were not calculated from t. Rather, the data were treated in the form $\ln t(T)$, which by Eq. (3) can be written

$$\ln t(T) = \ln(n_M \sigma_0) - \ln f_a(T).$$

For a harmonic solid, Eq. (1) yields

$$\ln t(T) = \ln(n_M \sigma_0) - k^2 \langle x^2 \rangle_T ,$$

so that $\ln t(T)$ is proportional to $\langle x^2 \rangle_T$, with an additive constant independent of the lattice-vibration properties of the solid. The resulting data are shown in Fig. 1.

Figure 2 shows the source velocity V_0 at resonance for each absorber as a function of temperature. In the cases of metallic Fe and sodium nitroprusside, the centroids of the spectra are given. All velocities are relative to sodium nitroprusside at 293 °K. From Eq. (4), we see that $V_0(T)$ is proportional to $\langle v^2 \rangle_T$ with an additive constant δ_0.

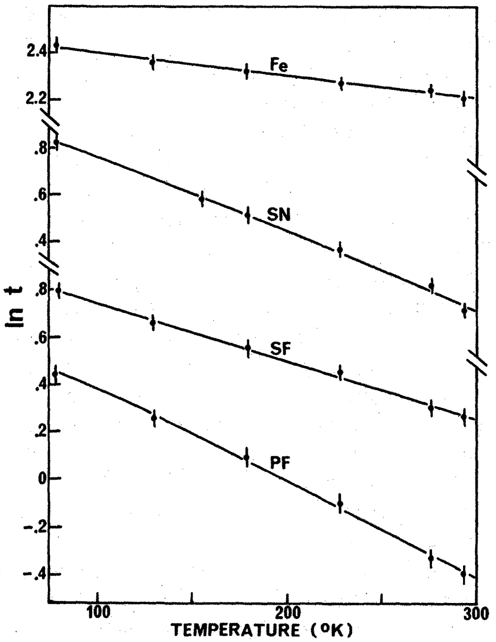

FIG. 1. Temperature dependence of ln$t$ in metallic iron (Fe), sodium nitroprusside (SN), sodium ferrocyanide (SF), and potassium ferrocyanide (PF), where $t \equiv n_M \sigma_0 f_a(T)$. In a harmonic solid, $\ln t(T) = \ln(n_M \sigma_0) - k^2 \langle x^2 \rangle_T$. The error bars are ±1 standard deviation, and the solid curves are the Einstein models given in Table I.

The data shown in Figs. 1 and 2 were fitted to Einstein and Debye lattice models, Eqs. (7)-(10), by means of an iterative least-squares computer program. χ-square tests were applied in each case to ensure the statistical significance of the fit. Table I shows the "best-fit" models obtained in each spectrum. The solid curves in Figs. 1 and 2 represent the Einstein models in Table I.

In Table I, certain trends can be seen in the behavior of the characteristic temperatures Θ_E and Θ_D. First, Θ_E and Θ_D are always lower for the ln$t(T)$ data than for the $V_0(T)$ data. This relationship results from the fact that ln$t(T)$ is related to $\langle x^2 \rangle_T$ of the Mössbauer nucleus, while $V_0(T)$ is determined by $\langle v^2 \rangle_T$. Because of the weighting factors w_i^{-1} and w_i for each term in Eqs. (5) and (6), respectively, $\langle x^2 \rangle_T$ is weighted toward lower frequencies than is $\langle v^2 \rangle_T$. Hence the lower characteristic temperature for ln$t(T)$.

This effect is much greater in the salts than in metallic Fe because of the existence of high-frequency optical modes of vibration in the former. These modes are responsible for the infrared absorption lines exhibited by these salts as discussed below. These optical modes involve intramolecular vibrations in which ion-ion (short-range) interactions are involved. Because these interactions are generally stronger than metallic bonds, they usually involve higher frequencies. Thus, Θ_E and Θ_D based on $V_0(T)$ measurements are larger for the salts than for the metallic Fe.

In the case of metallic Fe, there is a relatively small difference in the values for Θ_D calculated from ln$t(T)$ and from $V_0(T)$. This indicates that both the Mössbauer fraction and thermal shift in Fe can be described quite well by a single Debye model of $\Theta_D \simeq 390$ °K. The Debye temperatures for Fe in Table I agree well with previous work. Thermal-shift studies by Preston *et al.*[4] resulted in $\Theta_D = (400 \pm 30)$ °K, which agrees with our value of (421 ± 30) °K. Using neutron diffraction data, calculations by Housley and Hess[5] predict that the thermal shift in metallic Fe above ~ 200 °K should be characteristic of an Einstein solid of $\Theta_D = (422 \pm 3)$ °K, in excellent agreement with our value. Finally, de Launay[20] gives a value $\Theta_D = 420$ °K based on specific-heat data for Fe at temperatures when the specific heat is about one-half the Dulong-Petit value.

Hazony[21] has calculated an Einstein temperature $\Theta_E = (700 \pm 50)$ °K from thermal-shift measurements

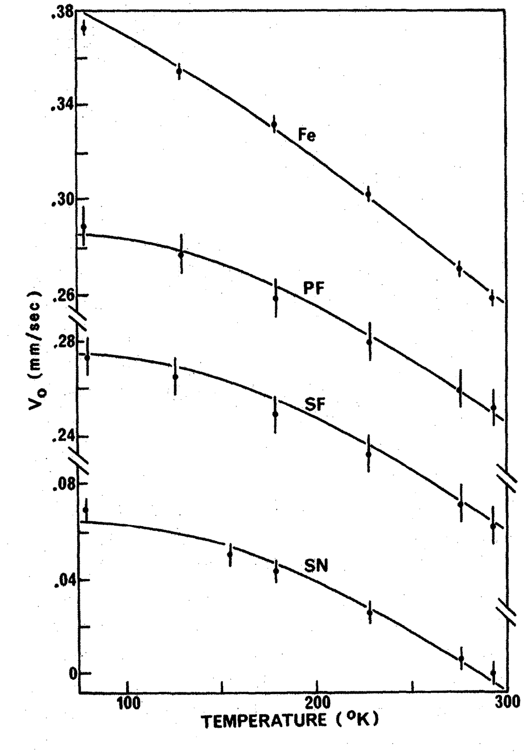

FIG. 2. Temperature dependence of the resonant source velocity V_0 in metallic iron (Fe), potassium ferrocyanide (PF), sodium ferrocyanide (SF), and sodium nitroprusside (SN), relative to sodium nitroprusside at 293 °K. In general, $V_0(T) = \delta_0 - \langle v^2 \rangle T/2c$. The error bars are ±1 standard deviation, and the solid curves are the Einstein models listed in Table I.

in potassium ferrocyanide. However, he treats the oscillator mass and frequency as variable parameters, using $m = 78$ amu in the thermal-shift data. If a value $m = 57$ amu were used (as in this work), Hazony's value for Θ_E would be reduced almost proportionally and would be much closer to that given in Table I. No other determinations of Θ_E or Θ_D from either Mössbauer-fraction or thermal-shift measurements in the salts studied here have been found.

The strongest infrared absorption lines[8,9] that are interpreted as vibrational modes involving the Fe atoms in the salts[10] are given in Table II. The higher-frequency lines are associated with the Fe-C-N bending mode, and the lower frequencies, with Fe-C stretching. The frequencies of absorption are given in terms of $\bar{\nu}$ in cm^{-1} as well as characteristic temperature Θ defined by $k_B\Theta = 2\pi c\bar{\nu}$. Also shown in Table II are the thermal-shift Debye temperatures for the salts from Table I. The relative closeness of the Θ_D values to the average Θ values is not unreasonable; in the Debye model of a solid, Θ_D corresponds to the maximum vibration frequency, while in the real solid, the infrared frequencies are the highest frequencies in the true vibration spectrum. The lack of systematic correlation in Θ and Θ_D from one salt to the next is rather disappointing, however.

In the case of potassium ferrocyanide, the Mössbauer fractions seem to indicate anharmonic behavior. If σ_0 is calculated using $\ln(n_M\sigma_0)$ from Table I, one obtains values for metallic iron, sodium nitroprusside, and sodium ferrocyanide which are all within experimental uncertainty of an average value $\sigma_0 = (2.7 \pm 0.2)\times 10^{-18}$ cm^2. (A recent measurement[19] of $\alpha_T = 8.17$ for the internal conversion coefficient in Fe^{57} gives $\sigma_0 = 2.57\times 10^{-18}$ cm^2.) The value one obtains for potassium ferrocyanide, however, is $\sigma_0 = (2.1 \pm 0.1)\times 10^{-18}$ cm^2, which is considerably lower than the above values. This apparently unrealistic value indicates that the Einstein and Debye models for the Mössbauer-fraction data for potassium ferrocyanide are not physically meaningful.

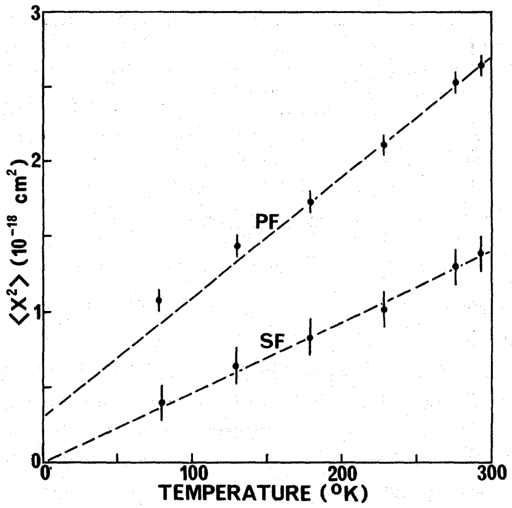

FIG. 3. Temperature dependence of $\langle x^2 \rangle$ in potassium ferrocyanide (PF) and sodium ferrodyanide (SF), using the data from Fig. 1 and assuming $\sigma_0 = 2.57\times 10^{-18}$ cm^2. If the harmonic approximation were valid in potassium ferrocyanide, the extrapolation of the high-temperature linear behavior would go through $\langle x^2 \rangle = 0$ at $T = 0$, as is the case in sodium ferrocyanide.

A more graphic demonstration of the apparent anharmonicity in potassium ferrocyanide is shown in Fig. 3. According to Eq. (5), in a harmonic lattice, the curve of $\langle x^2 \rangle$ versus T becomes linear at high temperatures, approaching a straight-line asymptote which originates at $\langle x^2 \rangle = 0$ and $T = 0$ has a slope dependent on the lattice properties. This is in accordance with the classical equipartition limit. If one assumes a value for σ_0, the data in Fig. 1 can be converted to a curve of $\langle x^2 \rangle$ versus T for each absorber. Figure 3 shows the results for potassium ferrocyanide and, for comparison,

TABLE I. Einstein and Debye lattice models for the data shown in Figs. 1 and 2. The uncertainties expressed are ±1 standard deviation.

		Metallic Fe	Sodium nitroprusside	Sodium ferrocyanide	Potassium ferrocyanide
$\ln f(T)$ data					
Einstein model:	$\ln(n_M\sigma_0)$	2.54 ± 0.02	1.13 ± 0.03	1.03 ± 0.02	0.82 ± 0.03
	Θ_E (°K)	206 ± 10	117 ± 2	133 ± 3	106 ± 2
Debye model:	$\ln(n_M\sigma_0)$	2.54 ± 0.02	1.13 ± 0.03	1.03 ± 0.02	0.82 ± 0.03
	Θ_D (°K)	358 ± 18	203 ± 4	231 ± 4	184 ± 3
$V_0(T)$ data					
Einstein model:	δ_0(mm/sec)	0.494 ± 0.003	0.274 ± 0.015	0.479 ± 0.023	0.477 ± 0.011
	Θ_E (°K)	318 ± 22	574 ± 40	560 ± 46	526 ± 31
Debye model:	δ_0(mm/sec)	0.495 ± 0.005	0.282 ± 0.016	0.485 ± 0.023	0.483 ± 0.013
	Θ_D (°K)	421 ± 30	788 ± 58	779 ± 67	716 ± 40

TABLE II. Infrared absorption lines involving vibrations of iron atoms in the salts studied in this work.

Absorber	$\bar{\nu}$ (cm^{-1})[a]	Θ (°K)	Θ_D (°K)[b]
Sodium nitroprusside	425 (stretching)	612	788 ± 58
	500 (bending)	720	
Sodium ferrocyanide	430 (stretching)	619	799 ± 67
	588 (bending)	846	
Potassium ferrocyanide	419 (stretching)	603	716 ± 40
	588 (bending)	846	

[a] Reference 10. [b] From Table I.

sodium ferrocyanide, where $\sigma_0 = 2.57 \times 10^{-18}$ cm^2 has been used. The behavior in sodium ferrocyanide is typical of a harmonic solid, but in potassium ferrocyanide, although the data fit well to a linear asymptote at high temperatures, the line intersects the $\langle x^2 \rangle$ axis decidedly above the origin. This indicates anharmonicity in the solid; in particular, there exists a rather large mean-square nuclear displacement at low temperatures. A similar effect in $FeCl_2$ has been observed by Johnson and Dash.[6] They observed in that substance that $\langle x^2 \rangle$ is less sensitive to temperature than can be expected from a general harmonic lattice and attribute this to low-temperature anharmonicity.

The anharmonic behavior in potassium ferrocyanide is perhaps related to the fact that this substance demonstrates ferroelectricity below 251 °K.[22] It is well known[23] that ferroelectricity can often be associated with a lowering of the frequency of the zero wave-vector transverse optical mode of lattice vibration. Hazony *et al.*[24] have proposed the existence of such an effect in potassium ferrocyanide and have used single-crystal measurements of the area of the Mössbauer absorption line through the ferroelectric transition temperature to support their argument. Equation (5) shows that a lowering of the frequency of any vibrational mode(s) results in a higher value of $\langle x^2 \rangle$ than if the frequency were unchanged as in a harmonic lattice. Inelastic neutron scattering has shown that in some ferroelectrics the frequency of the transverse optical mode actually decreases monotonically with decreasing temperature[23]. Although no such effect has been demonstrated in potassium ferrocyanide, this would explain qualitatively the behavior of $\langle x^2 \rangle$ in Fig. 3.

---

*Based on a dissertation submitted by L. Dwynn Lafleur in partial fulfillment of the requirements for the Ph. D. degree at the University of Houston.

†Supported by the National Aeronautics and Space Administration through a predoctoral traineeship and Grant No. NGR-44-005-021.

‡Present address: Physics Department, University of Southwestern Louisiana, Lafayette, La. 70501

[1] W. A. Steyert and R. D. Taylor, Phys. Rev. 134, A716 (1964).

[2] R. H. Herber and G. K. Wertheim, in *The Mössbauer Effect*, edited by D. M. J. Compton and A. H. Schoen (Wiley, New York, 1962), p. 105.

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

[4] R. S. Preston, S. S. Hanna, and J. Heberle, Phys. Rev. 128, 2207 (1962).

[5] R. M. Housley and F. Hess, Phys. Rev. 164, 340 (1967).

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

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

[8] F. A. Miller and C. H. Wilkins, Anal. Chem. 24, 1253 (1952).

[9] F. A. Miller, G. L. Carlson, F. F. Bentley, and W. H. Jones, Spectrochim. Acta 16, 135 (1960).

[10] L. Tosi and J. Danon, Inorg. Chem. 3, 150 (1964).

[11] H. Frauenfelder, *The Mössbauer Effect* (Benjamin, New York, 1962).

[12] G. Lang, Nucl. Instr. Methods 24, 425 (1963).

[13] G. K. Wertheim, *Mössbauer Effect, Principles and Applications* (Academic, New York, 1964).

[14] V. I. Goldanskii and E. F. Makarov, in *Chemical Applications of Mössbauer Spectroscopy*, edited by V. I. Goldanskii and R. H. Herber (Academic, New York, 1968), p. 26.

[15] R. M. Housley, J. G. Dash, and R. H. Nussbaum, Phys. Rev. 136, A464 (1964).

[16] Austin Science Associates, Model K3 Transducer, Model S3 Control Electronics.

[17] M. Kalvius, in *Mössbauer Effect Methodology*, edited by J. J. Gruverman (Plenum, New York, 1965), Vol. 1, p. 172

[18] A. H. Muir, Jr., K. J. Ando, and H. M. Coogan, *Mössbauer Effect Data Index* 1958–1965 (Interscience, New York, 1966); R. W. Grant, R. M. Housley, and U. Gonser, Phys. Rev. 178, 523 (1969).

[19] William Rubinson and K. P. Gopinathan, Phys. Rev. 170, 969 (1968).

[20] J. de Launay, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1956), Vol. 2, p. 219.

[21] Y. Hazony, J. Chem. Phys. 45, 2664 (1966).

[22] S. Waku, H. Hirabayshi, H. Toyada, H. Iwaski, and R. Kiriyama, J. Phys. Soc. Japan 14, 973 (1959).

[23] W. Cochran, in *Ferroelectricity*, edited by Edward F. Weller (Elsevier, New York, 1962), p. 62.

[24] Y. Hazony, D. E. Earls, and I. Lefkowite, Phys. Rev. 166, 507 (1968).