Time Dependence of Recoil-Free Resonance following Electron Capture in Co57

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The use of delayed-coincidence techniques in conjunction with the Mössbauer effect permits measurements of the time evolution of the Mössbauer resonance following formation of the resonant nuclear level. A series of measurements are reported in which the time dependence of Fe^{57} chemical charge states was studied for sources of Co^{57} (which decays to Fe^{57}) embedded in various compounds: CoO, NiO, $Fe(NH_4)_2$-$(SO_4)_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$, and $CoCl_2 \cdot 4H_2O$. These are systems in which the resonance spectra had previously been interpreted in terms of metastable chemical charge states possessing lifetimes comparable to the nuclear life time (100 nsec). In no case were time effects observed which could not be attributed to "time filtering" of the emitted radiation by the resonant absorber. The appearance of multiple emission lines is interpreted in terms of equilibrium between ferric and ferrous ions, the relative intensities probably being determined by the amount of deviation of the samples from stoichiometry.

I. INTRODUCTION

THE Mössbauer effect (hereafter denoted by the abbreviation ME) has been used in a wide variety of solid-state experiments. One application is as a means to study time-dependent processes occurring on time scales comparable to the lifetimes of the particular nuclear levels used.

Such experiments are difficult, and the only cases in which time-dependent effects have been directly observed are related to the quantum-mechanical nature of the decay process. These experiments showed the phenomena usually designated as "time filtering." Several experiments have been performed in which the time development of the ME spectra was not directly observed, but in which the measurements were interpreted in terms of processes occurring on time scales comparable to those of the nuclear levels. We shall be concerned with measurements designed to test the interpretation of one class of such experiments—those interpreted in terms of the occurrence in certain chemical compounds of metastable multiple-charge states of Fe processing intermediate-state lifetimes comparable to the 140-nsec mean lifetime of the 14-keV level of Fe^{57}. Our major conclusion is that, in the systems we have thus far investigated, no significant effects occur on this time scale. A discussion of some of the results presented in this paper has previously appeared.[1]

II. BACKGROUND

A. Nuclear Properties and Auger Processes

The nuclide most commonly used in ME experiments, and the one used exclusively in the experiments reported

here, is Fe^{57}. This is formed by electron capture of the parent nuclide Co^{57}. The nuclear properties of this decay, and the reasons why this isotope is well suited for ME studies, have been extensively discussed.[2-4] Co^{57} (half-life 270 days) decays by electron capture, with a K/L conversion ratio of about 8.9. The resulting nuclear state is Fe^{57} excited to 137 keV. After about 8 nsec this level decays, about 9% of the time to the Fe^{57} ground state with the emission of a 137-keV gamma, and about 91% of the time to the 14-keV level with the emission of a 123-keV gamma ray. The mean lifetime of the 14-keV level is 140 nsec, and its decay is either by emission of a 14-keV gamma ray or through internal conversion (internal conversion coefficient $\alpha = 9$).

In order to discuss the concept of metastable multiple-charge states and their possible occurrence in chemical compounds, it is necessary to discuss the events which may occur following electron capture in the parent Co^{57}. Electron capture takes place predominantly from the K electronic shell, and with reduced probability from the L, M, etc., shells. Simultaneously, a neutrino is emitted with an energy spectrum having a maximum energy of 600 keV. The neutrino emission produces recoil of the emitting atom with a maximum energy of 3.4 eV. Under certain circumstances this energy might be great enough to cause radiation damage through displacement of the decaying atom, but such effects have as yet not been observed. (The recoil energy following neutrino emission greatly exceeds the recoil energy of 0.14 eV associated with the decay of the 123-keV level.) The decaying nucleus is now left in the 137-keV level, while the electron struc-

[1] W. Triftshäuser and P. P. Craig, Phys. Rev. Letters 16, 1161 (1966).

[2] H. Frauenfelder, *The Mössbauer Effect* (W. A. Benjamin and Company, New York, 1962).
[3] H. Wegener, *Der Mössbauer Effekt und Seine Anwendung in Physik und Chemie* (Bibliographisches Institut Mannheim, Mannheim, Germany, 1965).
[4] *Nuclear Data Sheets*, compiled by K. Way *et al.* (Printing and Publishing Office, National Academy of Sciences—National Research Council, Washington 25, D.C.).

ture is that of Co^{57}, but with one low-lying electron missing. A rapid redistribution of electrons (the time scale is probably 10^{-15} sec) next occurs[5] through Auger processes, in which outer orbital electrons fall into and fill vacant electronic levels. The resultant energy release can have various effects, of which an important one is the ejection of some of the electrons (Auger electrons). Should the decaying atom be located in a gas, no electrons are available to neutralize the system and the end result can be very highly charged atoms. Distribution of final charge states up to about charge $+30$ have been experimentally observed in gases (such as Xe) by means of mass spectrometry.[6]

In solids the situation is considerably different, for highly charged atoms following the Auger processes possess a very high Coulomb potential, and may be expected to rapidly accumulate electrons from the local environment. In the case of Auger processes in a metal, the great abundance of conduction electrons assures that within a rather short time the Fe^{57} nucleus will come into complete equilibrium with its surroundings.

In an insulating medium there exists a possibility for the later stages of the equilibration process to proceed at a relatively slow pace, possibly slow enough as to permit experimental observation. The first experiments which were amenable to this interpretation were those of Wertheim using the ME to study Co^{57} in CoO.[7]

B. Previous Experiments and Interpretations

CoO is fcc with the NaCl structure.[8] It is a semiconducting material with a room temperature resistivity of about 10^7 Ωcm, which is, however, strongly dependent upon stoichiometry.[9] The Co normally exists in a $+2$ charge state. The lattice parameter of 4.24 Å suggests that Fe^{57} formed as a result of decay of an impurity radioactive Co^{57} atom will be somewhat compressed if it exists in the ferrous ($+2$) charge state (Fe^{+2} radius about 0.76 Å) but will fit loosely if it is in the ferric ($+3$) charge state (Fe^{+3} radius about 0.644 Å) because the ionic radius of the Co^{2+} is 0.74 Å.[10,11] It may thus be anticipated that most of the Auger processes will take place rapidly, but that in the final stages, when the Fe has an excess of only one or two charges beyond the anticipated equilibrium value of $+2$ (i.e., it is in a $+3$ or $+4$ charge state) the probability of capturing extra electrons may be retarded, and there is a possibility that the lifetimes of states with a slight excess charge may be comparable to nuclear lifetimes.
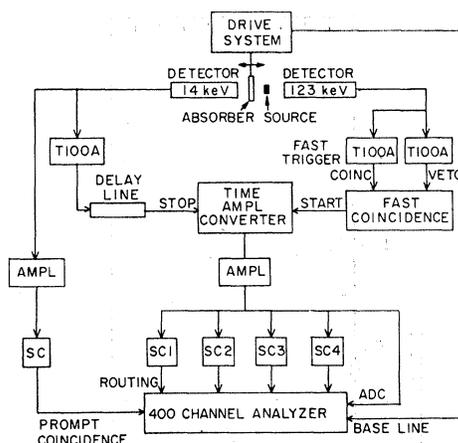

FIG. 1. Schematic diagram of the fast-slow coincidence system used in the two-dimensional Mössbauer spectrometer. The $T100A$ units are fast discriminators, those designated AMPL are slow pulse amplifiers, and those designated SC are single-channel pulse-height analyzers. Four 100-channel Mössbauer spectra can be determined simultaneously, corresponding to four delay time intervals.

Should this occur, the ME offers an excellent possibility for verifying the fact, for the position of the ME resonance is influenced by the s-electron charge density at the nucleus, which is dependent upon the chemical charge state. Thus, the position of the ME resonance lines yields a measure of the chemical charge state of the resonant atom.[12]

The original measurements were performed on a sample of CoO into which Co^{57} had been diffused.[7] At room temperature, two partially resolved lines were found which were identified as arising from $+2$ and $+3$ charge states. The relative intensities of the two lines were about equal. Below 291°K, CoO undergoes an antiferromagnetic transition. In the low-temperature regime two sets of magnetic hyperfine split lines were found, with hyperfine magnetic fields of such a magnitude as to confirm the high-temperature identification of the chemical states.

Since Co^{57} is expected to enter the CoO lattice substitutionally on Co sites, it is expected that there is a unique Co^{57} site, and that all Co^{57} atoms are equivalent. In this case, the observation of two lines in the ME resonance suggests that the $+3$ line is associated with a metastable state having a lifetime about equal to the nuclear level lifetime, which then decays to the stable $+2$ charge state. This picture was elaborated upon by Pollak,[11] who considered the details of the Auger processes and estimated that in a time short compared to 100 nsec, 5% of the Co^{57} decayed to Fe^{+2}, whereas 95% of it decayed to Fe^{+3}. The subsequent decay of Fe^{+3} to Fe^{+2} he estimated to occur at room temperature with a decay life time of 140 ± 20 nsec.

[5] K. Siegbahn, *Alpha- Beta- and Gamma-Ray Spectroscopy* (North-Holland Publishing Company, Amsterdam, 1965) Vol. I, p. 1523.

[6] A. Snell, Phys. Rev. **102**, 1419 (1956).

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

[8] A. F. Wells, *Structural Inorganic Chemistry* (Clarendon Press, Oxford, England, 1962).

[9] B. Fisher and D. S. Tannhauser, J. Chem. Phys. **44**, 1663 (1966).

[10] L. Pauling, *The Nature of The Chemical Bond* (Cornell University Press, New York, 1960).

[11] H. Pollak, Phys. Status Solidi **2**, 720 (1962).

[12] S. de Benedetti, L. G. Lang, and R. J. Ingalls, Phys. Rev. Letters **6**, 60 (1961); L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).
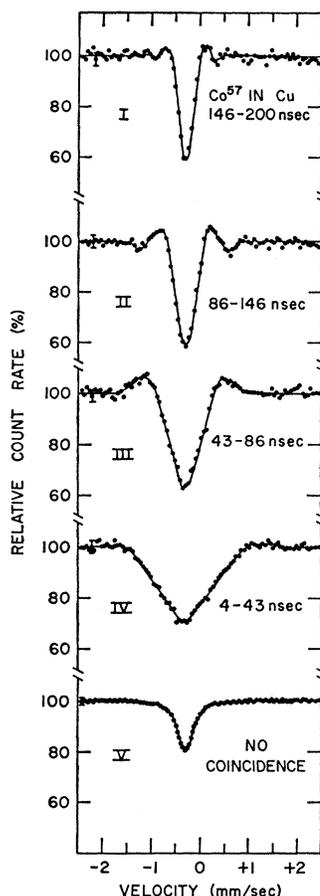
FIG. 2. Delayed coincidence Mössbauer studies using a source of Co^{57} in Cu and an absorber of potassium ferrocyanide. The "time filtering" effects displayed with this unsplit source were used to permit resolving more complex spectra in systems displaying multiple charge states. Note the "negative absorption" which is particularly strong in curves II and III. The last curve (taken without coincidence) is shown for comparison.

This viewpoint was further supported by the observation that the Fe^{+3} linewidth was slightly greater than that of the Fe^{+2} line. Such line broadening is expected from the uncertainty principle, since the $+3$ line is destroyed after a short time, and is therefore well defined in time and hence more poorly defined in energy than is a normal nondecaying line. The $+2$ line is created sometime after the 14-keV level is populated, and from a similar argument based on the uncertainty principle may be expected to be narrowed over the ideal linewidth.[13] The maximum possible narrowing is to about 64% of the normal linewidth (see appendix) and would be difficult to observe.

C. The Principle of the Experiment

The hypothesis of Wertheim and Pollak can be directly tested, since the predicted time scales are

[13] J. G. Dash and R. H. Nussbaum, Phys. Rev. Letters 16, 567 (1966).

comparable to the nuclear lifetime, and this time scale (for the Fe^{57} resonance) is well within the range of conventional electronics. The 123-keV gamma ray which populates the 14-keV level is used as a time marker, indicating that nuclear decay has occurred. After some predetermined time delay interval, a ME spectrum is measured using the 14-keV gamma radiation. The situation is then qualitatively as follows: If the Co^{57} decays initially to the $+3$ state, and thereafter decays exponentially to the $+2$ state with a characteristic time constant θ, then the probability at time t of a given atom being in the $+3$ state is $e^{-t/\theta}$ and the probability of the atom being in the $+2$ charge state is $1-e^{-t/\theta}$. Since the nuclear state is itself decaying exponentially with decay constant $1/\tau$ the effective time constant for the decay of the $+3$ charge state is $\theta/(\theta+\tau)$. For θ comparable to τ large time-dependent effects are expected. The actual line shapes expected when the emitted radiation is filtered by a resonant absorber are complex and are discussed in Sec. IV below and in the appendix.

III. EXPERIMENTAL

A. Samples

We have studied the oxide systems CoO and NiO, and the hydrated salts $(NH_4)_2Fe(SO_4)_2 \cdot 6H_2O$ (ferrous ammonium sulfate, abbreviated FAS), cobalt sulfate $CoSO_4 \cdot 7H_2O$ and cobalt chloride $CoCl_2 \cdot 4H_2O$.

Sources were prepared from commercially obtained Co^{57}. The CoO source was prepared by heating $Co(NO_3)_2$ (chemical grade 99.98), to which a small quantity of Co^{57} solution had been added, in an argon atmosphere to a temperature of 1000°C, for about 4 h. The sample was cooled slowly to room temperature. Samples of CoO without Co^{57} were also prepared in this manner and were subject to x-ray analysis. No evidence for diffraction rings not ascribable to CoO were observed, thereby confirming the purity of our samples. The radioactive sample (a brown-green powder) was packaged in a thin-walled aluminum container containing an argon atmosphere for use in the experiments.

The NiO source was similarly prepared by heating $Ni(NO_3)_2$ to which Co^{57} had been added in argon for 4 h at 1000°C. The result of this process was a green powder.

The FAS was grown as small crystals from a water solution to which a small amount of Co^{57} had been added. Crystallization was performed by slow cooling of the solution. About 95% of the Co^{57} appeared in the resultant crystallites.

Cobalt sulfate crystals containing Co^{57} were grown from a water solution of $CoSO_4$. The cobalt chloride was grown from a water solution of $CoCl_2$.

B. Electronics

The electronics amounted to a simple two-dimensional multichannel pulse-height analyzer displaying

counts as a function of delay time and Doppler shift velocity. Four different ME spectra were recorded simultaneously corresponding to four different selected delay time intervals following the population of the 123-keV level in Fe^{57}. The four resonances were stored in the four quadrants of a RIDL (Radiation Instruments Development Laboratories) 400-channel multichannel analyzer.

The apparatus is diagrammed in Fig. 1. The resonant absorber was potassium ferrocyanide enriched to 90% in Fe^{57} (0.68 mg/cm of Fe^{57}). This absorber was replaced by a natural iron foil for calibration of the ME Doppler shift apparatus. The linewidth obtained running a Co^{57} in Cu source against a natural Fe absorber of thickness 0.001 in. was 0.356 ± 0.005 mm/sec, in contrast to the ideal minimum of 0.2 mm/sec. The 123-keV photomultiplier (RCA type 56 AVP) was equipped with a lead-loaded plastic scintillator yielding a fast pulse (2.1-nsec rise time). The energy resolution was 80%. The output from the last dynode of this counter triggered two fast discriminators (Edgerton Germeshausen and Grier (EGG) Type T 100 A) which drove an anticoincidence circuit which selected the 123-keV gamma ray. The output of the anticoincidence circuit started a time-to-amplitude convertor (TAC) (EGG type TH 200) which was stopped by the arrival of a pulse from the 14-keV counter.

The 14-keV counter was a Harshaw integral line unit with a 0.1-mm-thick NaI (Tl) crystal. The output from the last dynode was coupled into a fast discriminator (EGG type T 100 A), and was fed through an adjustable delay line into the stop input of the TAC. The TAC output was then amplified and fed into the RIDL direct conversion input, and simultaneously to four single channel analyzers used for time interval selection. Energy information on the 14-keV γ ray was obtained by a conventional slow amplifier and single-channel analyzer combination.

The amplified output signal from the TAC provided the direct conversion input to the RIDL analyzer and also input to four single-channel pulse-height analyzers. These analyzers produced routing pulses which selected the particular quadrant of the RIDL into which TAC output pulses in selected amplitude intervals were to be stored. Adjustment and time calibration was done as follows: The RIDL was first connected as a multichannel analyzer, and the TAC output spectrum recorded. This spectrum yielded an exponentially decaying curve with a half-life of 100 nsec corresponding to the 14-keV half-life. The RIDL was then switched to "external routing" and the four single-channel analyzers were adjusted to route pulses of amplitudes corresponding to selected time intervals into the four RIDL memory quadrants, so as to assure that there was no overlap of the timing channels. The upper level discriminator in the RIDL was used to reject all pulses corresponding to delay times longer than those of interest, and the RIDL sensitivity control was used to
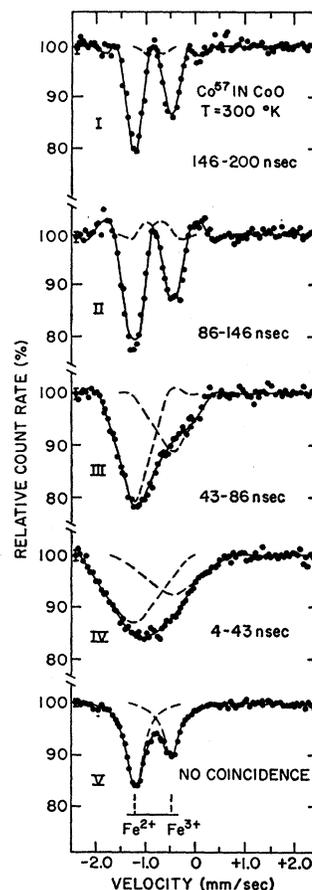

FIG. 3. Delayed coincidence ME spectra for Co^{57} in CoO at 300°K. No evidence for metastable charge states is found. In all measurements, an unsplit absorber of potassium ferrocyanide was used.

reject some small spurious pulses produced by the TAC.

The RIDL was then switched to "baseline input," in which mode the output of the velocity servo determined the channel in a given memory quadrant in which a pulse was to be stored. The particular quadrant was determined by the settings of the four single-channel analyzers. Thus, four independent ME spectra could be measured simultaneously.

In coincidence experiments a problem of importance is signal-to-noise ratio. Since the true counting rate is proportional to the source strength, whereas the accidental counting rate is proportional to the square of the source strength, it is necessary to use weak sources, and to maximize the solid angles subtended by the two counters. In our geometry the solid angles were approximately 36% and 17% of 4π. The source strengths were chosen such that the random counting rate equalled the true counting rate at a delay time of about 850 nsec, corresponding to about 6 mean lives for the 14-keV level. The random counting rate at the longest delay times used (200 nsec) was only about 15% of the
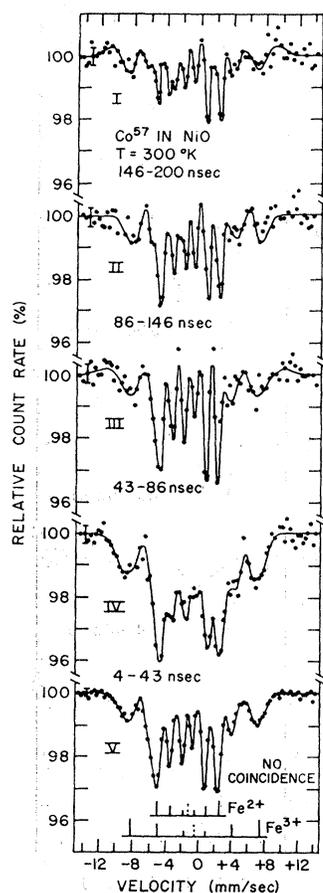
Fig. 4. Delayed coincidence spectra on Co^{57} in NiO at 300°K (below the Néel temperature). No time-dependent effects are found which are not associated with "time filtering."

true counting rate. Typical coincidence counting rates were about 10 counts per second. To obtain sufficient counting statistics required runs lasting from a few days to several weeks.

IV. TIME FILTERING

In ME experiments involving delayed coincidence measurements "time filtering" must be considered. This effect results from the filtering of the time-dependent emitted radiation through the resonant absorber and leads to complex line shapes. Qualitatively the lines are broadened at short delay times and narrowed at long times in agreement with the uncertainty principle. In addition oscillations appear in the line wings. Time filtering has been both experimentally[14,15] and theoretically investigated.[14-16]

We present here a summary adopted from Wegener.[3] The recoil-free radiation emitted from a decaying

nucleus as a function of energy E, at time t, following the formation of the excited level moving at Doppler velocity v is

$$n(E, t, v) = \frac{|M|^2}{[E-E_0(1+v/c)^2+\Gamma^2/4]}$$

$$\times \left\{ 1-\exp\left\{ \frac{i}{\hbar}\left[E-E_0\left(1+\frac{v}{c}\right)+\tfrac{1}{2}i\Gamma\right]t\right\}\right\}. \quad (1)$$

Here M represents matrix elements for the nuclear transition and for the lattice (Debye-Waller factor), the nuclear level width $\Gamma=\hbar/\tau$, the gamma energy is E_0 and the Doppler shift of energy for Doppler velocity v is $(v/c)E_0$.

This expression when integrated over time yields the usual Lorentzian emission spectrum, and when integrated over energy yields the usual exponential decay of a resonant level. When the radiation passes through a resonant absorber, its attenuation is a function of time and energy. The resulting expression is quite complex, but in the case that the absorber is thin, one obtains a simple expression for the intensity $I(v, t)$ transmitted at velocity v, in a small time interval δt occurring at t following the formation of the nuclear level. This expression is

$$I(v, t) = \frac{I_0 nff'\sigma}{\pi}\exp(-\Gamma t/\hbar)\frac{\sin(E_0 vt/\hbar c)}{v/c}. \quad (2)$$

The constants of proportionality involve the source and absorber Debye-Waller factors f and f', the source strength I_0, absorber thickness and cross section, etc.

In a practical experiment the measured time intervals must be finite so as to achieve a reasonable counting rate. The observed counting rate becomes for a counting interval Δt

$$I(v, t_0, \Delta t) = \int_{t_0}^{t_0+\Delta t} I(v, t)dt. \quad (3)$$

The oscillations in resonance intensity as a function of delay time and Doppler shift velocity predicted by Eqs. (2) and (3) have been observed experimentally, and are known as "time filtering."[14,15] In the limit when $t_0 \rightarrow 0$ and $\Delta t \rightarrow \infty$ (corresponding to no measurement of time) the usual Lorentzian ME line shape is obtained.

For fixed values of the measuring interval Δt, resonances observed at short delay times t become broad (as is predicted from the uncertainty principle $\Delta E \gtrsim \hbar/t$) whereas for large values of t, small changes in v produce large numbers of oscillations in the sine function except near resonance centers, and hence the observed lines become narrowed over their natural width. Some possible uses of this narrowing are mentioned at the end of this paper.

The resonant absorbers used were not ideally thin and did not possess ideal linewidths. Even if all quantities are treated as carefully as possible, unaccounted discrepancies exist between theory and experiment (as

[14] F. J. Lynch, R. E. Holland, and M. Hammermesh, Phys. Rev. **120**, 513 (1960).
[15] C. S. Wu, Y. K. Lee, N. Benczer-Koller, and P. C. Simms, Phys. Rev. Letters **5**, 432 (1960).
[16] S. M. Harris, Phys. Rev. **124**, 1178 (1961).

in the thickness parameter β of Ref. 14, which is too small by a factor of about 2). In order to circumvent these difficulties we experimentally determined the "time filtered line shapes" directly, using an unsplit source of Co^{57} in Cu, and the absorber, time intervals, and experimental geometry identical to those used in the actual experiments. For each time interval of interest a resonant spectrum was obtained which included the effects of time filtering but did not include any other factors, and which could be used in analyzing the results obtained with the more complex sources.

Figure 2 presents a series of spectra demonstrating these effects. The source is Co^{57} in Cu. The lowest resonance in the series (V) was taken with no coincidences and shows a single absorption line with a width of (0.40 ± 0.02) mm/sec. The upper four curves were obtained with timing intervals of (I) 146–200 nsec, (II) 86–146 nsec, (III) 43–86 nsec, and (IV) 4–43 nsec. Oscillations resulting from "time filtering" are particularly evident in the second and third curves, but are in all curves partially averaged out by the relatively large timing intervals used in order to increase the counting rate. At short delay times the expected line broadening is observed and at long delay times the expected narrowing. The time required to obtain all four of the resonances I–IV was about 48 h at a counting rate of about 2 counts per min and per channel.

V. SEARCH FOR METASTABLE CHARGE STATES

A. Cobalt Oxide

In Fig. 3 are shown results obtained on a source of CoO at room temperature. The experimental conditions

FIG. 6. Delayed coincidence studies on Co^{57} in iron ammonium sulfate. Multiple charge states are found not to arise from metastable effects. More probably Co is not strongly bound in this compound and occasionally occupies interstitial sites. Differences between the spectra of sources and absorbers do not necessarily indicate the presence of time-dependent effects.
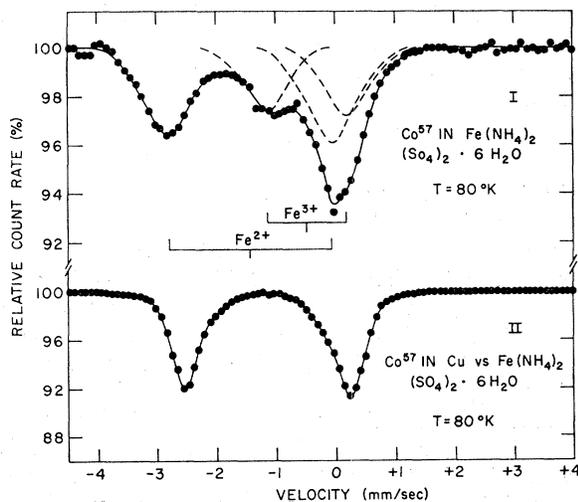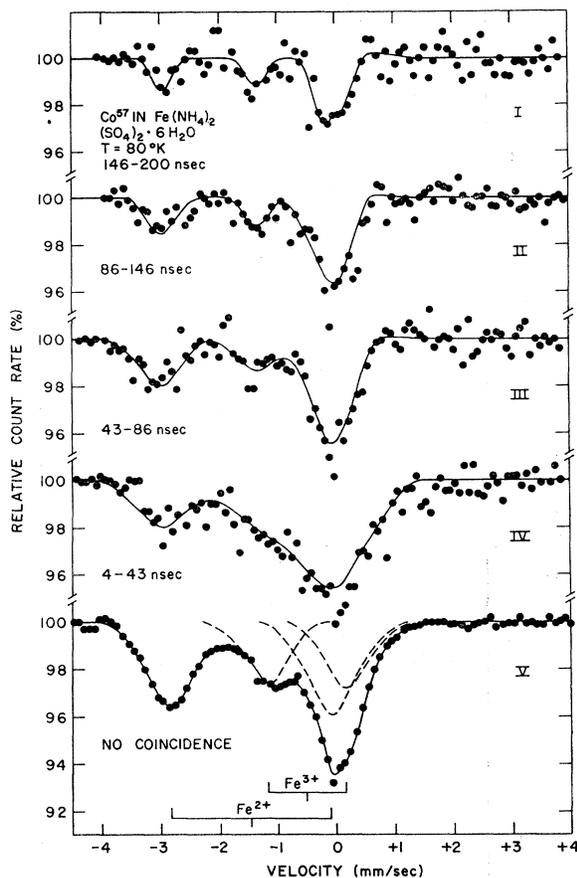

FIG. 5. Mössbauer spectra of iron ammonium sulfate. In (I) Co^{57} replaces part of the Fe. In (II) the same sample is used as an absorber. The difference in spectra in these two cases had been interpreted as evidence for metastable charge states associated with the decay of Co^{57}. The velocity scale in (II) is reversed to facilitate intercomparison of the two curves.

were identical to those used with the Cu source (Fig. 2). The lowest curve (V) was obtained without coincidences and shows the expected two resonance lines. The relative intensity of these lines is $I^{3+}/I^{2+}=0.61\pm0.02$ which is slightly different from the ratio of 47/53 found by Wertheim,[7] whose identification of the lines from their positions is followed. Resonances obtained using short delay times show pronounced broadening which smears the two peaks together. Our analytical approach to this data was to synthesize each observed spectrum as the sum of two separate lines. Each of these component lines was assumed to have the position and relative intensity associated with the normal spectrum without coincidences, and the line shape obtained for the corresponding time interval using the Cu source.

The solid curves drawn through the coincidence data of Fig. 3 were calculated in this manner, and offer an excellent fit to the data. A feature of interest is the effect of the oscillations apparent in spectrum III. Here the negative contribution to the Fe^{+2} line cancels part of the
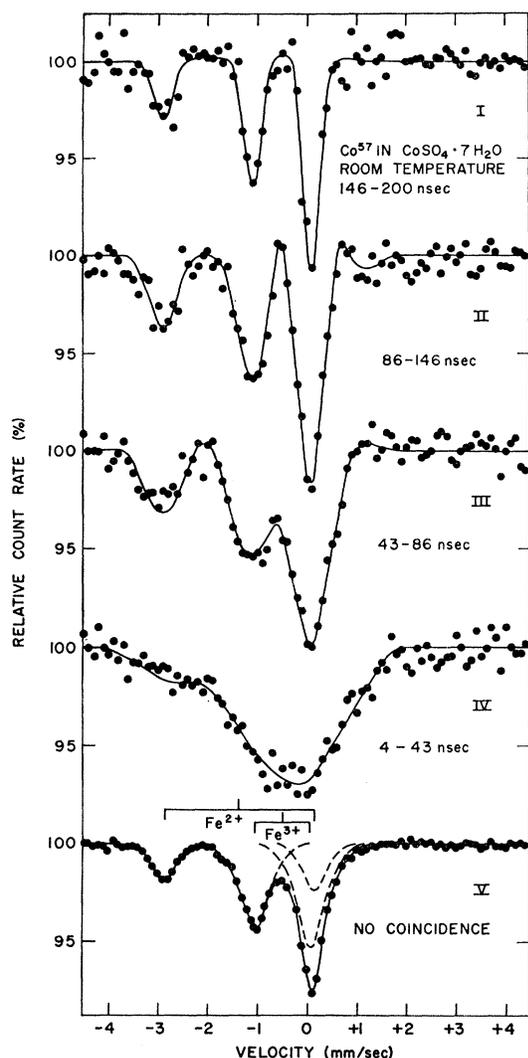
FIG. 7. Delayed coincidence ME spectra of Co^{57} in hydrated cobalt sulfate. Despite the presence of multiple-charge states, no evidence for metastable states is found.

Fe^{+3} resonance, thereby accounting for the inflection observed in the experimental curve.

From this analysis we find, by comparing the areas under the separate curves, that the relative intensity ration I^{+3}/I^{+2} remains constant at 0.61 ± 0.04 in the four time intervals studied. On the metastable-state model the expected relative intensities in the four time intervals studied are $I^{+3}/I^{+2}=4.7$, 1.4, 0.74, and 0.39, for the time intervals designated I, II, III, and IV. These calculated ratios were obtained by integrating the exponential decay predicted by Pollak[11] over the resolving time used in each of our coincidence intervals, and are in marked contrast to the predictions of the metastable charge state model discussed in Sec. II.

The behavior of Co^{57} has also been studied as a function of temperature. At 80°K (below the Néel temperature) the intensity ratio I^{+3}/I^{+2} was found to decrease

slightly compared to room temperature. Bhide and Shenoy[17] measured the ME spectra over the range 78 to 1000°K and found that at high temperatures the +2 line gradually vanished. We have confirmed these results above room temperature in a series of experiments without coincidence. Bhide and Shenoy interpreted their results in terms of an increase in the lifetime of the +3 state at high temperatures to values greatly in excess of the nuclear lifetime.

This interpretation was disproved by delayed coincidence experiments at a temperature of 389°K. At this temperature the average ratio $I^{+3}/I^{+2}=1.21\pm0.03$. The resolution of the coincidence data performed in the same manner as at room temperature again shows this ratio to be time-independent. The same conclusion was drawn from measurements at 508°K, where the intensity ratio was $I^{+3}/I^{+2}=3.70\pm0.05$.

B. Nickel Oxide

Bhide and Shenoy have performed a series of measurements on Co^{57} in NiO.[18] Their results and ours on this system are qualitatively similar to those on CoO. The Neel temperature of NiO is 523°K. NiO has the $NaCl$ structure, and here too the Co^{57} is expected to enter the lattice substitutionally. Our coincidence measurements at room temperature are shown in Fig. 4. Because the sample is below the Néel temperature the spectra consist of two sets of six finger patterns displaced from each other by an isomer shift. The chemical state identification shown for the two sets of lines agrees with that of Bhide and Shenoy and is based upon the observed isomer shifts and hyperfine fields. The resonance is relatively weak (about 3% in the strongest lines), and the curve shown required 12 days of counting. The intensity ratio I^{+3}/I^{+2} here of 0.65 ± 0.05 is independent of time and in agreement with Bhide and Shenoy. A shorter run made at 77°K showed an intensity ratio of 0.63 ± 0.08 at all times, with again no evidence for a time-dependent intensity ratio.

C. Ferrous Ammonium Sulfate (FAS)

FAS had been studied previously both as a source and as an absorber.[19] Differences observed between the source and absorber spectra were interpreted as arising from metastable-charge states. A lifetime of 5×10^{-8} sec was deduced for the +3 charge state at room temperature.[19] Figure 5 shows our measurements at 80°K on a sample of FAS containing Co^{57} used first as a source, [Fig. 5(I)] and then as an absorber [Fig. 5(II)]. The conventional definition that positive velocity corresponds to the source moving toward the absorber is reversed in Fig. 6(b) as to make the resonances correspond. Differences between the two spectra are evident and agree with the previous findings.[19]

[17] V. G. Bhide and G. K. Shenoy, Phys. Rev. **147**, 306 (1966).
[18] V. G. Bhide and G. K. Shenoy, Phys. Rev. **143**, 309 (1966).
[19] G. K. Wertheim and H. J. Guggenheim, J. Chem. Phys. **42**, 3873 (1965).

Figure 6 presents delay coincidence data on FAS at 80°K for the same four delay times previously used. The data are decomposed as before using the resonances obtained with the Co in Cu source. The ratio $I^{+3}/I^{+2}=$ 0.64±0.02, so that any time effects are at least an order of magnitude less than those predicted from the Pollak model.[11]

At room temperature changes in the relative intensities between the time interval 4–43 nsec and the interval 146–200 nsec were less than about 15%, in contrast to the predicted change of 1200%.

D. Cobalt Sulfate

Cobalt sulfate has been studied by Ingalls et al.,[20] who found three resolved ME lines at room temperature and atmospheric pressure which were identified as arising from Fe atoms in ferrous and ferric states. The ratio I^{+3}/I^{+2} was found by these authors to be 1.86 at room temperature, to be essentially unchanged at 143°K, and to decrease somewhat at higher temperatures. The highest temperature results were felt not to be totally reliable because of dehydration of the samples, but the qualitative conclusion was firm, and in the opposite direction to the change in intensity ratio found in CoO.

Our results at room temperature are presented in Fig. 7. This identification of charge states is based upon the isomer shifts of the centroids of the quadrupole split ME resonances and may be in error. No time-dependent effects beyond "time filtering" were observed. The intensity ratio at room temperature was found to be $I^{+3}/I^{+2}=2.45\pm0.09$, slightly higher than that obtained by Ingalls et al.[20] At liquid-nitrogen temperature the (time-independent) intensity ratio was found to be 2.64±0.12.

E. Cobalt Chloride

Cobalt chloride had been previously studied[21] and showed partially resolved ME lines at different temperatures which were contributed to Fe atoms in +2 and +3 states.

Our measurements at 80°K with and without delayed coincidence are shown in Fig. 8. The intensity ratio I^{+3}/I^{+2} at all delay times is 0.79±0.06 again showing no evidence for metastable-charge states.

VI. DISCUSSION

A. Oxides

The absence of time-dependent effects in the CoO spectra suggests at the outset two general types of explanation: (a) in terms of rapidly produced but long-lived metastable states, and (b) in terms of nonequivalent Co sites in the sample. By possibility (a) we mean

[20] R. Ingalls, C. J. Coston, G. de Pasquali, H. G. Drickamer, and J. J. Pinajian, J. Chem. Phys. 45, 1057 (1966).
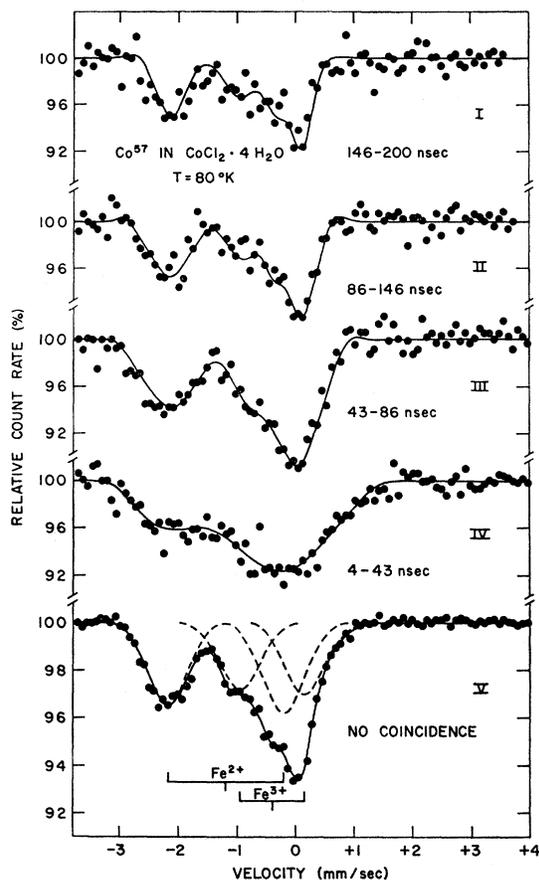[21] R. Ingalls and D. De Pasquali, Phys. Letters 15, 262 (1965).

FIG. 8. Co[57] in cobalt chloride at 80°K shows no evidence for metastable-charge states. The timing intervals are the same as for the previous curves, and a reference spectrum without timing is shown (V).

the following: The Auger processes occurring after electron capture in Co[57] rapidly (in times much shorter than 100 nsec) lead to the decay of all charge states higher than +3. Of the atoms in the +3 state, some decay very rapidly to the +2 state while others remain in the +3 state for times long compared to the nuclear lifetime. No processes take place in times comparable to the nuclear lifetime. The fraction of atoms remaining for long times in the +3 state is determined by variation in the local chemical environment. Measurements performed on such a system on a time scale of (say) minutes would show no evidence of the +3 state charge state. By possibility (b) we mean that all equilibration processes take place in times short compared to the nuclear lifetime. In this case the ME experiments are measuring equilibrium processes and should be in agreement with studies made on an arbitrarily slow time scale. In order to distinguish between these two processes absorbers were prepared containing $\frac{1}{2}\%$ and 1% Fe (natural Fe) in CoO. In addition to differing in Fe concentration these absorbers also differed in that the $\frac{1}{2}\%$ sample was prepared from an Fe^{+3} compound
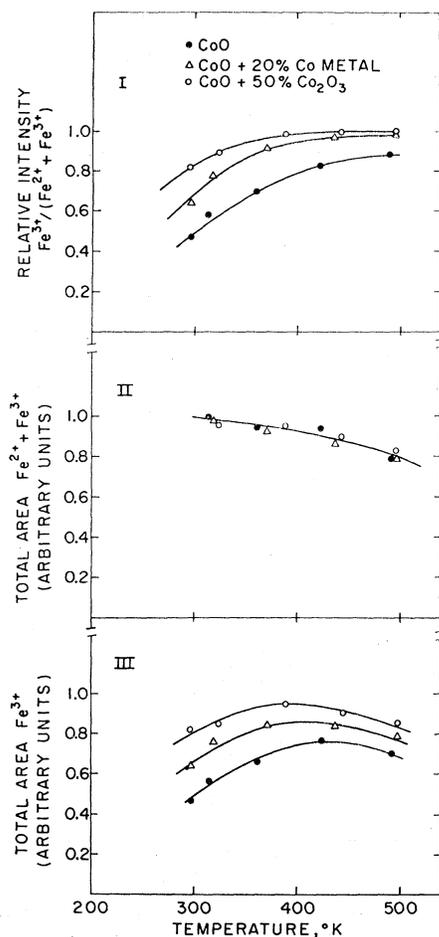
FIG. 9. Evidence for interconversion of ferrous and ferric Fe in CoO. Fig. 9 (I) shows the ratio of the ferric to ferrous peak areas versus temperature. At high temperature only a ferric peak is observed. Fig. 9 (II) shows the total area of the two peaks. Fig. 9(III) shows the temperature dependence of the ferric peak alone. The increase in intensity with increasing temperature up to about 500°K can be accounted for only by assuming conversion of ferrous Fe to ferric Fe. The intensity is a reversible function of temperature, showing the state of the total system to be one of chemical equilibrium. The three symbols refer to samples prepared by heating in argon slightly different starting compositions, as indicated.

[Fe$_2$(NO$_3$)$_3$] while the 1% sample was prepared using Fe in a +2 compound (FeCl$_2$). Measurements using these samples as absorbers showed spectra essentially identical to those obtained using the CoO source. Because natural Fe was used the resonances were quite weak. The only significant difference between the spectra obtained was found in the relative intensities of the ferrous (+2) and ferric (+3) lines. At room temperature the ratio I^{+3}/I^{+2} for the sample prepared from Fe^{+2} was about 0.6, while for the sample prepared from Fe^{+3} the ratio was about 0.9.

In the absence of time-dependent effects we conclude that the multiple ME emission lines results from non-equivalent sites in the CoO lattice. Since the ME experiments are made on Fe, it is not known whether the inequivalence is associated only with the Fe im-

purities, or whether there may be inequivalent Co sites as well. A number of mechanisms could be responsible for inequivalent sites. Among these might be included deviations from stoichiometry resulting from cation vacancies, interstitial oxygen, or the simultaneous existence of two different oxides of Co.

While the mechanisms involved remain as yet unclear, recent work by Mullen and Ok[22,23] offers a possible interpretation. Mullen and Ok have been able to prepare two oxides of Co, with certain remarkable similarities. These oxides, which they designate as CoO(I) and CoO(II) hold Fe impurities in the ferrous and ferric state, respectively. The Néel temperatures of the two oxides are approximately equal, and the x-ray diffraction patterns are almost identical. The major differences occur in the bulk density which is 6.4±0.1 g/cm^3 for CoO(I) and 3.3±0.2 g/cm^3 for CoO(II). The large difference in densities, combined with slight differences in the x-ray spectra lead to the conclusion that CoO(II) has the same NaCl structure as does the normal CoO(I), but that about 50% of the total sites are occupied by Schottky defects. Upon heating form (I) is found to remain stable up to 1000°C, whereas form (II) converts irreversibly to form (I) above about 400°C. The ME recoil-free fractions (f factors) observed in both materials behave normally, and decrease monotonically with increasing temperature.

The connection between these isolated oxides and the samples used in the various ME experiments is not entirely clear. Some indication of the mechanisms involved is found in the temperature dependence of the recoil free fractions. The relative intensities of the ferric and ferrous lines have been measured as a function of temperature by Bhide and Shenoy, who found the ratio to increase monotonically with increasing temperature so that by 600°K only ferric ions are observed. We have repeated and extended these measurements, [Fig. 9(I)]. Figure 9(II) presents the temperature dependence of the total area under the two peaks, which decreases monotonically with temperature as is expected as the Debye-Waller factor drops. The product of the data of Figs. 9(I) and 9(II) yields the temperature dependence of the resonance strength of the ferric (+3) peak alone, shown in Fig. 9(III). This curve is quite remarkable, in that the intensity of the ferric peak *increases* with increasing temperature up to about 500°K. The Mössbauer recoil-free fraction, or f factor, is determined by Debye-Waller factors which can only decrease with increasing temperature.[2] The occurrence of a peak which increases in intensity shows that this peak is gradually produced as the temperature is raised. The results presented in Fig. 9 are independent of thermal cycling, showing the origin of the ferric peak to be reversible oxidation of the ferrous ion as the temperature is raised.

It appears likely that the materials we have used in our work are similar to those used by Wertheim[7] and

[22] J. G. Mullen and H. N. Ok, Phys. Rev. Letters 17, 287 (1966).

[23] J. G. Mullen and H. N. Ok (to be published).

by Bhide and Shenoy.[17] These materials probably exhibit significant deviations from stoichiometry, and are probably composed of intermixtures of the two oxides found by Mullen and Ok. The intermixing probably occurs on a microscopic rather than on a macroscopic scale, for otherwise the time constants for the interconversion of the two species would become exceedingly long. (It is not as yet known just what the interconversion time constants are. Certainly they must be more rapid than the nuclear lifetime, or else only a single line rather than resolved ferric and ferrous lines would be observed. The interconversion rate must also be more rapid than hours, for in that case time-dependent effects would have shown up in the thermal-cycling experiments shown in Fig. 9. Experiments are underway at Brookhaven to determine directly the interconversion rate.)

The semiconductivity of CoO may bear upon these questions. Fisher and Tannenbaum[9] have studied the CoO phase diagram and find that the electrical properties are functions of the amount of excess oxygen present in the lattice. They found that up to 1.2% excess oxygen (or possibly Co deficiency) could be stabilized in the temperature region near 900°C, and that the actual amount was a function of the sample preparation temperature and of the excess oxygen pressure.

The role of sample stoichiometry in the CoO system is probably responsible for the seemingly anomalous early results of Bearden et al.,[24] who studied a source of Co^{57} in CoO and found no evidence whatever for a Fe^{+3} line. Their samples must have been almost exactly stoichiometric, with few cation vacancies present to stabilize Fe^{+3}. Coston et al.[25] have also speculated that time-dependent effects probably play a minimal role in this system.

A characteristic feature of measurements on the CoO system is a greater linewidth associated with the +3 line than with the +2 line. This effect was noticed by Wertheim,[7] and studied by Bhide and Shenoy.[17] The oxidation model offers a qualitative understanding of this line broadening in terms of an inhomogenous local environment of those atoms in the +3 state. On this model, the vacancies occur at random. Since the Fe atoms also occur at random, the distances of the vacancies from the local environment of the +3 atoms will be inhomogeneous and hence there will be a distribution of isomer shifts and small quadrupole splittings, leading to line broadening.

B. Insulators

In good insulators it seems probable that under the correct circumstances metastable charge states may exist. The Mössbauer spectra obtained in FAS, cobalt sulfate, and cobalt chloride using the coincidence technique show that in these systems metastable-charge states with lifetimes corresponding to 100 nsec do not occur. Since in FAS the differences in spectra between source and absorber do not permit us to distinguish between the alternatives (a) and (b) above (Sec. VIA), we cannot say whether there are very long-lived metastable-charge states or whether the source is in chemical equilibrium. While the most obvious interpretation is to assume that very long-lived charge states (greater than 100 nsec) are present, there are other mechanisms which might lead to differences in behavior between source and absorber. The most likely explanation is a difference in the local environment of Fe atoms which occur normally in the crystal, and Co atoms grown into the crystal impurities. The ionic sizes of Fe and Co differ slightly (Fe^{+2}: 0.76 Å; Co^{+2}: 0.74 Å),[8] and the Co could occasionally occupy interstitial positions. The Fe resulting from the decay of these interstitial Co atoms could produce a distribution of isomar shifts which would broaden the ME lines. This possibility could be investigated by growing a series of crystals with increasing stable Co content, and studying the effect of this upon the ME resonance. Such studies have not as yet been attempted. Differences in the local environment of the Co atoms could also arise from variation in the number of water of crystallization molecules per unit cell throughout the lattice. Finally, it is possible that stoichiometry is more difficult to obtain in the Co compounds than the Fe compounds.

C. Radiation Damage

A mechanism which could give rise to multiple Fe sites is radiation self-damage. There are at least two mechanisms which could lead to atomic displacements of Fe^{57}. Both of these are plausible in low Debye temperature, relatively weakly bound materials. The first of these is conventional radiation damage resulting from the relatively large maximum neutrino energy associated with electron capture. The second mechanism is radiation damage resulting from the Coulombic forces acting upon the charged Fe atom before the Auger processes have been completed. The forces acting on an atom with excess charge of two or three units are substantial. In an insulating material the time required to acquire the missing electrons could be many lattice vibration periods (but still much shorter than the 100 nsec nuclear lifetime), so that these Coulomb forces would have time to act. Such a mechanism has been proposed and discussed, but experimental evidence in support of it has not as yet appeared.[26] It would be rather difficult to separate radiation damage from this mechanism from that resulting from other mechanisms. The possibility for such separation exists, however, using the ME technique to study the variation of line shape, position and intensity with the electrical con-

[24] A. J. Bearden, P. L. Mattern, and T. R. Hart, Rev. Mod. Phys. 36, 470 (1964).
[25] C. J. Coston, R. Ingalls, and H. G. Drickamer, Phys. Rev. 145, 409 (1966).

[26] J. Durap and R. L. Platzmann, Discussions Faraday Soc. 31, 156 (1961).

ductivity of the source, varied by means of temperature, pressure, etc.

VII. CONCLUSIONS

It is now clear that if multiple-charge states are to be unambiguously observed, sample stoichiometry must be excellent. It also seems likely that the insulating properties of the source must be quite good, for if the electrical conductivity of the samples is not extremely low the probability of capturing the electrons required for charge equilibration becomes inordinately large, and the time scales involved short. For multiple-charge states to be observed using the ME, it will be necessary to embed radioactive impurity atoms into highly insulating host lattices. The positions in which the impurities are located must be cells large in comparison to the host size to insure that interactions of the impurity with its environment be small. It may be surmised that favorable circumstances might be found in noble element nuclides embedded in compounds with large interstices, such as the clathrates.

Evidence for multiple-charge states has been found in ME experiments in several systems other than Fe^{57}. These include the 35.6-keV resonance in I^{125} embedded in a host of $NaIO_3$[27] and the rare-earth resonances of Eu^{153} in Eu_2O_3.[28] The first system offers a good possibility for delayed coincidence verification of the metastable-charge state origin of the presently unaccounted four lines. The half-life of the second one is very short (0.228 nsec) and requires sophisticated coincidence techniques.

There exist several other areas in which time-dependent effects may occur. One of these involves the study of the transition behavior in certain paramagnetic substances from a region in which relaxation times are fast and single resonance lines are observed to a region in which relaxation effects take place slowly and hyperfine splitting appears. (See the review article of Wickman and Wertheim.[29]) This transition behavior has been experimentally observed in several systems, and discussed theoretically from several viewpoints. Each of the theories has as a free parameter a relaxation time (which is in most cases identified as the flipping rate of a hypothetical external field identified in one way or another with an electronic flipping rate). This relaxation rate is generally a function of temperature so that by variation of temperature both paramagnetic and magnetic ME resonances may be observed. The transition between the two regions occurs at a flipping rate comparable to the Larmor precision frequency of the nucleus in the magnetic field due to the electrons. Resolution of the hyperfine split lines

requires that the inverse of the Larmor precision frequency be greater than the nuclear-state lifetime. The delayed coincidence technique would appear to be inapplicable, for the requirement of measuring short times implies, through the uncertainty principle, that the ME lines will be hopelessly broadened. However, if measurements are made some time after the population of the resonant level, lines narrower than the natural linewidth may be obtained, even though the measuring time interval is short. The reason for this result may be seen by inspection of Eq. (1). At long delay times the argument of the sine function varies rapidly with velocity, yielding cancellation at velocities far removed from the center of the resonance. At long delay times the resonant detector is sensitive for a short time δt. However, the source has been emitting radiation for a long time t, and the absorber has responded to the incident radiation for this long time. The ME line shape is a function of both the delay time and the time the measuring window is open. It is thus possible to choose a very small resolution interval δt occurring a long time after the population of the resonant level, and so to obtain linewidths even narrower than the natural linewidth, thereby permitting the study of phenomena occurring in time scales considerably less than the nuclear lifetime.

An area in which delayed coincidence may prove useful is lattice dynamics. A possible effect to be searched for is time dependence of f factors (the probability of recoil-free gamma emission). Such effects could result from the excitation of localized modes with long decay times. A search for effects of this type in metals yielded negative results.[30] Insulating materials may turn out to offer much more favorable environments, especially since in insulators it should be possible to achieve much larger ratios of host to impurity mass than is feasible with metals.

ACKNOWLEDGMENTS

APPENDIX: LINE SHAPES OF METASTABLE CHARGE STATES

The formation and decay of metastable-charge states can lead to changes in the line shapes and intensities. We consider here the line shapes expected in the following two related problems:

(a) Following some decay a metastable state is

[27] C. E. Violet and R. Booth, Phys. Rev. 144, 225 (1966); 149, 414 (E) (1966).

[28] E. Steichele, W. Henning, S. Hüfner, and P. Kienle, in Conference on Applications of the Mössbauer Effect in Chemistry and Solid State Physics (International Atomic Energy Agency, Vienna, 1966) p. 233.

[29] H. H. Wickmann and G. K. Wertheim, in Chemical Applications of Mössbauer Spectroscopy, edited by V. I. Gol'danskii and R. H. Herber (to be published).

[30] P. P. Craig, O. C. Kistner, B. Mozer, and R. Segnan, Rev. Mod. Phys. 36, 361 (1964).

created (such as Fe^{+3}) which exists for a certain time and is then destroyed. The probability that the state exists at a certain t is $p(t) = e^{-\alpha t}$. When the state is destroyed the resultant state is assumed to have a different isomer shift and therefore does not influence the old state.

(b) The state created by the decay of a case (a) atom does not exist before time t, but after t exists as a stable entity. We expect from the uncertainty principle that case (a) will yield a line broadened over the natural width while case (b) will yield a narrowed line.

Consider first case (a). The emitted ME intensity at velocity v and delay time t following the formation of the state is given by Eq. (2):

$$I(v, t) = A \frac{\sin \Sigma tv}{v/c} e^{-\Gamma t/\hbar}, \qquad (A1)$$

where A is a constant and $\Sigma = E_0/\hbar c$.

This state lives from $t = 0$ until it is destroyed at time T. The emitted intensity is

$$M(v, T) = \int_0^T I(v, t) dt$$

$$= \frac{A\Gamma^2}{(E_0v/c)^2 + \Gamma^2}$$

$$\times \left[1 - \exp\left[-(\Gamma T/\hbar)\left(\cos\Sigma Tv - \frac{\Gamma c}{E_0 v} \sin\Sigma Tv \right) \right] \right]. \quad (A2)$$

As $T \to \infty$ the term in the brackets approaches unity yielding the usual Lorentzian line shape. An ensemble of such states has a probability of existing at a time of $p(T) = e^{-\alpha T}$ where α is a decay constant for the metastable state. The transmitted ME intensity at velocity v if no time measurement is made is then

$$M(v) = \int_0^\infty M(v, T) \frac{dp}{dT} dT$$

$$= \frac{A\Gamma^2}{(E_0v/c)^2 + \Gamma^2} \left[1 - \frac{\alpha^2}{(E_0v/c)^2 + (\Gamma + \alpha)^2} \right]. \quad (A3)$$

As $\alpha \to 0$ the metastable state approaches stability and the usual Lorentizian shape is obtained. As $\alpha \to \infty$ the metastable state decays rapidly and the total intensity approaches zero. Equation (A3) represents a non-Lorentzian shape with half-width greater than Γ.

The line shape associated with the created line [case (b)] may be similarly calculated by evaluating the integral in Eq. (A2) from T to ∞. The result is

$$M(v) = \frac{A\Gamma^2\alpha^2}{[(E_0v/c)^2 + \Gamma^2][(E_0v/c)^2 + (\Gamma + \alpha)^2]}. \quad (A4)$$

As $\alpha \to \infty$, the metastable state decays rapidly and the normal line shape is regained.

For finite values of α the line shape is non-Lorentzian with a half-width less than the natural width Γ. As $\alpha \to 0$ the intensity vanishes, and the line shape approaches

$$M(v, \alpha \to 0) = \frac{A\Gamma^2\alpha^2}{[(E_0v/c)^2 + \Gamma^2]^2}. \quad (A5)$$

The resonance drops off much more rapidly than Lorentzian and has a width at half-maximum of $(\sqrt{2} - 1)^{1/2}\Gamma = 0.64\Gamma$. The minimum linewidth possible with this model is thus 64% of the ideal width.

The decay constant α of the metastable level may be determined by comparison of line shapes and intensities of the created and the destroyed states. Comparison of the line half-widths must be done graphically or numerically. Comparison of the intensities at the line centers yields

I (created state)$/I$ (destroyed state) $= \eta^2/(1 + 2\eta)$,

$$(A6)$$

where $\eta = \alpha/\Gamma$. The two intensities are equal at

$$\alpha = (1 + \sqrt{2})\Gamma = 2.414\Gamma.$$

Comparison of the line areas A may also be done in closed form, yielding

A (created state)$/A$ (destroyed state) $= \eta^2/(2 + 3\eta)$.

$$(A7)$$

The two areas are equal at $\alpha = [3 + (17)^{1/2}]/2\Gamma = 3.56\Gamma$.