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Mössbauer Studies in Uncolored and Colored Co^{57} Diffused Single Crystals of KCl and NaCl

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Mössbauer spectra of uncolored, additively colored, and x-irradiatively colored KCl and NaCl single crystals diffused with Co^{57} are reported. Evidence of electron trapping effects by iron impurity ions was observed. It was also observed that the degree of ionicity and the mean-square amplitude of impurity-ion vibrations changed after additive coloration. The changes resulting from x-irradiation and the effect of optical bleaching are discussed. Efforts to find the site (interstitial or substitutional) for the Fe^{57} impurity ions in KCl as well as in NaCl were also made.

I. INTRODUCTION

Impurity ions in alkali halides are known to reside in various charge states and environments.[1,2] Electrons and holes which are released during the diffusion of excess alkali atoms (additive coloration) and on x irradiation of doped alkali halides are known to be trapped by the impurity ions.[1] Consequently, two important effects are observed: (i) the change of charge states of the impurity ions and (ii) the change of environment around the impurity ions owing to the movement of charge-compensating vacancies. Various techniques have been used to study these effects.[1] However, so far the Mössbauer technique has not been used in such studies. One of the motivations of the present work is to gather Mössbauer spectroscopic evidence for the above effects.

Exposure of irradiated alkali halides to optical wavelengths results in the bleaching of colored crystals. During this process a considerable rearrangement of thermally generated and impurity-induced cation vacancies takes place. In such a process, therefore, the immediate environment of the vacancies may change.[1] This can be detected using the Mössbauer technique. An attempt to study these effects has also been made and is reported here.

Recent electron paramagnetic resonance (EPR) experiments,[3] optical absorption studies,[4] and *F*-center growth-rate measurements[5] of cobalt-ion-doped alkali and silver halide crystals suggest the possibility of cobalt ions at the interstitial site. Iron ions in NaF are found to reside at the substitution site,[6] whereas no definite conclusion was drawn about the iron ion site in NaCl.[7] It is not clear, therefore, whether the Fe^{57} impurity ion formed by the decay of the parent Co^{57} radioactive impurity ion will reside at the interstitial site or at the substitutional site in NaCl and KCl. Efforts to find the site of the Fe^{57} impurity ions in KCl and NaCl are also made in the present work.

II. EXPERIMENTAL DETAILS

Single crystals of KCl and NaCl were grown by the Kyropoulos method from reagent-grade materials having less than 8-ppm background concentration of iron-group impurities. These crystals were heated to a temperature of 650 °C and were maintained at this temperature for 2 h. The crystals were then cooled to room temperature (RT) very slowly (at the rate of about 2 °C/min) in order to keep the strains in the crystals to a minimum. To diffuse Co^{57} in these crystals, 0.2 to 0.5 mCi of carrier-free $Co^{57}Cl_2$ was gradually evaporated at RT on the surface of the freshly cleaved crystals approximately $5\times4\times1$ mm^3. The crystals were kept at 110 °C for about 20 min inside a furnace in which dry and oxygen-free argon was flushed continuously. This was done in order to remove any residual moisture from the crystal surface. The temperature near the crystal was then raised to (545 ± 5) °C, and the crystal was kept at this temperature in a dry inert atmosphere for nearly 23 h. The crystal was then quenched from this temperature to RT to distribute the introduced impurity vacancy dipoles uniformly and to avoid the aggregation of the introduced impurity atoms. After this the crystal was etched in high-purity concentrated HCl and then washed in pure ethyl alcohol to remove any cobalt oxide or cobalt chloride from the crystal surfaces. The above diffusion procedure is essentially the same as the one used by De Coster and Amelinckx[8] and by Mullen[9] in the earlier work on KCl and NaCl, respectively. These Co^{57}-diffused crystals did not show any *F* color band when studied on a Unicam SP 500 spectrophotometer. We shall refer to these crystals as the uncolored crystals.

The additive coloration of the crystals was done as follows. A hard glass tube was "necked" down to form two sections. The potassium metal chips were placed in one section and the Co^{57}-diffused crystal in the other. The tube was then sealed under a vacuum of less than 10^{-2} Torr and was heated to a temperature of (560 ± 5) °C. The temperature of the section containing the potassium metal chips was about 30 to 50 °C lower than the other section. The stoichiometric excess of K^+ ions was thus introduced into the crystal owing to the diffusion of K atoms at high temperature. To achieve a uniform distribution of the excess potassium, the glass tube was kept at the above-mentioned temperature for about 30 h. After this prolonged heating, the crystal was quenched in the dark to RT in a time span of about 3 min. The crystal was then wrapped in thin black paper (to protect it from daylight which has been found to introduce new defect centers in such crystals[1]) and was mounted on a Mössbauer drive. The above procedure was used for the additive coloration of all crystals investigated. After recording the Mössbauer spectra, the crystals were unwrapped and mounted on Unicam SP 500 spectrophotometer to study their optical absorption. An intense *F* absorption band at 555 $m\mu$ in KCl and at 460 $m\mu$ in NaCl was observed in the additively colored crystals.

The coloration by x irradiation of the crystals was performed with the help of a Phillips x-ray diffraction unit operated at 30 kV and 20 mA with molybdenum as the target. The crystals were irradiated for about 7 h. These Co^{57}-diffused x-irradiated crystals will be referred to henceforth as x-colored crystals. As expected, these crystals also showed the characteristic colors of the *F* band.

The optical bleaching of these irradiated crystals was done by keeping the crystals at a distance of 30 cm from a 60-W tungsten lamp for about 10 min and then by keeping them in ordinary daylight for about 24 h. No color or *F* absorption band was seen in the optically bleached crystals thereby suggesting that the characteristic *F*-band color had vanished. Identical Mössbauer studies were made on these uncolored, colored, x-colored, and optically bleached crystals.

The Mössbauer spectra at RT were recorded using a mechanically operated constant-velocity drive. The orientation of the samples was such that the [100] direction was parallel to the direction of motion of the Mössbauer source. An Fe^{57} type-310 enriched stainless-steel foil was used as absorber.

A Co^{57}-diffused copper source (prepared by diffusion at 950 °C in a hydrogen atmosphere) was made to facilitate evaluation of *f*, the recoilless fraction in various crystals (see the Appendix).

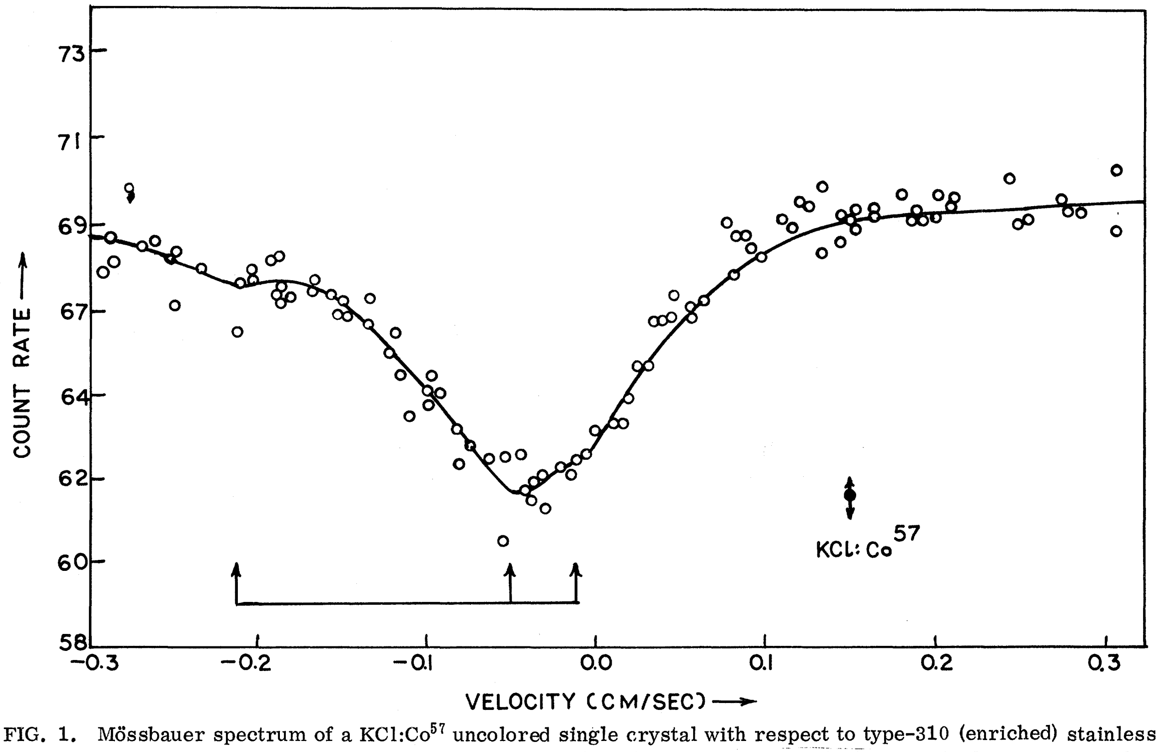

FIG. 1. Mössbauer spectrum of a $KCl:Co^{57}$ uncolored single crystal with respect to type-310 (enriched) stainless-steel absorber. Arrows show the peak positions and solid line the best-fit curve which gives the least-squares deviation.

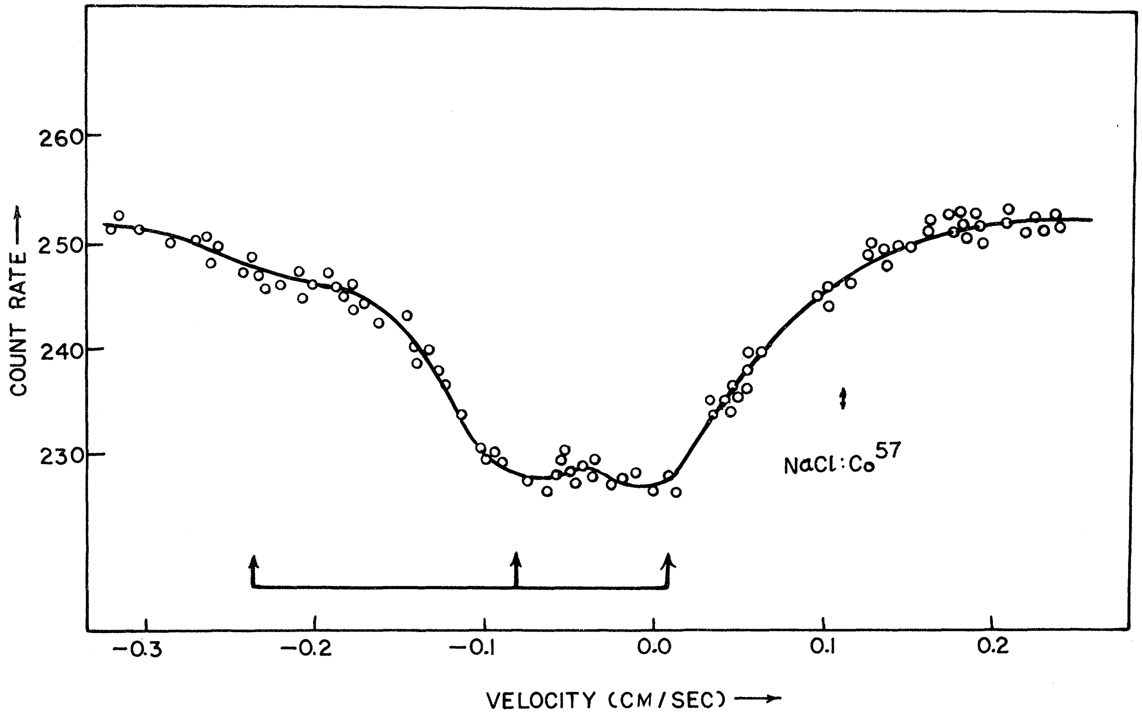

FIG. 2. Mössbauer spectrum of a NaCl:Co^{57} uncolored single crystal with respect to type-310 (enriched) stainless-steel absorber. Arrows show the peak positions and solid line the best-fit curve which gives the least-squares deviation.

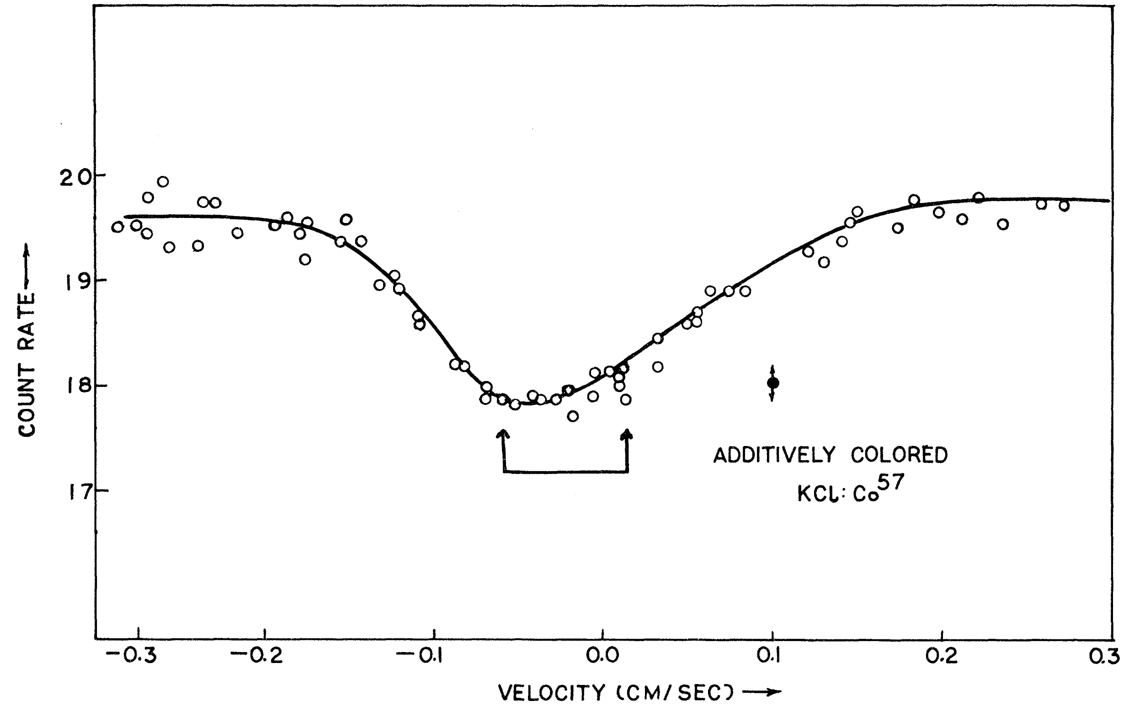

FIG. 3. Mössbauer spectra of KCl:Co^{57} additively colored single crystal with respect to type-310 (enriched) stainless-steel absorber. Arrows show the peak positions and solid line the best-fit curve which gives the least-squares deviation.

This source gave full widths of 0.050, 0.030, and 0.270 cm/sec at half the resonance absorption peaks with type-310 stainless steel, sodium nitroprusside, and potassium ferrocyanide, respectively, as the absorbers. The linewidth with type-310 stainless steel as absorber (0.050 cm/sec) was nearly the same as obtained by Mullen[9] in an earlier work. The enriched stainless steel was chosen in preference to potassium ferrocyanide and other narrow-line absorbers in the present study because of the fact that it gave the maximum absorption intensity of the resonance lines, which was necessary in view of significant statistical variations (~0.75%).

The geometry of the experimental setup was kept the same during all the measurements. The diffusion and coloration procedures were kept identical in both the NaCl and the KCl crystals. The background correction to the count rate for each activated sample was determined separately using a modified Housley method[10] (see the Appendix). All the spectra reported here were recorded at RT.

III. EXPERIMENTAL RESULTS AND ANALYSIS

A. Results

The Mössbauer spectra of uncolored KCl and NaCl single crystals are given in Figs. 1 and 2, respectively. The observed Mössbauer spectra of additively colored crystals (Figs. 3 and 4) are significantly different from those of uncolored crystals. The Mössbauer spectra of these colored crystals after they were exposed to daylight for about 24 h were exactly similar to the ones given in Figs. 3 and 4. As expected, the original color still persisted since the *F* centers in the additively colored crystals are difficult to bleach. As is clear from these figures, on coloring the NaCl crystal the area under its resonance line decreases appreciably. It was further observed that the thermal treatment of the colored NaCl crystal, by keeping the crystal at (470 ± 5) °C for 12 h in air and then slowly cooling to RT (a procedure called thermal bleaching), resulted in an increase in the area under the resonance lines. This spectrum is shown in Fig. 5. The Mössbauer spectra of x-colored KCl and NaCl crystals are shown in Figs. 6 and 7, respectively. The changes in the Mössbauer spectra on x irradiation of the crystals were only slight compared with the changes on additive coloration; a possible reason for which is discussed in Sec. IV B. The visible color in these x-colored crystals vanished after 10 to 15 min of optical bleaching. The Mössbauer spectra of these optically bleached x-colored crystals were recorded and were found to be exactly identical to Figs. 6 and 7.

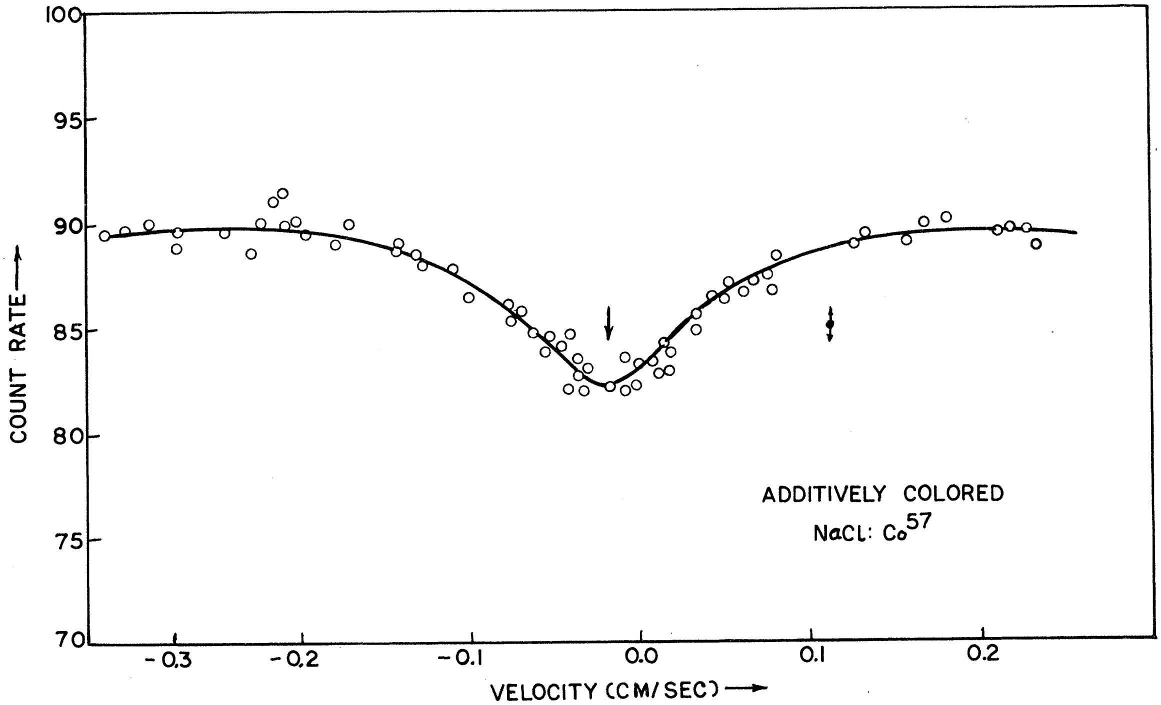

FIG. 4. Mössbauer spectra of a NaCl:Co^{57} additively colored single crystal with respect to type-310 (enriched) stainless-steel absorber. Arrows show the peak positions and solid line the best-fit curve which gives the least-squares deviation.

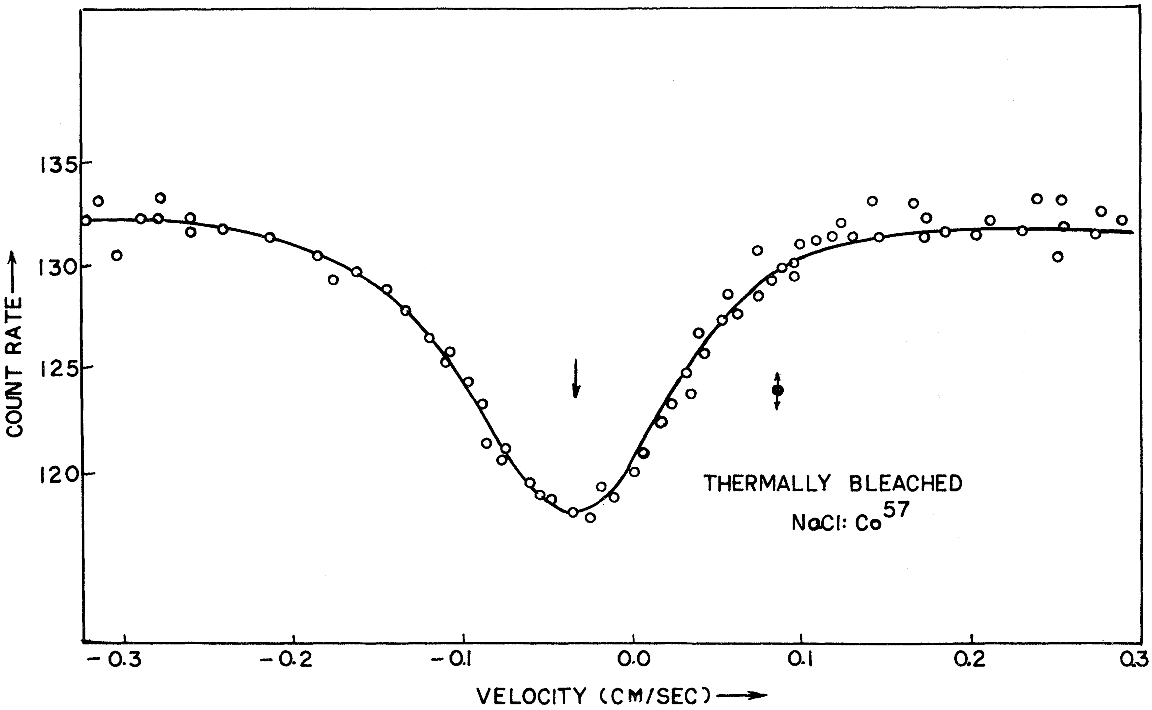

FIG. 5. Mössbauer spectra of a NaCl:Co^{57} crystal thermally bleached after additive coloration with respect to type-310 (enriched) stainless-steel absorber. Arrows show the peak positions and solid line the best-fit curve which gives the least-squares deviation.

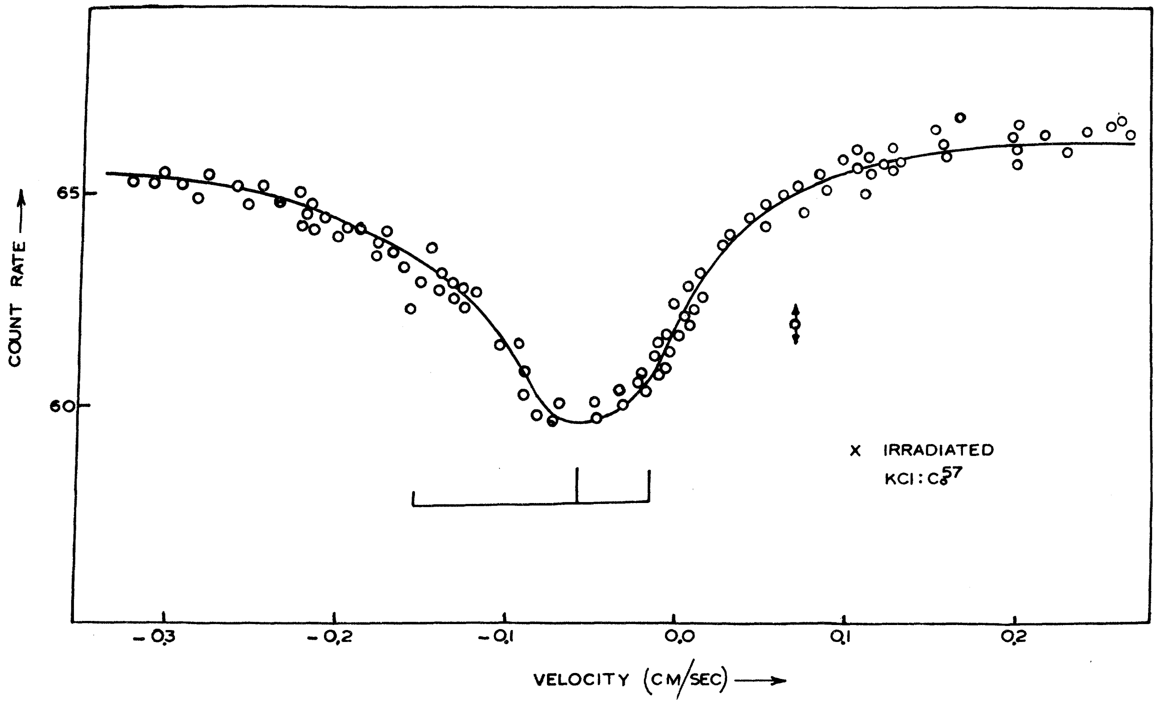

FIG. 6. Mössbauer spectra of a KCl:Co^{57} x-irradiatively colored single crystal with respect to type-310 (enriched) stainless-steel absorber. Arrows show the peak positions and solid line the best-fit curve which gives the least-squares deviation.

B. Analysis

It is clear from the various spectra that the individual lines are not well resolved and there is an appreciable broadening of the lines. The broadening of lines can be because of the inhomogeneous hyperfine interaction owing to the presence of lattice defects at various distances from the Mössbauer nuclei or to the relaxation of nonequilibrium charge states formed by Auger electron relaxation process, etc. As the nature of the spectra is complex, it was necessary to introduce certain assumptions to analyze the observations. It was assumed that the nonequilibrium charge states which could give rise to multiple charge states did not exist. This is supported by the fact that Fe^{1+} and Fe^{2+} charge states were found to be no less broadened than the Fe^{3+} state. Other assumptions were made: (a) Line shapes were assumed to be Lorentzian; (b) the number of lines, their widths, positions, and intensities which gave the minimum least-squares deviation using a least-squares differential correction technique and best-fit parameters were assumed to represent the spectra; (c) the isomer-shift (IS) diagram of Walker, Wertheim, and Jaccarino (WWJ)[11] was assumed to give the correct covalency and charge states; and (d) the iron charge states were assumed to be high-spin ionic in the case of highly ionic crystals such as KCl and NaCl.

The computer analysis of the uncolored KCl spectrum (Fig. 1) showed a single line at − 0.210 cm/sec, and on the basis of the IS diagram it was assigned a Fe^{1+} charge state.[8,9] The remaining portion of this spectrum could be fitted best with two lines, each 0.071 cm/sec wide, at − 0.015 and − 0.051 cm/sec, respectively. The possibility of a single broad peak instead of the above-mentioned two peaks was discarded due to the reasons that (a) a single line would clearly result in asymmetry in shape around the peak position and (b) the least-squares deviation had taken a much larger value. The interpretation of the two lines as the quadrupole partners of a Fe^{3+} state rather than two lines belonging to two different charge states (say, Fe^{2+} and Fe^{3+}) is based on the following reasonings. In the latter case, one of the lines will have an IS relative to sodium nitroprusside of 0.069 cm/sec. This would correspond to a Fe^{2+} state with more than a 30% 4*s* electron contribution,[11] in contradiction with the already mentioned assumption regarding the ionic character of iron ions. Further, Fe^{3+} and Fe^{2+}, if present, would induce cation vacancies to achieve the charge compensation. This would make the crystal field around these ions noncubic, resulting in the quadrupole splitting of the lines, and at least for Fe^{2+} it

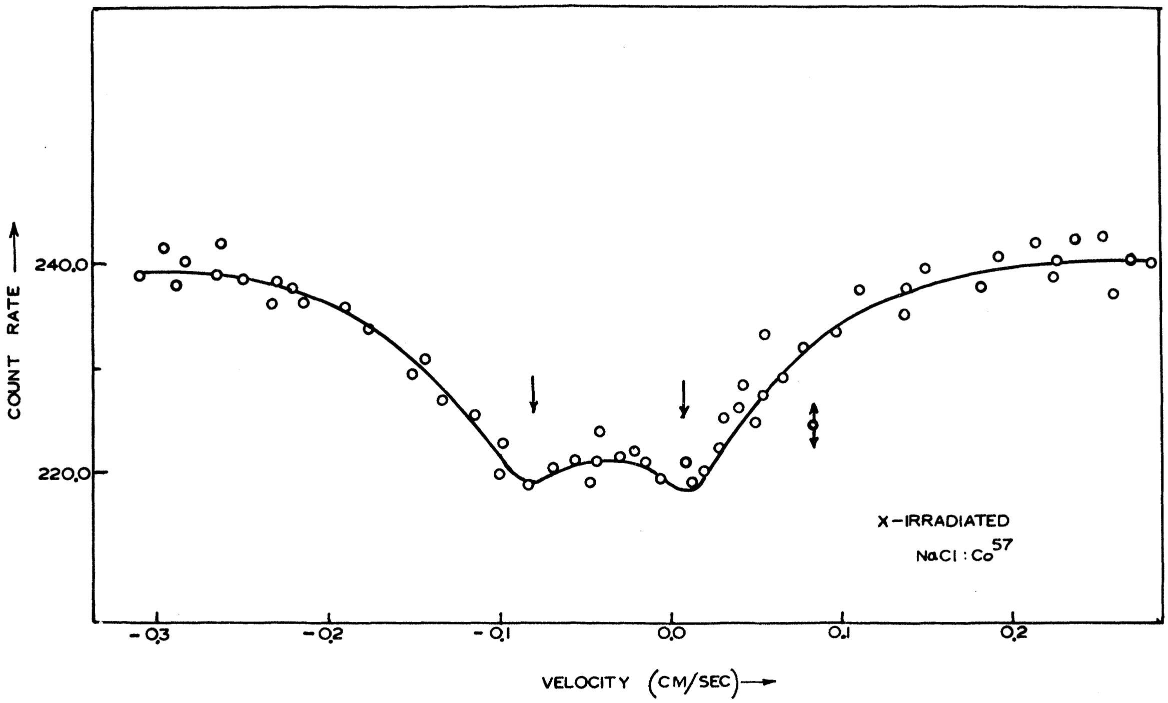

FIG. 7. Mossbauer spectra of a NaCl:Co^{57} x-irradiatively colored single crystal with respect to type-310 (enriched) stainless-steel absorber. Arrows show the positions and solid line the best-fit curve which gives the least-squares deviation.

would have been immediately detected.

The uncolored NaCl crystal spectrum (Fig. 2) when computer analyzed indicated a single line at − 0.220 cm/sec and was assigned a Fe^{1+} charge state. For the remaining portion of the spectrum, the assumption of two broad peaks 0.096 cm/sec wide each gave the lowest least-squares deviation and the best-fit parameter (96%). The interpretation of these two peaks as the quadrupole partners of a Fe^{3+} state rather than two lines belonging to the different charge states is based on the following arguments: In the colored NaCl crystal spectrum (Fig. 4), a single broad resonance line instead of a quadrupole doublet was observed. It is difficult to conceive of a mechanism by which two different charge states (say, Fe^{2+} and Fe^{3+}) can trap electrons released during additive coloration to produce a single unique charge state. However, if one considers that the charge states in the present spectrum are formed because of Auger electron relaxation effects then it might be possible that after additive coloration the energetics of the system favor Fe^{3+} formation only. But the ionicity and the charge-compensation considerations do not support this proposition.

The spectrum of a colored NaCl crystal (Fig. 3) showed a single broad line. Attempts were made to fit two or more lines but they all converged to a single line. This line corresponds to the Fe^{3+} charge state. In contrast to the colored NaCl spectrum, the colored KCl spectrum (Fig. 4) showed two resonance lines (quadrupole partners) which are partially overlapping, and a charge state of Fe^{3+} was assigned to these lines. The spectrum of Fig. 5 was analyzed in a way identical to the one used for the spectrum in Fig. 3. The analysis showed only one broad resonance line and this line was assigned to the Fe^{3+} state. X-colored KCl and NaCl spectra have the same features as the corresponding uncolored crystals, the major difference being the vanishing of the Fe^{1+} resonance lines on x irradiation. The spectra of these crystals were thus analyzed in the same way as the spectra of uncolored crystals. Tables I and II sum up the various quadrupole splittings and IS, etc., obtained from the analysis of various spectra (Figs. 1-3).

IV. EFFECT OF COLORATION ON IRON IMPURITY IONS

A. Additively Colored Crystals

Mössbauer spectra of additively colored KCl and NaCl crystals did not show a Fe^{1+} resonance. The absence of Fe^{1+} resonances after coloration can be explained by closely examining the coloration mechanism. On heating alkali halide in potassium vapor at (560 ± 5) °C, the K atoms (vapors) diffuse into the crystal (the vapor pressure of K is about 55 Torr at 560 °C). The K atoms then dissociate into K^+ ions and electrons. On quenching such a crystal to RT, the excess alkali ions occupy normal lattice sites, and the electrons are trapped in the anion vacancies forming F centers.[1,12] In the presence of impurity ions, these electrons may get trapped by the impurity ions too. This would result in lowering the valence state of impurity ions. The above argument is a well-established fact in color-center spectroscopy and, in fact, some indirect evidence of the electron trapping by the divalent impurity ions in the alkali halides has been reported from optical and ionic-conductivity measurements in impurity-doped additively colored crystals.[1,13] The Fe^{1+} ion in the alkali halide might trap an electron resulting in the formation of Fe^0. The Fe^0 center thus formed may have electronic structure $3d^8$ or $3d^7 4s$ depending upon the energetics. According to the WWJ IS diagram, the $3d^8$ and the $3d^7 4s$ states should have ISs relative to stainless steel of 0.19 and 0.0 cm/sec, respectively. The 0.19-cm/sec line was not seen in KCl or in NaCl. Hence, the $3d^8$ state, if present, should have very weak binding with the host. The resonance owing to the $3d^7 4s$ state of the Fe^0 center, if present, would be completely masked by the strong resonance lines of Fe^{3+} resonance. Another possibility is that the cobalt ions (presumably Co^{2+}) could also capture an electron before the transition, and this might change the probabilities for various valence states after the transition and the Auger readjustments. However, it is difficult at present to make conclusions one way or the other but the observation of the effect discussed above is clear and important and needs further investigation.

Another interesting observation was the decrease in the ISs of the Fe^{3+} state in both KCl and NaCl on coloration. According to the WWJ plot, this decrease should represent a decrease in the degree of ionicity of Fe^{3+} ions. A possible explanation of this observation is as follows. In alkali halides, the charge states higher than 1+ result in the formation of impurity vacancy dipoles. Each of the Fe^{3+} ions, therefore, is surrounded not only by six neighboring Cl^{1-} ions but also by the cation vacancies. A cation vacancy behaves effectively as a negative charge in the lattice, and thus the total negative charge surrounding the Fe^{3+} ion will be greater than the total negative charge surrounding the Fe^{1+} ion. An electron released during the dissociation of K^+ atoms in an additive-coloration process will thus have larger probability of penetrating the negatively charged shield around Fe^{1+} than around Fe^{3+}. In such a case, therefore, while the charge state of Fe^{1+} can change completely, the charge state in Fe^{3+} may still remain the same and only the change in the degree of ionicity might be observed.

As is apparent from the quadrupole splitting data (Table I), while the crystal field around Fe^{3+} in the case of NaCl becomes cubic after additive coloration the same is not observed in KCl, and an appreciable change in the magnitude of the quadrupole splitting is seen. In fact, the field around Fe^{3+} becomes more noncubic. Further, the area under the resonance lines in NaCl shows a significant decrease, while in KCl there is a noticeable increase in the total area under the resonance lines. A possible explanation for the different behaviors in KCl and NaCl can be that the lattice site of iron impurity ions in KCl is substitutional while in NaCl it is interstitial. This point will become more apparent in Sec. V when we take up the discussion on recoilless fraction and quadrupole splitting in the uncolored crystals.

From the area under the resonance line, the Mössbauer–Debye temperature Θ_M for the Fe^{3+} ions in colored crystals is about 173 °K, while in the uncolored crystal it is about 255 °K (see the

TABLE I. Isomer shift relative to sodium nitroprusside (cm/sec), quadrupole splitting (cm/sec), and area of the resonance lines (after correction for background and assuming area with Cu : Co^{57} source as unity) in Co^{57}-diffused samples using a type 310 stainless-steel absorber.

Host lattice	Crystal	Experimental parameter		Valence state	
			Fe^{3+}	Fe^{1+}	Fe^{2+}
KCl	Uncolored (KCl : Co^{57})	IS	0.051 ± 0.003	0.230 ± 0.005	...
			0.052[a]	...	...
		Quadrupole splitting	0.036 ± 0.003	...	...
			0.042[a]	...	...
		Area	0.52 ± 0.04	0.035 ± 0.005	...
	Additively colored KCl : Co^{57} (K^+)	IS	0.040 ± 0.003	...	...
		Quadrupole splitting	0.072 ± 0.003	...	...
		Area	0.60 ± 0.03	...	...
	x irradiated KCl : Co^{57} (X)	IS	0.051 ± 0.003	...	0.171 ± 0.005
		Quadrupole splitting	0.046 ± 0.005	...	...
		Area	0.48 ± 0.03	...	0.040 ± 0.005
NaCl	Uncolored (NaCl : Co^{57})	IS	0.056 ± 0.003	0.238 ± 0.005	...
			0.061 ± 0.003[b]	...	...
		Quadrupole splitting	0.098 ± 0.004	...	...
			0.051 ± 0.006[b]	...	...
		Area	0.69 ± 0.02	0.010 ± 0.004	...
	Additively colored NaCl : Co^{57} (K^+)	IS	0.038 ± 0.004	...	...
		Quadrupole splitting	...	...	...
		Area	0.36 ± 0.02	...	...
	Thermally bleached NaCl : Co^{57} (T)	IS	0.050 ± 0.003	...	...
		Quadrupole splitting	...	...	...
		Area	0.53 ± 0.03	...	...
	x irradiated NaCl : Co^{57} (X)	IS	0.055 ± 0.003	...	...
		Quadrupole splitting	0.098 ± 0.004	...	...
		Area	0.69 ± 0.02	...	...

[a] Reference 8.

[b] Reference 9.

TABLE II. Recoilless fraction f and Mössbauer–Debye temperatures Θ_M at RT for an Fe^{3+} state in uncolored and colored Co^{57}-diffused KCl and NaCl.

Sample	State	f	Θ_M (°K)
KCl : Co^{57}	Fe^{3+}	0.36 ± 0.04	203 ± 10
NaCl : Co^{57}	Fe^{3+}	0.51 ± 0.04	246 ± 10
KCl : Co^{57} (K^+)	Fe^{3+}	0.44 ± 0.04	223 ± 10
NaCl : Co^{57} (K^+)	Fe^{3+}	0.26 ± 0.03	173 ± 8
NaCl : Co^{57} (T)	Fe^{3+}	0.37 ± 0.04	205 ± 10

Appendix and Table II). The localized modes or gap modes [14,15] owing to the foreign impurity ions are known to influence Θ_M. However, both these modes are absent in the present case since (i) the additively diffused K^{1+} ions are heavier than Na^{1+} and Cl^{1-} ions, and (ii) the phonon spectrum of NaCl is known to exhibit no gaps. The change in Θ_M in NaCl on additive coloration can be explained as follows. The additively diffused K^{1+} ions occupy the neighboring cation vacancies around the Fe^{3+} impurity ion and thereby reduce the binding of the impurity with the host. Support to the above proposition came from the following additive result: It is well known[1] that on heating an additively colored crystal to a temperature of about 250 °C and then slowly cooling the crystal, the colloids of K atoms and the F aggregate centers are formed. By this process, called thermal bleaching, the concentration of K^{1+} ions in the interior of the crystal is very much reduced. This is because of the thermal diffusion of excess cations from the interior to the crystal surface owing to the higher vapor pressure of cations at high temperatures. On slowly cooling the crystal subsequently, the excess cations do not redistribute to the original configuration. Therefore, if Θ_M had decreased because of the excess K^{1+} ions at the cation vacancy sites around the Fe^{3+} impurity ions, on removal of these excess cations in the thermal bleaching process, Θ_M should increase. We have indeed observed that on thermal bleaching of the additively colored NaCl crystals, Θ_M for Fe^{3+} ions increased from 173 to 205 °K (Table II).

No change in the Mössbauer spectrum following an exposure of the additively colored crystals to visible light could be detected in either of the Co^{57}-doped crystals. The Mössbauer technique sees only the Mössbauer isotope and it can therefore be concluded that the exposure of additively colored crystals does not affect the impurity centers and the neighboring vacancies. It implies therefore, that the bleaching effects observed in optical spectra are associated with the effects produced at the F centers and not at the impurity ions and their vicinity.

B. X-Colored and Optically Bleached Crystals

As pointed out in Sec. III A, the changes in the Mössbauer spectra on x coloration are only slight compared to the ones observed on additive coloration. This can be attributed to the fact that (i) the x coloration does not normally change the stoichiometry of the crystal and (ii) it is mostly the surface layers that are affected on x irradiation. While no optical absorption measurements in the uncolored and in the x-colored iron-doped alkali halides have been reported so far, several EPR studies in these alkali halides have been made.[3,6,7] In the EPR work of Hayes[3] and of Andrews and Kim[6] the Fe^{2+} state in the uncolored NaF, though speculated, could not be observed possibly due to the influence of the lattice defects resulting in the large broadening of the EPR signal. After x irradiation, Hayes[3] could see only Fe^{1+}, while Andrews and Kim[6] had seen both Fe^{1+} and Fe^{3+}. Wertheim and Guggenheim[16] had observed the Fe^{3+} state in Co^{57}-doped NaF in the uncolored crystals also when the sample preparation was done in air. All these studies have one thing in common: Charge conversion of the impurity ions takes place on x irradiation owing to the trapping of the released electrons and holes by the impurity ions. Results obtained in the present samples showed Fe^{1+} and Fe^{3+} prior to x coloration and on x coloration it was observed that (i) no charge conversion of Fe^{3+} ions was observed; (ii) unlike additive coloration, no significant changes could be noticed for Fe^{3+} resonances; and (iii) no Fe^{1+} resonances were observed; instead, a weak line corresponding to almost ionic Fe^{2+} state was observed in the case of KCl only. Observation of the vanishing of the Fe^{1+} resonances following x coloration can be explained on the arguments identical to the ones advanced in Sec. IV A for additive coloration. The appearance of a weak Fe^{2+} resonance in KCl is an interesting and important observation and is perhaps due to the trapping of the holes released during x irradiation by some of the Fe^{1+} impurity ions. However, in the absence of detailed work, nothing definite can be concluded.

V. LATTICE SITE OF IRON IN UNCOLORED CRYSTALS

Optical absorption[4] and F-center growth-rate measurements[5] in cobalt-doped alkali halides suggested the possibility of cobalt at the interstitial site and the same state is favorable from ionic radii considerations also. (Co^{2+} ionic radius is much smaller than many other transition-metal ions.) No such studies are available for iron-doped alkali halides. The EPR studies[6] in iron-doped NaF give evidence for the iron impurity at the substitutional site. One is not in a position, therefore, to predict the site of iron impurity ions at the time of Mössbauer transition since in the present study Co^{57} parent nuclei decay to Fe^{57m}, which in turn return to the ground state following the Mössbauer transition. In this section, we make some attempts to discuss the lattice site of iron at the time of Mössbauer emission from recoilless fraction and quadrupole splitting results in Co^{57} diffused uncolored KCl and NaCl crystals. As pointed out earlier, the characteristics of the Fe^{3+} charge state in colored NaCl are different from that in colored KCl. Different iron sites in these two cases could possibly be a reason for this behavior.

Since the masses of K^{1+} and Cl^{1-} are nearly equal, we assume KCl to be a monatomic crystal. If the iron impurity of mass m_0 occupies a substitutional site, the Debye-Mössbauer factor Θ_M can be written in terms of the Debye temperature Θ as [17]

$$\Theta_M = \Theta\ (m/m_0)^{1/2}, \qquad (1)$$

where m is the mass of the host atom. The force constants for the impurity-host atoms and the host-host atoms are assumed to be the same. From the RT value of $\Theta = 235$ °K, [18] Eq. (1) gives $\Theta_M = 191$ °K. Thus, if the Fe^{3+} occupies a substitutional site in $KCl: Co^{57}$, Θ_M is expected to be around 190 °K. To stabilize a Fe^{3+} ion the required binding force is greater at the interstitial site than at the substitutional site. For example, Triftshäuser and Schroeer[19] have observed $\Theta_M = 600$ °K for an interstitial iron ion and $\Theta_M = 250$ °K for a substitutional iron ion in $Cu_2O : Co^{57}$. No theoretical attempts have so far been reported to obtain a relation for the Debye temperature for an *interstitial* impurity in any host material. Equation (1) follows from the fact that the Debye temperature is proportional to the Debye frequency and hence is inversely proportional to the square root of the masses of the atoms and therefore to the density of the lattice points. For an interstitial iron atom, the local lattice density will roughly be eight times greater than that for a substitutional iron atom. Using this lattice density argument, if the value of Θ_M for iron at the substitutional site is taken as 191 °K, correspondingly the value for the interstitial iron site should be around 540 °K. The experimentally observed value of Θ_M equal to (203 ± 10)°K for the Fe^{3+} ions in $KCl: Co^{57}$ (Table II), therefore, suggests that the Fe^{3+} ions are at the substitutional site. It should be mentioned that the above arguments are based upon the presumption that cation vacancies which are induced by the higher charge state of an iron impurity do not alter the force constants. Equation (1) cannot be used to estimate the value of Θ_M for iron in NaCl since the masses of Na^{1+} and Cl^{1-} are different. As stated earlier (Table I), the quadrupole splitting of the Fe^{3+} ion in NaCl was 0.098 cm/sec. Such a large quadrupole splitting suggests Fe^{3+} ions at the interstitial site. This is due to the fact that the various vacancies that create the distortion are nearer to a Fe^{3+} ion located at an interstitial site than if the Fe^{3+} ion is located at a substitutional site. If one qualitatively extends the KCl discussion to NaCl, one would expect Θ_M for an interstitial Fe^{3+} ion in NaCl to be around 540 °K. The experimentally observed value, however, is (246 ± 10) °K. Hence, there is an apparent contradiction of results obtained from quadrupole splitting and from Θ_M values. Further, for the uncolored crystals, while the KCl results are in agreement with the ones of De Coster and Amelinckx, [8] (Table I), the NaCl results for Fe^{3+} ions are different from those of Mullen. [9] These are interesting observations and need further investigation.

APPENDIX

Besides the 14.4-keV γ rays, one also counts in any experimental setup some radiation due to low-energy x rays, and 122- and 136-keV γ rays. These undesirable counts which are velocity independent are referred to as the background counts. The area under the Mössbauer spectrum, if corrected for the background, is directly proportional to the recoilless fraction f_m. This can be seen from the following well-known expression:

$$s = f_m \pi t_A e^{-t_A/2} \left[I_0(\tfrac{1}{2} i t_A) + I_1(\tfrac{1}{2} i t_A) \right] , \qquad \text{(A1)}$$

where $t_A = n f^1_m \sigma(\epsilon_0)$; $I_0(\frac{1}{2} i t_A)$ and $I_1(\frac{1}{2} i t_A)$ are the zero- and the first-order Bessel functions, respectively, of the imaginary argument t_A; n is the number of resonantly absorbing nuclei per cm^2 of the absorber; and f_m and f^1_m are the Mössbauer emission and absorption probabilities in the source and the absorber, respectively. $\sigma(\epsilon_0)$ is the resonant absorption cross section of the absorbing nucleus for γ energy ϵ_0. This equation is based on the assumption that self-absorption in the source is negligible. This is usually justified and works well provided that the concentration of Mössbauer nuclei is not large. It is clear from the above discussion that for a particular absorber (enriched type-310 stainless steel in the present work) and a fixed geometry of the setup, the ratio of the background-corrected areas under the resonance will be in the ratio of the corresponding recoilless fractions in the two different sources to a fairly good degree of accuracy. Precise measurements of f_m for Co^{57} diffused in copper using the black-absorber technique are available from the work of Nussbaum, Howard, Nees, and Steen. [20] Using their value of f_{Cu} as 0.710 at RT, we evaluated f in NaCl and KCl for the Fe^{3+} state of Fe^{57} by the above-mentioned area ratio method. Background correction for areas was determined separately for each run of the spectrum by finding the intensity ratio of 14.4-keV γ rays and the other x rays and γ rays using the method suggested by Housley, Erickson, and Dash.[10] It should be noted that Eq. (A1) strictly holds only if one charge state is present. However, since the intensity of Fe^{1+} resonance lines is much smaller than the Fe^{3+} lines, Eq. (A1) holds to a good approximation.

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Symmetrized Multipulse Nuclear-Magnetic-Resonance Experiments in Solids: Measurement of the Chemical-Shift Shielding Tensor in Some Compounds[*]

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An experimental study of the properties of one form of the three-state reflection-symmetry cycle is presented. The cycle and its compensated form are used to measure the chemical shielding tensor of ^{19}F in polytetrafluoroethylene [$(C_2F_4)_n$], and ^{31}P in powdered zinc phosphide (Zn_3P_2). The effect of phase errors is discussed and the principle of phase compensation is demonstrated in a phase-alternated sequence. Amplitude-modulation effects of phase errors are also discussed.

I. INTRODUCTION

In most solids which have a nuclear-spin species the dominant spin-spin magnetic interaction is via the nuclear dipole-dipole coupling. It was recognized a long time ago[1,2] that high-speed rotation of the specimen about the so-called "magic axis" could substantially reduce the magnetic dipolar interaction tensor but not the isotropic parts of the chemical shift or shielding tensor or the isotropic part of the electron-coupled nuclear pseudodipolar interaction or exchange interaction. Indeed, as with random motion in a mobile liquid, one obtains the familiar structured high-resolution spectra.

More recently,[3-11] it has been shown both theoretically and experimentally that irradiation of solids with certain multipulse sequences can also selectively remove or reduce the dipolar interaction thus revealing previously hidden and usually more interesting interactions in solids. This is because these smaller interactions reflect the