Study of Iron Ions in NaCl Using the Mössbauer Effect.
I. The CoCl₂ Precipitated State*

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Single crystals of $CoCl_2$ containing tracer Co^{57} were grown by precipitation within NaCl at low temperatures. The observed Mössbauer spectrum for Fe^{57} indicates an isomer shift of 1.32 ± 0.04 mm/sec above stainless steel and a quadrupole splitting of 1.14 ± 0.06 mm/sec at 80°K, which is significantly less than has been observed in ionic-Fe^{2+} compounds. The small splitting can be largely explained by assuming a doubly degenerate ground state with the appropriate wave functions. The measured quadrupole splitting is reduced about 20% at room temperature which can be explained by arguments analogous to those used to interpret the temperature dependence of the splittings in iron compounds. The observed angular distribution of the intensities of the two lines demonstrates that the precipitated crystals near the surface are partially aligned in their spatial orientation. The data indicate only one charge state (Fe^{2+}), showing that higher charge states resulting from the emission of Auger electrons reach equilibrium in less than 10^{-7} sec.

I. INTRODUCTION

WHEN aliovalent positive ions are introduced into an alkali halide crystal, these ions are generally found to reside in a number of environments. In the case of Mn ions in NaCl, for example, Watkins[1] found, using electron-spin-resonance techniques, spectra which he was able to identify with precipitated $MnCl_2$, isolated Mn ions, and Mn ions which had a charge compensating positive ion vacancy associated with the divalent impurity ion. These three environments are in accord with theoretical expectations,[2–4] and there is much indirect experimental evidence which seems to correlate with this picture.[2] The present paper[5] (I) and the one that follows (II) are concerned with the study of the charge states and environments of Fe^{57} ions in NaCl using the Mössbauer effect as a microscopic probe to measure internal crystalline fields and electronic charge densities at the Fe^{57} nuclei. The spins of the ground state and 14.4-keV level of Fe^{57} are $\frac{1}{2}$ and $\frac{3}{2}$, respectively. Thus, an electric-field gradient at the nucleus will split the 14.4-keV level into two levels by means of interaction with the nuclear quadrupole moment. This effect has been observed in many ferrous and ferric compounds,[6–10] although the effect is generally small for the ferric compounds. The centroid of the Mössbauer resonance,

commonly referred to as the isomer shift, can be related to differences in the electronic charge density at the source nuclei compared with that at absorber nuclei,[9–11] which with the aid of calculated free ion wave functions can be useful in inferring the electronic configuration of ions in different environments.

The experiment described in I is intended to identify the charge state and quadrupole splitting for Fe ions in cobalt chloride which has been precipitated in a single crystal of NaCl. The possibility of multiple charge states resulting from Auger transitions, proposed by Wertheim,[12] is examined in the light of the present experimental data. Also, the possibility of using the precipitation technique for growing anhydrous and oriented single crystals is demonstrated.

II. EXPERIMENTAL TECHNIQUES

A. Velocity Spectrometer and Dewar Assembly

The Mössbauer resonances were observed using a mechanical velocity spectrometer, which produced a crank motion at the absorber. A schematic drawing of this mechanical system and the associated electronics is shown in Fig. 1. The synchronous motor and 100:1 gear reducer were shock mounted from the crank assembly and power was transferred to the crank via an elastic belt (made by Tilton Company). The pulleys used were measured to be concentric to 0.0002 in. in assembly, which meant that the error resulting from variations in pulley ratio were negligible. A large flywheel was attached to the crank to prevent any loss of synchronism between the motor and the crank assembly. Oilite bushings were used with clearances of less than 0.0002 in., and attempts to measure the net play in the crank assembly indicated that it was less than 0.0001 in. When a calibration experiment was performed using an iron source and absorber the full width at half-maximum approached that predicted from the lifetime

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[1] G. D. Watkins, Phys. Rev. **113**, 79 (1958).

[2] For a general discussion of the subject see A. B. Lidiard, in *Handbuch der Physik*, edited by S. Flügge (Springer-Verlag, Berlin, 1957), Vol. 20, p. 246.

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

[10] For a number of recent results, see *Proceedings of the Second International Conference on the Mössbauer Effect* (John Wiley & Sons, Inc., New York, 1962).

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

[12] G. K. Wertheim, Phys. Rev. **124**, 764 (1961).

FIG. 1. Schematic diagram of apparatus.

of the 14.4-keV level, which meant that vibrational broadening was certainly negligible for the present experiment involving an intrinsically broadened stainless steel absorber.

While the absorber executed a continuous reciprocating crank motion in time, γ rays from Fe^{57} nuclei were analyzed with a 20-mil-thick NaCl(Tl) scintillation crystal, photomultiplier, and single-channel analyzer. The pulses from the 14.4-keV γ rays were then sent into a 400-channel RIDL multichannel analyzer, which was operated as a multichannel scaler, with the channel address being advanced linearly in time, via an independent oscillator. The analyzer system was reset synchronously with the reciprocating motion by a pulse generated from a photodiode. Synchronism in the reset was held to 0.01 channels by operating the sine wave oscillator at 100 times the channel-stepping frequency. This frequency attenuation was accomplished with two scaler units in series. After a reset pulse, the first fast oscillator pulse sent into the divide by 100 unit was random to within one cycle of the fast oscillator or to 0.01 channels. Because of this synchronism the 14.4-keV pulses registered in a given channel corresponded to a unique absorber velocity, which was evaluated from the measured parameters of the crank motion by means of an IBM 704 computer. The frequency of rotation of the crank was recorded on each experiment by counting the number of reset pulses generated during the experiment. A 16-μsec delay circuit was used to avoid any interference between reset and address advance pulses. Different velocity ranges could be obtained by using different pulley arrangements. The maximum velocity range used in this experiment was ± 4 mm/sec, although

the mechanical system was capable of a much greater range.

Low source temperatures were obtained by attaching the NaCl crystal to the bottom of a container of liquid coolant. To avoid straining the crystal and at the same time to keep a good thermal contact, the crystal was encapsulated in Al foil and fastened to a copper plate with silicon grease between the foil and plate, but not in contact with the crystal. The Dewar was made of stainless steel with a Be window for transmitting the 14.4-keV γ rays. With liquid nitrogen as coolant the Cu plate was at a measured temperature of 80°K. In the experiments described in I and II the temperature was not monitored in all cases, and it is possible that in some cases the temperature was slightly greater than 80°K.

B. Preparation of Source and Absorber

The absorber consisted of a 1-mil-thick 302 stainless steel foil (natural iron), which had been annealed for several hours between two plates of quartz. The foil was mounted between two $\frac{1}{32}$-in. Lucite plates and was kept at room temperature. With a Co^{57} in Cu unsplit source, this absorber gave a full linewidth at half-maximum of 0.45 mm/sec.

The source was made by diffusing cobalt ions into a Harshaw NaCl crystal. About 10 mg of $CoCl_2 \cdot 6H_2O$ were added to a tracer quantity of hydrous Co^{57} Cl_2 (purchased from Nuclear Science), and the mixture was evaporated under vacuum onto a face of an NaCl crystal, giving a visible film ($\sim$1 mg) of cobalt chloride. The crystal was placed in a long Vycor tube which was closed at one end, and was arranged facing a second NaCl crystal with a small quartz ring between the two crystals making contact at the corners. The purpose of the second crystal was to minimize the loss of NaCl which left the active crystal by evaporation during the diffusion anneal. The Vycor tube was filled with one atmosphere of chlorine gas to prevent oxidation of the cobalt chloride on the surface of the salt crystal.

Temperature quenching of crystals was achieved by removing the vertical Vycor tube from the furnace and placing it in cold water. The time required to remove the crystal from the furnace and the low thermal conductivity of both Vycor and NaCl meant that the quenching speeds were limited. A calibration experiment indicated that the time required for the salt crystal to arrive at a temperature below 100°C from a 700°C anneal was of the order of 3 min. This quenching speed was slow enough, however, that no obvious strain effects, such as cracking or plastic deformation, were observed.

After the diffusion anneal the NaCl crystals were etched in concentrated HCl and ethyl alcohol. This procedure was to remove any cobalt oxide or cobalt chloride from the crystal surface. The HCl etch was not always performed since the chlorine atmosphere appeared to completely inhibit the conversion of $CoCl_2$ to CoO.

In order to estimate the concentration of cobalt ions after diffusion, three rough measurements of diffusion were made, using an etching technique. Although the diffusion measurements were done with tracer quantities of activity ($\sim$0.1 mCi) these measurements should be satisfactory for an order-of-magnitude estimate of the mean-diffusion depth, even at the high concentrations used to produce the precipitated state.

The diffusion anneal for the crystal used in the present experiment was performed in the temperature interval 600 to 450°C for 90 min. Using the measurements of the diffusivity, the mean penetration was estimated to be of the order of 0.1 mm, giving a concentration of cobalt ions of the order of or greater than 1% of the concentration of sodium ions. After quenching the specimen from 450°C, a bluish precipitate of $CoCl_2$ was observed within the NaCl crystal.

III. EXPERIMENTAL RESULTS

After diffusing the Co ions into the NaCl crystal and quenching to room temperature, the Mössbauer effect was measured at room temperature and at 80°K with the NaCl crystal oriented so that the [100] direction
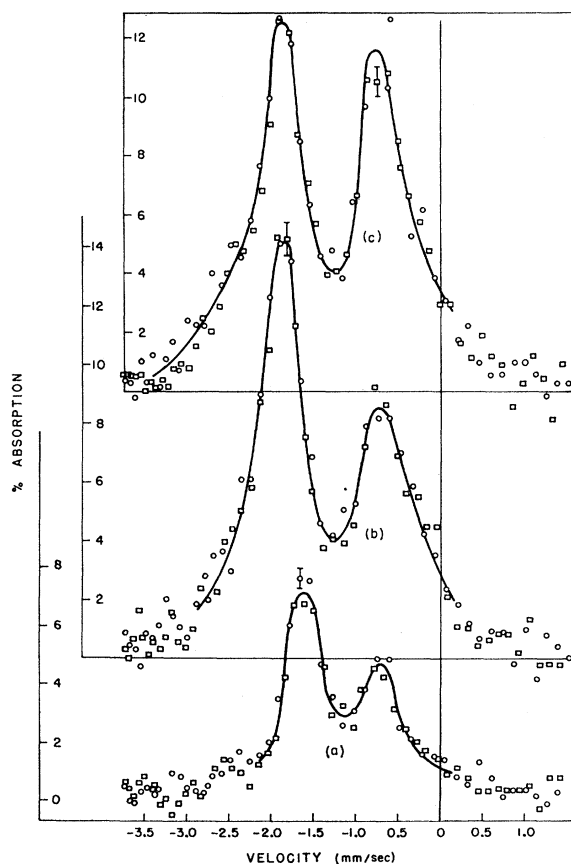
FIG. 2. Mössbauer spectra for precipitated $CoCl_2$ at different orientations and temperatures of the NaCl host (a) $T=296°K$, [100]; (b) 80°K [100]; (c) 80°K [110].

was parallel to the direction of motion. The resulting curves are shown in Figs. 2(a) and 2(b). The percent absorption has been calculated from the measured intensities, I, by the relation

$$\% \text{ Absorption} = 100[1 - I(v)/I(\infty)], \quad (1)$$

where $I(v)$ is the measured intensity at velocity v (taken as positive when source and absorber are approaching each other) and $I(\infty)$ is the measured intensity at velocities far from resonance. $I(\infty)$ was determined by averaging several values of I which were more than 20 times the natural line width from resonance. The absorption as determined by Eq. (1) is not corrected for background (B.G.). Even though the resolution of the scintillation system was good, it was estimated that only about 80% of the registered counts were from the 14-keV line, i.e., writing the absolute absorption as

$$\% \text{ Absorption absolute} = \gamma(\% \text{ Measured absorption}),$$

the measured value of $\gamma = I(\infty)/[I(\infty) - \text{B.G.}]$ was found to be 1.25. This measurement was made from time to time during the experiments described in I and II and values ranged from 1.2 to 1.4, which would indicate that this quantity is only accurate to about 10%. Because an accurate value for γ could not be established, the resonance curves are displayed without including this correction.

Two lines of different relative intensities are clearly resolved in Figs. 2(a) and 2(b), where the line drawn through the points represents a visual fit. In order to study the angular distribution of the emitted γ rays the NaCl crystal was reoriented with the [110] direction parallel to the direction of motion. The crystal was again lowered to 80°K and another resonance absorption curve was obtained. This is shown in Fig. 2(c). Since the relative intensities of the two lines has significantly changed, the angular distribution of the γ rays for the two lines is not isotropic, which indicates that a large fraction of the internally precipitated crystals had the same orientation.

It should be noted that the lines observed are broad. It is believed that this is because of an incomplete precipitation of cobalt chloride, resulting from quenching. The existence of isolated cobalt ions and vacancy-associated cobalt ions could explain this apparent broadening (see II).

After annealing the above crystal at 300°C and slowly cooling it to room temperature (rate was less than 1°C/min), the cyrstal was observed to have both a blue and white precipitate. By thoroughly etching the crystal it was possible to completely remove the blue precipitate leaving only the white. A Mössbauer resonance was again run at 80°K with the NaCl crystal oriented such that its [100] direction was parallel to the direction of motion, and the result is shown in Fig. 3. The absorption lines fall at the same velocities as before, although the intensities of the two lines are equal and the lines are as

narrow as could be expected for the particular stainless steel absorber used. Since the lines occur at the same velocities, the difference in color of precipitate is probably connected with the size of the precipitated crystals. Since the two lines were of equal intensity, it is reasonable to assume that only small crystalline precipitates exist after the heavy etch, and that these crystals are randomly oriented.

To verify that the precipitate studied was, in fact, $CoCl_2$, an experiment was performed on pure anhydrous $CoCl_2$ which was prepared with tracer $Co^{57}Cl_2$ on a quartz disk and encapsulated in black wax to avoid hydration. The Mössbauer spectrum was observed at 80°K and at room temperature and revealed two lines of nearly equal intensity occurring at the same velocities as found for the precipitated state. This experiment is not as informative as the study of the precipitated $CoCl_2$ and was only performed to verify the composition of the precipitate. It might also be noted in this connection that NaCl crystals prepared with high concentrations of precipitated $CoCl_2$ were found to be slightly porous following an initial etch so that the anhydrous $CoCl_2$ would slowly convert to a hydrated state in a period of days with the expected color changes. In a crystal in which some of the $CoCl_2$ had become hydrated a Mössbauer spectrum at room temperature indicated two quadrupole splittings, with the hydrated salt giving a splitting more than twice that corresponding to the anhydrous salt.

The experimental results for the precipitated state are summarized in Table I. Data for a Co^{57} in Cu source are also given, for purposes of reference, since the composition of stainless steel varies and there may be slight differences in the isomer shift as a result.

The lines drawn through the points represent a visual fit of the data. A procedure which is often used to evaluate peak positions and intensities is to fit either a Gaussian curve or a Lorentzian curve to data, allowing the linewidth and intensity to vary as parameters. Attempts by the writer to make such a fit did not prove satisfactory. When a Co^{57} in copper source was used
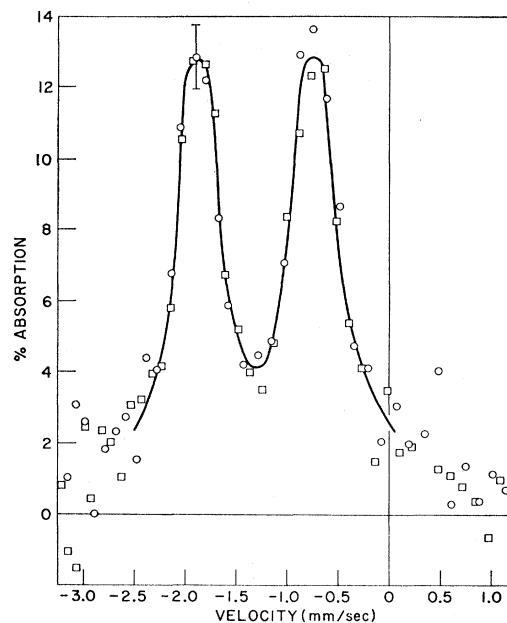
Fig. 3. Mössbauer spectra for precipitated $CoCl_2$ after considerable etching. The NaCl crystal was oriented with the [100] direction parallel to the direction of motion. In this case the absolute counting rate was about 10% of that for the data shown in Fig. 2.

with the stainless absorber, the single line of width 0.45 mm/sec could not be satisfactorily fitted with either a Lorentzian or a Gaussian distribution. When a good fit was obtained in the region of the resonance peak, the agreement in the wings of the resonance was completely outside of the experimental errors. Hence, the peak positions were determined by finding the points where the slope of the absorption curve went to zero. This was done by calculating the slope between each pair of measured velocities and fitting 4 to 6 slope values in the region of the peak to a straight line, from which the velocity at the point of zero slope was evaluated. The areas under the absorption curves were calculated on a computer in a straightforward manner.

Since the crank motion was reset once per revolution

TABLE I. Experimental results for high concentrations of cobalt.

Figure displaying related spectrum	Tempera- ture of run (°K)	NaCl Orientation rel. to direc- tion motion	Measured peak positions[a] (mm/sec)	Calculated quadrupole splitting[b] (mm/sec)	Calculated isomer shift above stainless steel absorber[b] (mm/sec)	Ratio of peak heights	Total area under absorption curve[c] (mm/sec) × (% absorp- tion)
2(a)	298	[100]	−1.62, −0.72	0.90±0.06	1.17±0.04	1.54±0.08	10.0±0.4
2(b)	80	[100]	−1.91, −0.72	1.19±0.06	1.32±0.04	1.64±0.08	20.9±0.6
2(c)	80	[110]	−1.90, −0.73	1.17±0.06	1.32±0.04	1.11±0.04	22.3±0.5
3	80	[100]	−1.89, −0.75	1.14±0.06	1.32±0.04	1.02±0.06	22.1±0.9
Fe⁵⁷ in Cu (not shown)	80		−0.44±0.02				20.5±0.5

[a] All errors are ±0.04 mm/sec, except where indicated otherwise.
[b] Calculation based on peak positions only.
[c] This number does not include the background correction $\gamma = 1.25 \pm 0.15$ necessary for calculating absolute absorption.

of the flywheel, all resonances were run twice. The circles and squares on the absorption curves are to differentiate the two half-cycles of the crank motion.

The systematic errors in the velocity for the present experiment were estimated to be less than ± 0.02 mm/sec. The errors resulting from limited counting statistics were about ± 0.04 mm/sec, as determined by the dispersion in the evaluated peak positions for the two half-cycles of the crank motion.

IV. DISCUSSION

The observed isomer shift of 1.32 mm/sec at 80°K is typical for ferrous compounds relative to stainless steel, and indicates that the Fe^{57} ion resides in the $CoCl_2$ lattice in the charge state $+2$. It is apparent that the precipitate is in a noncubic[13] crystalline form,[14] since a 1.14 mm/sec quadrupole splitting is observed at 80°K, with each line having a full width at half-maximum which is as narrow as could be expected for the particular stainless steel absorber used. This quadrupole splitting is much smaller than the 3 to 4 mm/sec splitting typically observed in ionic ferrous compounds[7–10] at this temperature. If it is assumed that the precipitate has trigonal symmetry[13] then the ^5D state is split into a doublet and a triplet, the latter being described by $Y_2{}^0$ and the appropriate linear combinations[15] of $Y_2{}^{\pm 1}$ and $Y_2{}^{\pm 2}$. If the triplet splits so that the state corresponding to $Y_2{}^0$ lies above the degenerate doublet, then the ground-state electric-field gradient will be $+\frac{2}{7}\langle r^{-3}\rangle$, or half of the magnitude of the $Y_2{}^0$ singlet. While the factor of 2 reduction in quadrupole splitting still does not completely account for the difference in the present observation compared with most iron compounds, the remaining difference can probably be accounted for on the basis of differences in covalency and Sternheimer polarization. The temperature dependence of the observed splitting can be explained by assuming that the singlet $(Y_2{}^0)$ is above the doublet ground state by an energy comparable to kT at room temperature. Thus, the reduction in splitting between 80 and 298°K would result from a superposition of all three states of the triplet, with the splitting decreasing as the temperature is raised, i.e., as the proba-

bility of occupying the $Y_2{}^0$ state increases. The magnitude of the reduction ($\sim 20\%$) is comparable to that observed for many ferrous compounds.[8]

It is clear from Fig. 2 that the angular distribution of emitted γ rays is not isotropic, indicating that the precipitate consists of partially aligned crystals of $CoCl_2$. It is interesting to note that if one assumes that 10% or more of the precipitated crystals are randomly oriented (the results shown in Fig. 3 indicate that this assumption is reasonable) then the ratio of the peak intensities in Figs. 1(a) and 1(b) is sufficiently great that the peak at $v=-1.89$ mm/sec, which lies higher in energy would correspond to the $m=\pm\frac{3}{2}$ state, since the relative intensities of the $\pm\frac{1}{2}$ to $\pm\frac{1}{2}$ transition is never greater than 5/3 of the $\pm\frac{3}{2}$ to $\pm\frac{1}{2}$ transition. This result indicates a positive electric-field gradient at the iron nucleus as is expected if the electronic ground state is the doublet rather than the $Y_2{}^0$ singlet. It is encouraging that the assumption of a doubly degenerate ground state is consistent with both the magnitude of the splitting and the relative intensities of the two lines.

It has been suggested by Wertheim[12] that higher charge states may exist for iron ions in insulating materials when they result from the decay of Co^{57}, because Auger transitions produce high charge states which may not reach electronic equilibrium in 10^{-7} sec, the lifetime of the isomeric transition. The present data on $Co^{57} \rightarrow Fe^{57}$ in crystalline cobaltous chloride does not seem to be in accord with this analysis. It does not seem likely that electrons are easier to obtain in a highly ionic material like $CoCl_2$ than in CoO studied by Wertheim. Also, it is easily seen why electronic equilibrium may be attained in 10^{-7} sec since the Auger electrons and the x rays that precede the 14-keV transition excite other electrons into the conduction band where they can be trapped by the excited, positively charged iron ions. Failure to observe higher charge states in $CoCl_2$ is encouraging, because it shows that these states are not likely to occur in other insulating materials. It is possible that Wertheim's results on CoO can be explained on the basis of Auger transitions by assuming that Fe^{+3} has only a slight affinity for electrons, and hence, is a poor electron trap, when in this particular environment. Such a fortuitous situation, however, is not likely to occur in many materials.

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[13] Wyckoff's tables of crystal structures indicate trigonal symmetry for $CoCl_2$.

[14] M. De Coster and S. Amelinckx [Phys. Letters **1**, 245 (1962)] observed a broad unsplit line which they attributed to a cubic precipitate for cobalt ions in KCl. Assuming there is not a fundamental difference between the precipitate in KCl and that in NaCl, the present results are not in accord with their findings. De Coster has indicated in a private communication that they are repeating their experiment and are finding "a larger half-width than with the earlier crystals," and that some of their latest specimens did not show any resonance absorption when prepared by the treatment which they had used in their earlier work. It should be noted in this connection that in the preliminary stages of the present investigation, the writer tried a technique for preparing sources which was similar to that used by De Coster and Amelinckx and found that cobalt chloride reacted with H_2O on the NaCl surface to form CoO, which has a similar Mössbauer spectrum at room temperature to that which they observed.

[15] See B. Bleaney and K. W. H. Stevens, Repts. Progr. Phys. **26**, 108 (1953), for explicit wave functions.