

Study of Iron Ions in NaCl Using the Mössbauer Effect. II. The Vacancy-Impurity Associated State*

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Two types of Mössbauer spectra were observed for dilute concentrations of Fe^{57} ions in NaCl. A doublet with a 0.5 mm/sec quadrupole splitting and a 0.5 mm/sec isomer shift relative to stainless steel (80°K) is interpreted as the result of either Fe^{2+} or Fe^{3+} associated with a positive ion vacancy. A broad unsplit line at -2.07 ± 0.07 mm/sec (80°K) is interpreted as the result of Fe^{2+} substitutionally replacing Na^+ . The data are used to make a rough estimate of the binding energy between positive ion vacancies and cobalt impurities, and the result is consistent with theoretical expectations. A study of the temperature dependence of these two resonances indicates that the ratio of the recoilless emitted γ rays from the isolated ions compared with the vacancy associated ions is 0.75 ± 0.15 at 80°K, 0.24 ± 0.08 at 296°K, and 0.16 ± 0.08 at 478°K. This huge effect is believed to be due to the difference in elastic constants and "mass-symmetry" contributions to the localized modes, for the two environments.

I. INTRODUCTION

THE purpose of the present experiment is to identify the two Mössbauer resonances corresponding to isolated iron ions substitutionally replacing Na^+ ions in the NaCl lattice and iron ions which are associated with charge-compensating positive-ion vacancies.¹ The temperature dependence of the number of ions in the two environments was studied by measuring the Mössbauer intensities of the two resonances as a function of temperature and also at 80°K after quenching from various high-temperature states. In this way we get an estimate of the temperature dependence of the thermodynamic equilibrium between the two types of environments, and are thereby able to estimate the binding energy of the vacancy-impurity associated states. We also attempt to answer questions concerning the charge state and electric-field gradients for these two environments by measurements of the isomer shift^{2,3} and quadrupole splitting.³⁻⁵

The temperature dependence of the Mössbauer intensity for the two types of environments was measured, and it was found that at room temperature about 4 times as many recoil-free γ rays were emitted from iron ions in the associated state as compared to iron ions in the isolated state. This indicates that the vibrational frequency spectrum for the two environments is very different and qualitative arguments are given to account for this large difference.

* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

¹ For a general discussion of different environments for alien ions in alkali halide lattices see A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

² L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

³ S. DeBenedetti, G. Lang, and R. Ingalls, *Phys. Rev. Letters* **6**, 60 (1961).

⁴ G. K. Wertheim, *Phys. Rev.* **121**, 63 (1961).

⁵ C. E. Johnson, W. Marshall, and G. J. Perlow, *Phys. Rev.* **126**, 1503 (1962).

II. EXPERIMENTAL TECHNIQUES

The same velocity spectrometer and stainless steel absorber described in I were used in the present study. The sources were prepared by essentially the same technique as discussed in I with the exception that no carrier CoCl_2 was added to the $\text{Co}^{57}\text{Cl}_2$ (typically ~ 0.1 mC) which was evaporated onto the NaCl crystal prior to diffusion. Thus, the concentrations of cobalt ions used in this study were at least two or three orders of magnitude lower than in the previous experiment. After the diffusion anneal, etching was performed to eliminate any surface⁶ CoCl_2 as discussed in I. High-temperature Mössbauer resonances were run with source temperatures between room temperature and 300°C. These were obtained by means of a furnace, interchangeable with the liquid nitrogen container, which was heated by means of a Watlow heater rod. Thermal contact between the heated copper block and the NaCl crystal was optimized by spring loading the crystal against the copper block.

III. EXPERIMENTAL RESULTS

Two distinct Mössbauer spectra were observed in the present experiment, and they will be referred to by the labels *A* and *B* in the following discussion. *A* is a doublet whose peaks occur at -0.78 ± 0.04 mm/sec, and -0.23 ± 0.04 mm/sec when the NaCl crystal is at a temperature of 80°K. At this same temperature *B* is a single broad line whose peak velocity occurs at -2.07 ± 0.07 mm/sec and whose full linewidth at half-maximum is about 1 mm/sec.

To understand the nature of the crystal environments which produced the *A* and *B* resonances a number of quenching experiments were performed. By this procedure it was possible to "freeze in" at high-temperature state and yet to examine the Mössbauer effect at 80°K

⁶ An abstract of preliminary data obtained in this experiment is given in *Bull. Am. Phys. Soc.* **7**, 345 (1962). The resonances reported at this meeting were complicated somewhat, as a result of a fraction of the activity being on the surface. The etching procedure eliminated this difficulty completely.

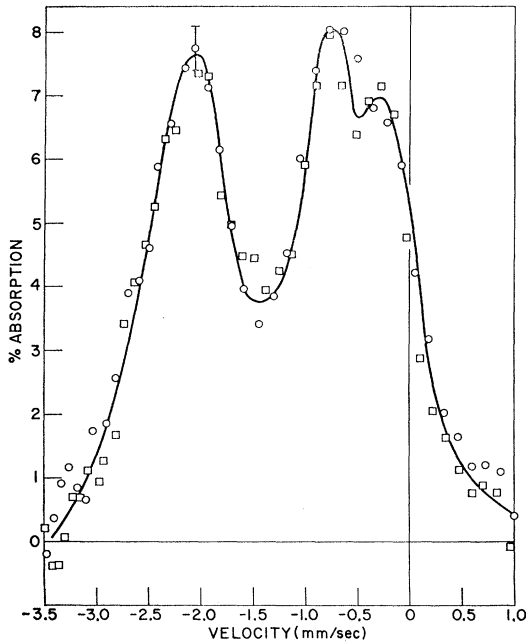


FIG. 1. The Mössbauer spectra at 80°K obtained after quenching from 600°C. The diffusion depth was $\approx 10^{-2}$ cm which permitted a large fraction of the *B* environment to be quenched in.

where the Debye-Waller factor, and hence, the total fraction of recoilless γ rays emitted, is large. Although quenching experiments using NaCl are generally difficult, because of the low-thermal conductivity of this

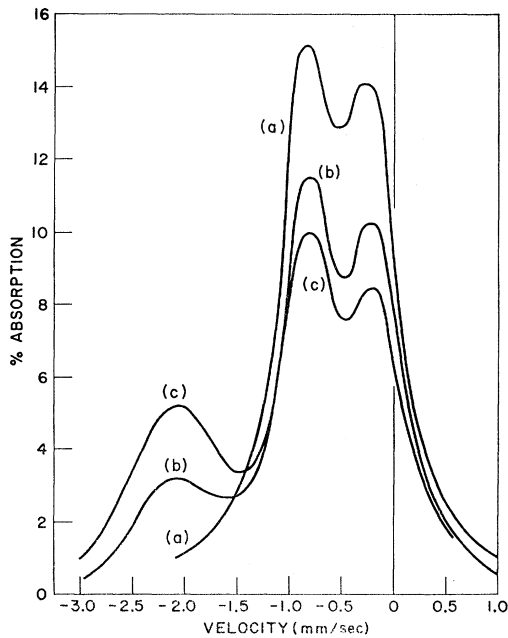


FIG. 2. Three Mössbauer resonances at 80°K showing the difference in the amounts of the *B* spectrum obtained after (a) slow cooling of NaCl crystal, (b) quenching from 300°C, and (c) quenching from 600°C.

material, these problems are less severe in the present experiment where the Co^{57} tracer ions are near to the surface. Thus, by reducing the diffusion depth the rate of cooling could be enhanced in the region of the crystal containing Co^{57} ions. When quenching occurred from a fixed temperature and the mean-diffusion penetration was varied, it was found that the ratio of *B*-type ions to *A* type increased as the diffusion depth was decreased. Although *B*-type ions have not yet been completely isolated by this technique, Fig. 1 shows a case where a large fraction of the ions are in the *B*-type environment.

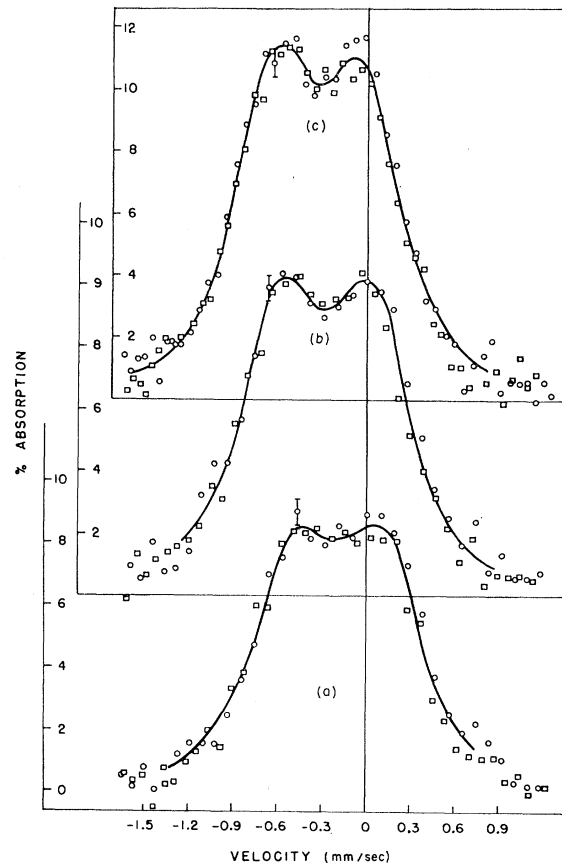


FIG. 3. Mössbauer spectra for the *A* resonance at (a) $T=579^\circ\text{K}$, (b) $T=473^\circ\text{K}$, and (c) $T=374^\circ\text{K}$.

On three quenches from about 600°C the fraction of *B* ions, F_B , was found to vary with diffusion depth, d , as follows: $F_B=0.66$, for $d\approx 4\times 10^{-3}$ cm, $F_B=0.55$ for $d\approx 11\times 10^{-3}$ cm, $F_B=0.32$ for $d\approx 2\times 10^{-2}$ cm. It should be noted that F_B was determined by a graphical measurement of F_A , the area under the *A* spectrum divided by the area under the *A* spectrum when only *A* ions are present. F_B was then determined by the relation $F_B=1-F_A$, to avoid any difficulties from the difference in Debye-Waller factor for *A*- and *B*-type ions. It should be noted that the observation of a dominant *B*

resonance precludes the possibility of its being connected with a "hidden" line under the A resonance.

A qualitative examination of the relative fraction of B ions quenched-in as a function of quench temperature is shown in Fig. 2. To keep the quenching rate constant, the diffusion depth was kept large enough that the anneal preceding the quenches could be performed without appreciably altering this depth of diffusion. Thus, the measurement is qualitative, since the quenched-in temperature is undoubtedly lower than the annealing temperature. The results do indicate that the amount of B environment quenched in increases as the annealing temperature is raised.

The B environment could be converted into the A environment by annealing at low temperatures. The rate of conversion of B to A depended on the concentration of cobalt ions, being a rapid conversion at high concentrations and a slow conversion at low concentrations. Thus, while F_B/F_A was largest when quenching with small diffusion depths, F_B/F_A went rapidly to zero on annealing in the temperature region 200 to 300°C. As the concentration was decreased by further diffusion the conversion of B to A was slower.

Using a crystal that was annealed at approximately 300°C and which gave only the A spectrum at 80°K [see Fig. 2(a)], the temperature dependence of the Mössbauer effect was measured at 579, 473, 374, 296, and 80°K. The results of these measurements are shown in Figs. 3 and 4, and the relevant data associated with these curves are shown in Table I.

It is evident from Fig. 4 that the intensities of the two peaks are not exactly equal at low temperature. This difference is quite small and might be due to a small amount of CoCl_2 precipitate at the low temperatures, which would enhance the -0.78 -mm/sec peak. The other line associated with the precipitated state, however (see I), was not observable, which might be due to its smallness coupled with its superposition on the wing of the main A resonance, or possibly it is a real effect resulting from the anisotropy of f in this environment. It should be pointed out, however, that this small difference in peak height was not generally

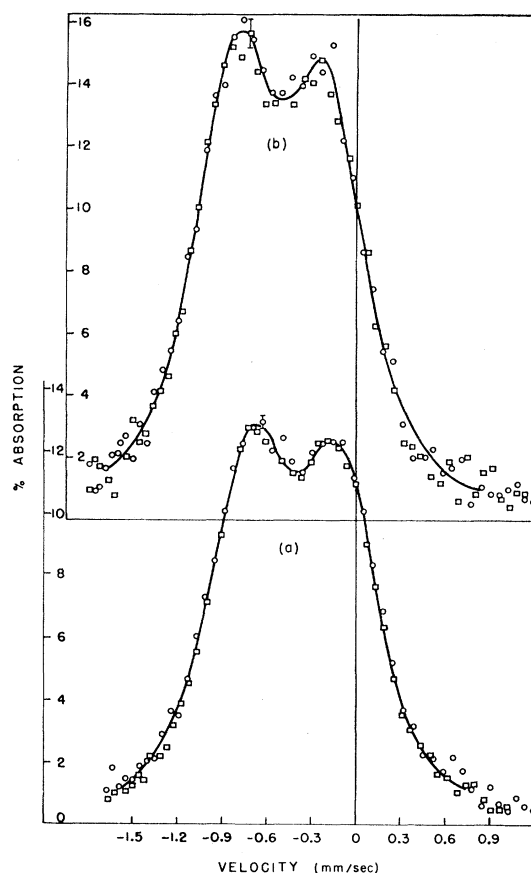


FIG. 4. Mössbauer spectra for the A resonance at (a) $T=296^\circ\text{K}$, and (b) $T=80^\circ\text{K}$.

reproducible, although the peak positions and intensity magnitudes were.

The temperature dependence of the Mössbauer effect for B -type ions was also measured at 80°, 296°, and 478°K, with some of the data displayed in Fig. 5. A difference in the temperature dependence of the Mössbauer intensities for A - and B -type ions is visually apparent from the differences in relative areas under the A - and B -type spectra. In Table II the relative in-

TABLE I. The temperature dependence of spectrum A .

Temperature (°K)	Relevant figure	A_A (% absorption) \times (mm/sec) ^a	$f_A(T)/f_A(80^\circ\text{K})$	Peak positions ^b (mm/sec)	Calculated quadrupole splitting (mm/sec)	Calculated isomer shift (mm/sec)
80		21.6 ± 0.6	1.00			
579	3(a)	11.6 ± 0.4	0.54 ± 0.04	-0.47 ± 0.06 , $+0.05 \pm 0.06$	0.52 ± 0.09	0.21 ± 0.05
473	3(b)	14.2 ± 0.4	0.67 ± 0.05	-0.55 ± 0.04 , -0.02 ± 0.04	0.53 ± 0.06	0.28 ± 0.03
374	3(c)	15.2 ± 0.3	0.71 ± 0.04	-0.57 ± 0.04 , -0.08 ± 0.04	0.49 ± 0.06	0.32 ± 0.03
296	4(a)	17.4 ± 0.2	0.81 ± 0.04	-0.68 ± 0.04 , -0.17 ± 0.04	0.51 ± 0.06	0.43 ± 0.03
80	4(b)	21.1 ± 0.3	1.00	-0.78 ± 0.04 , -0.23 ± 0.04	0.55 ± 0.06	0.50 ± 0.03

^a Background correction, $\gamma \cong 1.25$ has not been included in A_A (see I).

^b These numbers include a small (0.02 mm/sec) correction to account for the difference in true peak positions and the points of zero slope. The correction was estimated graphically using the data from the Co^{57} in Cu unsplit source, and it is such as to increase the quadrupole splitting 0.04 mm/sec.

^c In this case the statistics were poor and the positions were determined by a visual examination of the curve.

tensities are calculated directly by using the relation

$$A_B'(T)[f_A(T)/f_B(T)] + A_A'(T) = A_A(T),$$

where A_A is the total area under the absorption curve with only A -type ions [See Table I for values of $A_A(T)$], and A_A' and A_B' are the graphically determined areas under the A and B resonances, respectively. The errors indicated in Table II were visually estimated to make a reasonable allowance for errors in graphically partitioning a given resonance into the A_A' and A_B' . Although the above procedure should automatically account for any annealing of B into A , resonances were run at 80°K before and after the 296 and 478°K runs. Although some annealing of B into A did occur the effect was small. When $A_B'(80)$ is taken as the average of the runs before and after each "high-temperature" run, we can calculate $f_B(T)/f_A(80)$ without making reference to the measurement of $A_A(T)$, i.e.,

$$f_B(T)/f_A(80) = [f_B(T)/f_B(80)][f_B(80)/f_A(80)].$$

For $T=296$ and 478 we find $f_B(T)/f_A(80) = 0.19 \pm 0.07$ and 0.14 ± 0.07 , respectively, in excellent agreement with the values shown in Table II, which were calculated using the measured $A_A(T)$. It should be noted that the

reason for normalizing $f_B(T)$ relative to $f_A(80)$ is merely that this value is presumably near 1, and thus normalizing to $f_A(80)$ should give an estimate of the absolute f_B 's, i.e., $f_B(T) \cong f_B(T)/f_A(80)$. A summary of the relative f values is shown in Fig. 6.

IV. DISCUSSION

The quenching data and low-temperature annealing data indicate that at elevated temperatures the iron ions are predominately in the B environment and at low temperatures they are predominately in the A environment. This result can be explained by considering the B environment to correspond to an isolated iron ion substitutionally replacing a sodium ion, and the A environment to correspond to an iron ion which is associated with a positive ion vacancy. This interpretation is augmented by the observation of a quadrupole splitting for iron ions in the A environment and no resolvable splitting for those in the B environment, which is cubic in the absence of a positive ion vacancy.

As was discussed in I, the isomer shift, which measures changes in electronic charge density at the Fe^{57} nucleus, is useful in inferring the electronic configuration and charge state of an Fe ion in a particular environment.^{2,3} Resonance B was observed to have an isomer shift of 2.07 mm/sec (80°K) above stainless steel with respect to energy. This is a much larger shift than is observed for even the most ionic ferrous compounds and indicates a charge state of +1 for the iron ion in a $3d^7$ configuration. The isomer shift of resonance A was about 0.5 mm/sec (80°K) and this is typical for Fe^{3+} in ionic compounds, although Fe^{2+} is also a possibility, since covalency effects for an unclosed $3d^6$ configuration could account for the change in electronic charge density at the iron nucleus. It should be emphasized that the ambiguity in the interpretation of the associated state does not enter for the isolated state, since the large isomer shift in the latter case indicates a very low electronic charge density, $\rho_e(0)$, at the iron nucleus. The only effect which reduces $\rho_e(0)$ is polarization of the s electrons. To obtain sufficient polarization to explain the observed isomer shift it appears necessary to ascribe a $3d^7$ electronic configuration to the iron ion. It is encouraging that Hayes^{7,8} has observed electron spin resonance data for iron in NaF, which he is able to explain by attributing a $3d^7$ configuration to the iron ion. It is not certain whether Fe^+ is stable or is a metastable state which results from the local irradiation that precedes the 14.4 keV isomeric transition, although the observation of only Fe^+ for the isolated state suggests that it is energetically preferred to Fe^{2+} when no charge compensating positive-ion vacancy is present. The fact that Hayes did not see Fe^+ except upon irradiation at low temperatures may have been due to the intrinsic

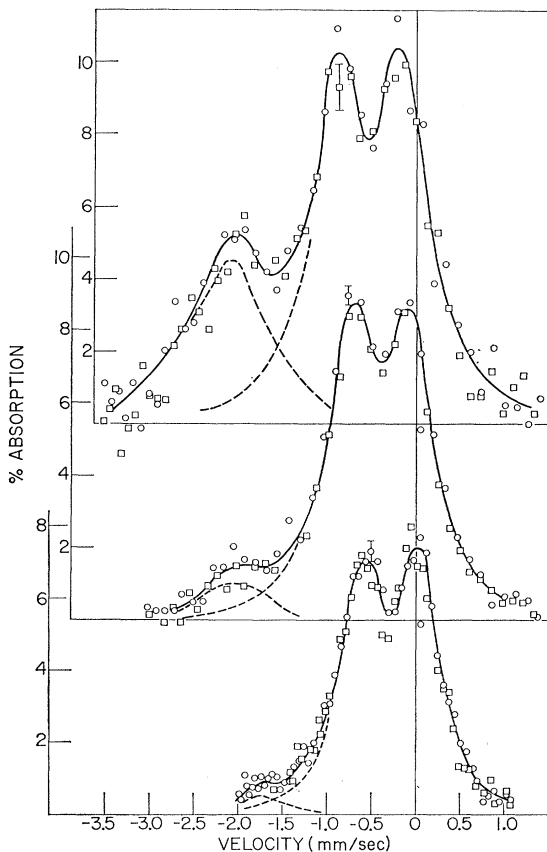


FIG. 5. Mössbauer spectra for the A and B resonance at $T=80$, 296 and 478°K (from top to bottom).

⁷ W. Hayes, Suppl. J. Appl. Phys. **33**, 329 (1962).

⁸ B. Bleaney and W. Hayes, Proc. Phys. Soc. (London) **B70**, 626 (1957).

TABLE II. Experimental results used in calculating relative f 's.

Temperature (°K)	Relevant figure where shown	A_A' (mm/sec) × (% absorption) ^a	A_B' (mm/sec) × (% absorption)	A_A (mm/sec) × (% absorption)	$f_B(T)/f_A(T)$	$f_B(T)/f_A(T)$ Av.	$f_B(T)/f_A(80)$
80		7.18	9.90	21.36	0.70	0.75±0.15	0.75±0.15
80	1	9.65	9.34	21.36	0.80		
296		4.95	2.38	17.36	0.19	0.24±0.08	0.19±0.08
296	5	12.55	1.40	17.36	0.29		
478	5	9.27	0.79	14.25	0.16	0.16±0.08	0.11±0.07

^a Background correction $\gamma \cong 1.25$ has not been included in A_A' , A_B' and A_A .

difficulty of quenching in the isolated state for large alkali-halide crystals, or possibly isolated Fe^{2+} is metastable in NaF as a result of the scarcity of free electrons in this environment.

It is possible to estimate the binding energy for the cobalt ions⁹ and positive-ion vacancies from the experimental data. The relationship¹ between the binding energy, E_B , and the probability of association, p , is

$$p/(1-p)^2 = 12c \exp(E_B/kT),$$

where c is the concentration of divalent impurities and the factor 12 is the number of positive-ion nearest neighbor positions, which for the present estimate is assumed to represent the only bound state. Although cobalt ion concentrations are not known in the present experiment, it is possible to estimate c and E_B by taking two values of p and T at a nearly constant concentration. In a quenching measurement from 854°K ($d \approx 0.04$ mm) the area under the A resonance indicated $p = F_A = 0.3$. After this quench the temperature dependence of A was measured (Figs. 3 and 4). The small variation of $f_A(T)$ indicates that $p \gtrsim 0.8$ at $T = 579^\circ\text{K}$. Using these two sets of values to solve for c and E_B from the above equation, we find $E_B \approx 0.55$ eV and $c \approx 30$ ppm. The theoretical estimate¹⁰ of the binding energy for a closed shell divalent ion is 0.4 eV. Thus, the estimated value is reasonable, particularly considering that Co^{2+} is not a closed-shell ion and covalency effects may enhance the binding at the nearest neighbor position. It should be noted that the systematic errors in this rough estimate of the binding energy would suggest a larger binding than calculated from the data.

The rate of annealing was not studied extensively, although it was noted that the annealing of B to A at low temperature was faster at high concentration, as expected on the basis of the present interpretation. At room temperature and at the concentrations typically used, it was noted that the conversion of B to A was very slow with a mean life greater than weeks. While this might be interpreted as evidence for the existence

⁹ Since the 14.4 keV isomeric transition of Fe^{57} occurs 10^{-7} seconds after the decay of Co^{57} , one measures the binding energy of the positive-ion vacancy to cobalt ions rather than iron ions, while the isomer shifts, field gradients and f values are those of the iron ion in its particular environment.

¹⁰ F. Bassani and F. G. Fumi, Nuovo Cimento **11**, 274 (1954).

of a charge state of $+1$ for isolated cobalt ions, the point will have to be investigated more carefully with known concentrations of cobalt before any conclusions can be drawn.

Perhaps the most interesting observation in the present experiment is that at high temperatures (300 to 500°K) the fraction of recoilless emitted γ rays from iron ions which are associated with vacancies is approximately four times as great as the fraction emitted from isolated substitutional impurities. This can be qualitatively understood on the basis of the difference in charge states for the two environments and the resulting difference in elastic constants. Since iron ions in the associated state have a charge of either $+2$ or $+3$ they will strongly attract the surrounding Cl^- ions to increase the binding of the iron ion and reduce the mean-square displacement of the ion, with a corresponding increase in the fraction of recoilless γ rays emitted. Possibly another important factor to consider is the difference in vibrational frequency spectra resulting from the difference in symmetry for the two environments and the difference in the net mass of the two defects, since the isolated state corresponds to replacing an Na^+ ion by

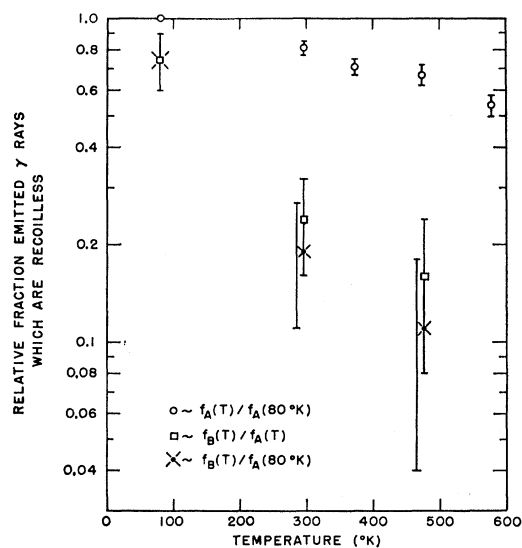


Fig. 6. Relative f values for the two types of Mössbauer spectra as a function of temperature.

an iron ion of approximately twice its mass while the associated state corresponds to replacing two Na^+ ions by an iron ion of about the same mass as the two ions it replaces. A quantitative estimate of the magnitude of these two effects will require a detailed theoretical treatment of the problem, which has not yet been attempted. The magnitude of the effect is so great, however, that even a crude calculation may be useful. It is interesting that the data on precipitated CoCl_2 indicate a temperature dependence of f which is between that found for the two cases considered here (see I).

The broad linewidth observed for the isolated iron ions (~ 1 mm/sec) may be the result of quadrupole broadening from a Jahn-Teller type distortion or a trapped hole in the vicinity of the iron ion, although no noticeable narrowing was observed as the temperature was raised.

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Neutron Scattering by an Anharmonic Crystal*

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Baym's treatment of coherent scattering of slow neutrons by a crystal is examined and modified to include effects due to the cubic-anharmonic term in the lattice potential to second order in the coupling constant. Corrections to the Debye-Waller factor and to the "one-phonon" resonance peak are obtained, which appear to be negligible ($\approx 0.01\%$) for the case of a Bravais lattice and certainly $< 1\%$ in other cases.

I. INTRODUCTION

WE would like to derive an expression for the coherent scattering cross section for slow neutrons, in which the anharmonic terms in the lattice potential are taken into consideration. Much work has been done on the problem of scattering from a perfect (harmonic) crystal,¹⁻³ where it is found that the coherent part may be written as a sum of terms representing scattering with absorption or emission of a number of phonons. The elastic term gives rise to peaks in the energy spectrum of the scattered neutrons (diffraction pattern) at the Bragg angles and the one-phonon term in the expression also gives rise to a δ -function peak at the phonon energy. It has been tacitly assumed that for a nonperfect crystal the one-phonon peak becomes broadened by the interactions into a Lorentzian shape whose width is the inverse of the phonon lifetime. Such lifetime effects may be described in terms of the phonon Green's function and it is the purpose of this study to see to what extent the singular features of the cross section are related to the Green's function.

The contribution from scattering with multiple phonon emission or absorption produces a continuous

background in the harmonic case and, by continuity arguments, also in the weakly coupled case.

Experiments by Brockhouse *et al.*⁴ have measured large widths in scattering from lead at high temperatures and some doubt has surrounded the form of the Debye-Waller factor. Although I have been unable quantitatively to explain these large widths (the theory, in any case, has treated the anharmonic nonmetallic crystal) the form of the result shows that for temperatures where such anharmonicities are considerable, one should expect a departure from the simple Lorentzian shape. This statement is very tentative because we have assumed weak coupling, working to second order in the coupling constant in a consistent manner.

The problem has been discussed by Brout,⁵ Baym,⁶ Krivoglaz,⁷ and Maradudin.⁸ Brout gives a general discussion of the energy spectrum of particles scattered from a system in terms of the widths and shifts of the states of that system. The approach of the other authors is a direct investigation of the formula for the coherent cross section. The present work follows on from Baym's analysis. We show that his result is applicable to a crystal with harmonic forces (including impurities and vacancies) but that it needs modification before being applied to the anharmonic case.

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¹ G. Placzek and L. Van Hove, *Phys. Rev.* **93**, 1207 (1954).

² A. C. Zemach and R. J. Glauber, *Phys. Rev.* **101**, 118 (1956).

³ L. S. Kothari and K. S. Singwi, *Proc. Roy. Soc. (London)* **A231**, 293 (1955).

⁴ B. N. Brockhouse, T. Arase, C. Caglioti, K. R. Rao, and A. D. B. Woods, *Phys. Rev.* **128**, 1099 (1962).

⁵ R. Brout, *Phys. Rev.* **107**, 664 (1957).

⁶ G. Baym, *Phys. Rev.* **121**, 741 (1961).

⁷ M. A. Krivoglaz, *Zh. Eksperim. i Teor. Fiz.* **40**, 1812 (1961) [translation: *Soviet Phys.—JETP* **13**, 1273 (1961)].

⁸ A. A. Maradudin and A. E. Fein, *Phys. Rev.* **128**, 2589 (1962).