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### Mössbauer Effect in Dilute Alloys of Iron in Aluminum<sup>†</sup>

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The Mössbauer spectrum of dilute alloys of  $^{57}\text{Fe}$  in aluminum has been studied. In the concentration range from 0.005 to 1.2-at.% Fe, the spectrum consists partly of a single-line component due to Fe in solid solution in aluminum metal and partly of a multiple-line component associated with Fe in  $\text{Fe}_4\text{Al}_{13}$ . These two components can be distinguished from each other by the differences in their behavior when either concentration or temperature is varied. In the course of this investigation we achieved some understanding of two peculiar observations that had led us to undertake this study. (i) Bara *et al.* had obtained a succession of unusual spectra for excited  $^{57}\text{Fe}$  nuclei formed by the decay of  $^{57}\text{Co}$  which had been diffused into aluminum metal. We can explain their results on the assumption that the  $^{57}\text{Co}$  first went into solid solution in the aluminum, was then converted to metallic cobalt during further heat treatments, and finally became oxidized. (ii) From recoil-implanted  $^{57}\text{Fe}$  in aluminum, Sprouse *et al.* had obtained a Mössbauer spectrum that appeared to consist of two poorly resolved broad lines instead of the expected single sharp line. We believe this modification of the spectrum must be attributed to radiation damage produced by the implantation of the  $^{57}\text{Fe}$  atoms. In the vicinity of the final position of each implanted atom this damage is probably in the form of lattice vacancies.

#### I. INTRODUCTION

Iron is only very slightly soluble in fcc metallic aluminum, as seen in its phase diagram<sup>1</sup> (Fig. 1). Except at extremely low concentrations, this solid-solution phase coexists with a phase that has a complicated monoclinic structure whose approximate composition<sup>2</sup> is represented by the formula  $\text{Fe}_4\text{Al}_{13}$ .

There seems to be no direct information (e.g., from x-ray diffraction) on the kinds of sites occupied by the iron atoms in the solid-solution phase. However, the atomic radius of iron is sufficiently close to that of aluminum that the iron atoms almost certainly substitute for aluminum atoms on regular lattice sites, and are too large to occupy interstitial locations. One expects this phase to have a single sharp Mössbauer absorption line because (a) there is no magnetic ordering in this phase, so there should be no magnetic broadening, (b) the iron concentration in this phase is always very low, so if the iron atoms are randomly distributed, there is little likelihood that a given iron atom will have a second iron atom near enough to it to affect its Mössbauer spectrum, and (c) although the substitutional iron atoms are not quite the right size, so

they probably distort the lattice locally, still the symmetry about these sites is normally cubic and so if (as expected) the substitution of an iron atom introduces only cubically symmetric distortions, the symmetry of the local environment about each site will remain cubic, and so there will also be no quadrupole fields to broaden the Mössbauer spectrum. However, if the iron atoms were to produce asymmetric distortions of the lattice (as they might, especially if the iron atoms tended to cluster, or as they would if iron atoms tended to have near-neighbor vacancies associated with them), then the Mössbauer spectrum could exhibit broadening from both quadrupolar effects and inhomogeneous isomer shifts.

As will be seen, there is no magnetic ordering in the chemically ordered  $\text{Fe}_4\text{Al}_{13}$  phase at temperatures down to 4°K. There are five sites for iron, four of which have similar, but not identical, near-neighbor environments, while the fifth has a quite different environment.<sup>2</sup> None of these sites have cubic symmetry, so there may be quadrupole hyperfine fields. Thus, the  $^{57}\text{Fe}$  Mössbauer spectrum should consist of five quadrupole doublets, each with its own splitting and isomer shift.

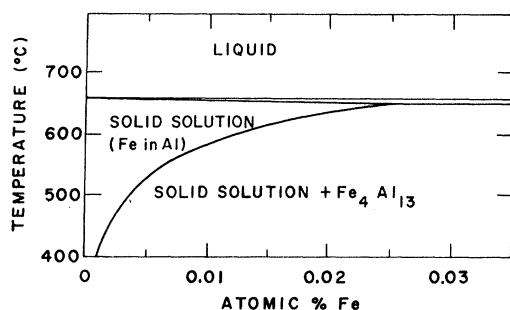


FIG. 1. Phase diagram for dilute alloys of iron in aluminum, based on data from Ref. 1.

Mössbauer spectra for dilute alloys of Fe in aluminum have been measured by a number of experimenters. Bush, Stickels, and Hobbs<sup>3</sup> observed just one Mössbauer absorption line for the solid-solution phase. Also, they were able to get more than the normal amount of iron into the solid solution by quenching samples from just below the melting temperature of aluminum (660 °C). They investigated the effects of cold work and further heat treatment on the Mössbauer spectra of these samples. In addition, they obtained spectra for  $\text{Fe}_4\text{Al}_{13}$  samples, and these turned out to consist typically of a broad line with little structure.

Janot and Lelay<sup>4</sup> made similar studies of the effects of cold work on dilute alloys of iron in aluminum. They interpreted the single Mössbauer line for the undisturbed solid solution as being due to atoms on substitutional sites.

Nasu *et al.*<sup>5</sup> measured the shift of the solid-solution line as a function of temperature, and from this they calculated how much of the total shift relative to metallic iron is due to thermal shift and how much is due to isomer shift.

Besides these absorber experiments, work has also been done with sources consisting of excited  $^{57}\text{Fe}$  nuclei in aluminum. Bara *et al.*<sup>6</sup> diffused radioactive  $^{57}\text{Co}$  into aluminum and observed the Mössbauer spectra of the 14-keV  $\gamma$  rays emitted by the excited  $^{57}\text{Fe}$  nuclei that are formed by the decay of the cobalt. Sprouse *et al.*<sup>7</sup> produced a Mössbauer source by introducing Coulomb-excited  $^{57}\text{Fe}$  nuclei into an aluminum foil by recoil implantation. The Mössbauer spectra were quite different in these two cases, and were also different from the results of the absorber experiments.

Bara and his co-workers<sup>6</sup> prepared their source by first drying an aqueous solution of  $^{57}\text{CoCl}_2$  on an aluminum foil. They then removed the water of hydration by heating the foil at 200–300 °C, and obtained a complicated room-temperature spectrum which they attributed to  $\text{CoCl}_2$ . Next, they heated the foil to 600 °C in an argon atmosphere for 100 min. After this the room-temperature spectrum

consisted of a single line, which they interpreted as a conventional single-line paramagnetic spectrum from fairly dilute  $^{57}\text{Fe}$  in aluminum. But after further successive heatings at 600 °C, the room-temperature spectrum changed so that the single line grew weaker and a magnetically split six-line pattern began to appear. They interpreted the six-line component as the result of long paramagnetic spin relaxation times such as might be associated with an extremely dilute solution of a magnetic iron impurity in a nonmagnetic aluminum lattice. When additional Mössbauer spectra were obtained while the source was being held at elevated temperatures, they found that the hyperfine splitting decreased very slowly with temperature up to about 260 °C. At 300 °C the magnetically split spectrum disappeared and only a doublet remained. They considered this to be a quadrupole doublet and attributed its occurrence to a structural change in the sample.

Sprouse and his colleagues<sup>7</sup> observed a broad asymmetrical line in the Mössbauer spectrum from recoil-implanted  $^{57}\text{Fe}$  source atoms in aluminum. This measurement was made as part of a series of recoil-implantation experiments involving various host lattices.

This paper describes experiments that were undertaken in an attempt to clarify the discrepancies among the results of the various Mössbauer measurements on dilute solutions of iron in aluminum. The first objective was to see whether the Mössbauer spectra for  $^{57}\text{Fe}$  impurities introduced into aluminum while the aluminum was molten could be fully understood in terms of the phase diagram for Fe-Al alloys. The second objective was to look for similarities between such spectra and the spectra obtained in the investigations with sources prepared by drying and subsequent heat treatment<sup>6</sup> or by recoil implantation<sup>7</sup> and to see if any of these similarities might lead to an understanding of the basically discrepant results of the various experiments.

## II. EXPERIMENT

The Mössbauer spectrometer was of the constant-acceleration type, with some unusual features.<sup>8</sup> The source was  $^{57}\text{Co}$  in chromium metal, and was held at room temperature for all of the measurements. With the help of a cryostat and a vacuum oven, the absorber temperature could be varied from liquid-helium temperature to the melting temperature of aluminum. The absorbers were prepared in various ways, and were subjected to various heat treatments before their spectra were measured, as will be described.

### A. Identification of the $\text{Fe}_4\text{Al}_{13}$ Spectrum and the Solid-Solution Spectrum

Specimens containing 0.005-, 0.02-, 0.05-, and 1.2-at. % iron enriched in  $^{57}\text{Fe}$  were prepared by

melting 99.999% pure aluminum together with the iron in an argon arc furnace. Each sample was rolled down to 0.025 cm thickness, and then annealed for 6 days at 540 °C. X-ray diffraction measurements on these samples detected only the face-centered-cubic structure expected for a solid solution of iron in aluminum metal. However, most of these samples had iron concentrations well above the solubility limit for iron in aluminum at either room temperature or 540 °C so that the  $\text{Fe}_4\text{Al}_{13}$  phase should also have been present. That this phase was not detected by x-ray diffraction is a consequence of the fact that at such low concentrations of Fe, the small quantity of  $\text{Fe}_4\text{Al}_{13}$  present occupies only a very small fraction of the total volume of the sample.

The room-temperature Mössbauer spectra for these samples are shown in Fig. 2. At the lowest concentrations, most of the intensity is in a single line at about 0.4 mm/sec. This line has already been identified<sup>3-5</sup> as the line for  $^{57}\text{Fe}$  in the solid solution. Other components are present, and their intensities grow with increasing iron concentration. Additional measurements were made to determine whether these other components are due to the  $\text{Fe}_4\text{Al}_{13}$  phase. Two special samples were prepared. One, which contained 0.02-at.% Fe, was vacuum annealed at 640 °C (just below the melting point) for

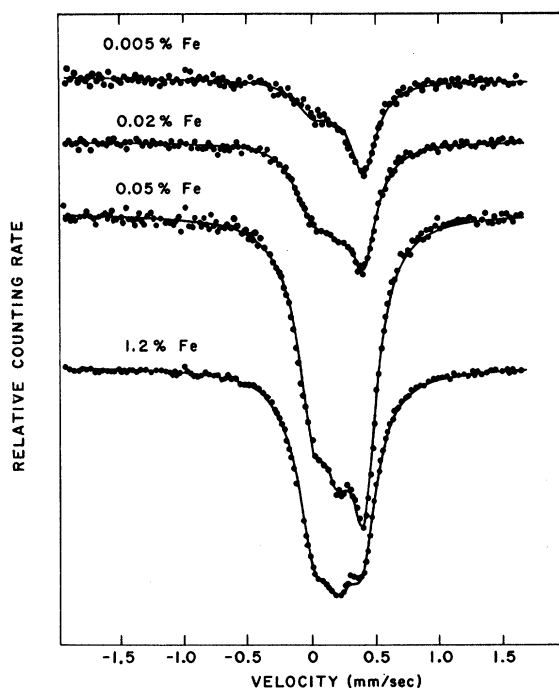


FIG. 2. Mössbauer spectra for various concentrations of iron in aluminum at room temperature. The solid lines represent fits to mixtures of the spectra for the solid solution and for  $\text{Fe}_4\text{Al}_{13}$ .

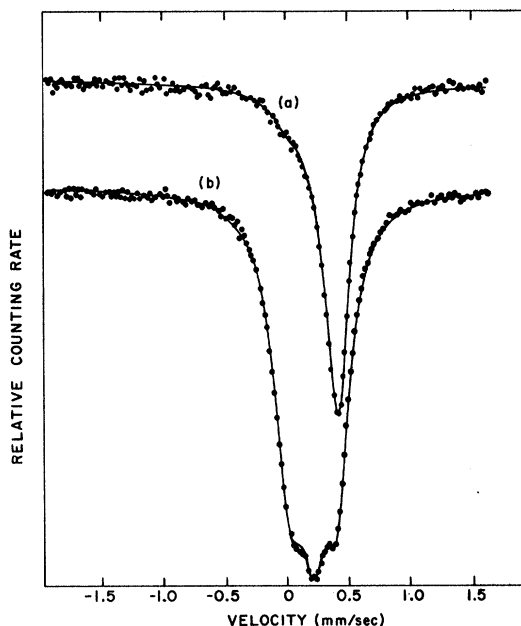


FIG. 3. Mössbauer spectra (a) for the nearly pure solid solution and (b) for the pure  $\text{Fe}_4\text{Al}_{13}$  phase.

6 days. Although this sample was not cooled especially rapidly (e.g., it took 8 min to cool from 640 to 540 °C) its room-temperature spectrum consisted almost entirely of a strong solid-solution line [spectrum (a) in Fig. 3]. The spectrum of such a sample can be restored to the form shown in Fig. 2 for 0.02% Fe by reannealing the sample at 540 °C for 6 days. If it is not reannealed, however, the spectrum does not exhibit any appreciable reversion to that form after six months of aging at room temperature.

The other special sample had a composition lying within the narrow range between  $\text{FeAl}_4$  and  $\text{Fe}_4\text{Al}_{13}$ . It was annealed at 540 °C for 7 days and then filed. The filings were reannealed at 540 °C for 2 h to remove strains, and were then used for both x-ray diffraction measurements and Mössbauer absorption measurements. The x-ray patterns agreed with those obtained by Black<sup>2</sup> for  $\text{Fe}_4\text{Al}_{13}$ .

It was found that the Mössbauer spectrum of this  $\text{Fe}_4\text{Al}_{13}$  sample could be fitted well by three lines of equal width and equal intensity, but nonuniform spacing. It did not seem worthwhile to try to fit this spectrum to five different quadrupole doublets representing the five different iron sites. The data and the best fit are shown as curve (b) of Fig. 3. The parameters determined from the fit are given in Table I. The spectrum of the 0.02% Fe sample [curve (a) in Fig. 3] was then fitted to a composite spectrum consisting of a small amount of the spectrum for  $\text{Fe}_4\text{Al}_{13}$  added to the spectrum for the solid solution. In this fitting, the  $\text{Fe}_4\text{Al}_{13}$  spectrum was

TABLE I. Parameters found from best fits to the room-temperature spectra of the  $\text{Fe}_4\text{Al}_{13}$  phase and the solid-solution phase. The  $\text{Fe}_4\text{Al}_{13}$  spectrum ought to contain five quadrupole doublets, but a satisfactory fit is obtained with three equal lines that turn out to be almost uniformly spaced.

Phase	Line position (mm/sec relative to iron metal at room temperature)	Linewidth (mm/sec)	Constraints used in fitting
$\text{Fe}_4\text{Al}_{13}$	$0.010 \pm 0.002$	$0.265 \pm 0.002$	All three lines equal in width and intensity
	$0.202 \pm 0.002$	$0.265 \pm 0.002$	
	$0.392 \pm 0.002$	$0.265 \pm 0.002$	
	(Mean: 0.20)		
Solid solution	$0.422 \pm 0.001$	$0.242 \pm 0.002$	

approximated by three lines with equal intensities and with the positions given in Table I. The solid-solution spectrum was represented by a fourth, independent, line. The parameters that were varied to produce the best fit were the (equal) intensities of the  $\text{Fe}_4\text{Al}_{13}$  lines, the position and intensity of the solid-solution line, and the (equal) widths of all four lines. The best fit is the solid line shown with the data for the 0.02% spectrum [curve (a) in Fig. 3]. The position of the solid-solution line, as determined by this fitting, is given in Table I.

The assumption that the spectra of Fig. 2 consisted of mixtures of the  $\text{Fe}_4\text{Al}_{13}$  spectrum and the solid-solution spectrum was then tested by fitting the data of Fig. 2 according to the same prescription, except that the position of the solid-solution line as well as the positions of the three lines representing  $\text{Fe}_4\text{Al}_{13}$  were now all constrained to be the values given in Table I. That is, two intensities and one linewidth were the only adjustable parameters. The solid curves in Fig. 2 illustrate the good quality of the fits. The variations of the intensities of the two components as functions of the Fe concentration agree qualitatively with our expectations which were based on the phase diagram of Fig. 1. That is, at all concentrations except the lowest the solution is saturated with iron and, as a consequence, the intensity of the solid-solution component is approximately constant over the concentration range investigated. Also, as expected, the intensity of the  $\text{Fe}_4\text{Al}_{13}$  phase increases with increasing iron concentration. (In the spectrum of the 0.005% sample, a noticeable part of the measured spectrum is actually due to iron impurities in the aluminum window of the  $\gamma$ -ray detector. The spectrum of these impurities is shown later in Fig. 6. The presence of this fixed background has been allowed for in obtaining all the results given in this paper. The dependence of the intensities on the concentration is not obvious from inspection of Fig. 2 because the spectra are plotted to different

vertical scales.)

Further evidence that the components of the spectrum for the solid-solution and the  $\text{Fe}_4\text{Al}_{13}$  phases have been correctly identified comes from a series of spectra for the 0.02% sample (annealed at  $540^\circ\text{C}$ ) taken at different temperatures. These spectra are shown in Fig. 4. The solid curves represent best fits made under the following conditions. The three lines for  $\text{Fe}_4\text{Al}_{13}$  were all kept equal in intensity, but this intensity was varied for best fit. The separations of these three lines were constrained to be the same as the separations found for pure  $\text{Fe}_4\text{Al}_{13}$  (Table I), but the absolute positions of these lines were varied for best fit. The intensity and the position of the solid-solution line were both varied for best fit. All four lines were constrained to have the same width, and this width was varied for the best fit. It was possible to get good fits to the data over a wide temperature range. The positions and intensities of the two components as determined from these fits are shown in Fig. 5.

For purposes of comparison, the data of Nasu *et al.*<sup>5</sup> for the solid solution are also shown in Fig. 5. They concluded from their treatment of their data that the shift falls off with temperature at almost the classical high-temperature rate, even at rather low temperatures. However, as may be seen here, the shift for the  $\text{Fe}_4\text{Al}_{13}$  falls off much more slowly. If interpreted as an ordinary thermal shift, this indicates that the mean-squared velocity of the iron atoms increases more rapidly with tem-

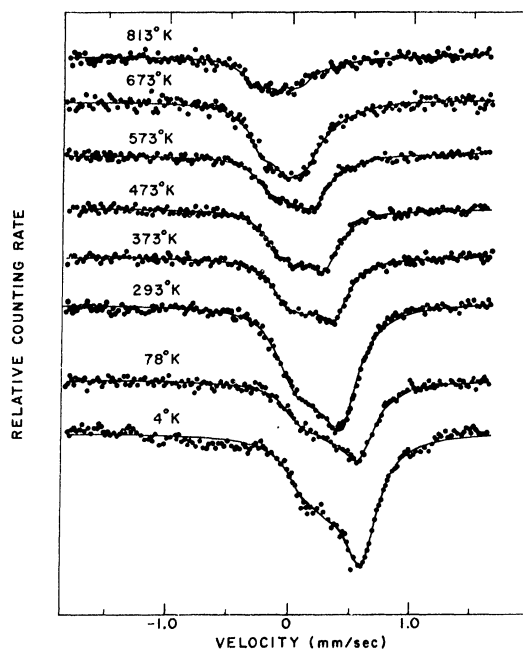


FIG. 4. Mössbauer effect for 0.02% Fe in aluminum at various temperatures.

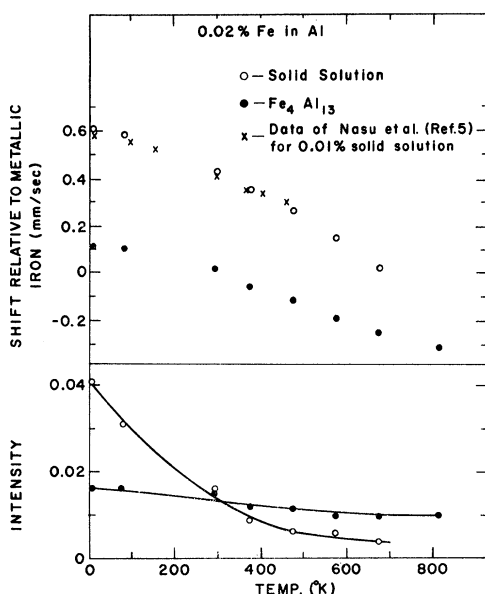


FIG. 5. Temperature dependence of the shifts and intensities of the components of the spectrum that represent the solid solution and  $\text{Fe}_4\text{Al}_{13}$ . The shifts are relative to metallic iron at room temperature. The shift plotted for  $\text{Fe}_4\text{Al}_{13}$  is the shift of one of the three lines chosen to represent the complex  $\text{Fe}_4\text{Al}_{13}$  spectrum. In the fitting, the other two lines were constrained to shift in step with this one.

perature in the solid solution than in  $\text{Fe}_4\text{Al}_{13}$ , and implies that the mean-squared displacement of the iron atoms from their equilibrium positions also increases more rapidly in the solid solution. Because of the dependence of the Mössbauer fraction on the mean-squared displacement, we thus expect that at low temperatures the intensity of the solid-solution spectrum will decrease more rapidly with increasing temperature than will the intensity of the  $\text{Fe}_4\text{Al}_{13}$  spectrum. As may be seen from the intensity data of Fig. 5, this is just what happens.

#### B. Reconsideration of the Results of Bara *et al.*

Bara *et al.* had concluded that the spectrum for a very dilute solution of  $^{57}\text{Co}$  in metallic aluminum is influenced by slow electronic spin relaxation at temperatures as high as  $250^\circ\text{C}$ , but this seemed open to some question. An alternative explanation of their data, suggested to us by Flinn,<sup>9</sup> was that if the relaxation had really been slow, it might have been because the  $^{57}\text{Co}$  had diffused into the protective aluminum oxide coating on the surface of the aluminum, and not into the metal itself. No effects of slow relaxation were seen at  $78^\circ\text{K}$  by Wertheim and Remeika<sup>10</sup> in the spectrum of a source made by diffusing  $^{57}\text{Co}$  into  $\alpha\text{-Al}_2\text{O}_3$ , but we considered it possible that the oxide coating might actually be  $\gamma\text{-Al}_2\text{O}_3$ , which is the form of the protective coating

formed in air at temperatures above  $500^\circ\text{C}$ .<sup>11</sup> We therefore made some inconclusive attempts to diffuse  $\text{FeCl}_2$  into powdered  $\gamma\text{-Al}_2\text{O}_3$ .

A sample of this powder that had been moistened in a solution of  $\text{FeCl}_2$  was heated in an argon atmosphere at  $600^\circ\text{C}$  for several hours. The room-temperature absorption spectrum of this sample consisted of a complex central component with a superimposed weak six-line spectrum that was readily identified as coming from  $\text{Fe}_2\text{O}_3$ . We attributed the production of magnetic  $\text{Fe}_2\text{O}_3$  to the presence of traces of oxygen in the argon gas, which we knew to be less pure than the argon used in the preparation of our metallic aluminum samples. We then reannealed the sample at  $600^\circ\text{C}$  in the same argon gas to which a small amount of hydrogen had been added. We hoped that the oxygen in the argon would combine with this hydrogen, rather than with the iron in the sample. However, we found that the hydrogen also tended to reduce the  $\text{Fe}_2\text{O}_3$  that had already been formed, so that the room-temperature spectrum now contained two six-line patterns, one for  $\text{Fe}_2\text{O}_3$  and the other for metallic iron.

While this result is not surprising, nor of special intrinsic interest, we mention it because it suggested still another possible explanation for the results of Bara *et al.*, namely, in the course of their heat treatment they produced three different forms of cobalt: (i) cobalt in solid solution in aluminum metal, (ii) cobalt in metallic cobalt, and (iii) cobalt in cobalt oxides. With this in mind we have estimated the shifts and splittings of some of their spectra from their published graphs. We find that the single broad line which they observed at room temperature after the initial heating for 100 min at  $600^\circ\text{C}$  is very similar to curve (a) of Fig. 3 of this paper. This corroborates their statement that this line is the normal line for the paramagnetic solid solution in aluminum (if the spin relaxation is fast).

The six-line spectrum they observed after further heating could very well be that of  $^{57}\text{Fe}$  in metallic cobalt. First, in the spectrum at room temperature the shift relative to a stainless-steel absorber is about  $-0.15$  mm/sec. From the results of Walker, Wertheim, and Jaccarino<sup>12</sup> we would expect a shift of  $-0.12$  mm/sec. Second, the rate at which the hyperfine field falls off with temperature is almost the same as, but slightly faster than, the rate for the spontaneous magnetization of cobalt metal.<sup>13</sup> Third, the room-temperature hyperfine splitting is about 320 kOe as compared with the known value of 316 kOe for  $^{57}\text{Fe}$  in cobalt.<sup>14</sup>

The two lines of the doublet that appeared in the spectrum of Bara *et al.* at  $350^\circ\text{C}$  after prolonged heating in argon probably represent  $^{57}\text{Fe}$  in oxides of cobalt. They are very similar to the two lines

obtained by Ok and Mullen<sup>15</sup> at nearly the same temperature from a source containing  $^{57}\text{Co}$  in oxides of cobalt. When allowance is made for the different absorber used by Ok and Mullen, their lines were at about  $-0.35$  and  $-0.95$  mm/sec relative to stainless steel, which may be compared with shifts of about  $-0.4$  and  $-0.9$  mm/sec for the lines observed by Bara and his colleagues.

### C. Interpretation of the Recoil-Implantation Spectrum of Sprouse *et al.*

The spectrum of Sprouse *et al.* for recoil-implanted  $^{57}\text{Fe}$  in aluminum is very broad [approximately 8 mm/sec full width at half-maximum (FWHM)], and is superficially similar to the absorber spectra of Fig. 2 for dilute alloys of Fe in aluminum. For purposes of comparison we show (Fig. 6) our spectrum for 0.02% Fe in Al, a spectrum for recoil-implanted iron in aluminum, and the spectrum of the aluminum window of our  $\gamma$ -ray detector. The recoil-implantation data are from recent unpublished results of Sprouse and Latshaw,<sup>16</sup> to whom we are indebted for permission to use these data here. The recoil-implantation spectrum has been reversed horizontally because of the change of sign between source and absorber experiments, and the velocity scale has been shifted so that it refers to velocities relative to Fe in metallic iron, as it does for the other two spectra.

The similarity of the three spectra might be thought to suggest that regardless of how the iron is introduced into aluminum – whether by controlled introduction (the top spectrum), by recoil implanta-

tion (middle spectrum), or by “accidental” introduction (bottom spectrum) – the iron atoms occupy the same kinds of sites and therefore give the same kinds of Mössbauer spectra. However, there are strong reasons to doubt this. The aluminum window of the detector probably does contain a good deal of iron; since it is not enriched in  $^{57}\text{Fe}$ , the iron would be difficult to detect otherwise. Therefore it ought to contain a mixture of the solid solution and the  $\text{Fe}_4\text{Al}_{13}$  phases and thus have a spectrum similar to the upper spectrum, as it does. But the recoil-implantation spectrum should not have any appreciable component due to  $\text{Fe}_4\text{Al}_{13}$ . One justification for this statement is that we have made Mössbauer absorption measurements on a piece of the original aluminum implantation-target material, and cannot find any  $^{57}\text{Fe}$  Mössbauer spectrum above the known background from our detector window. Second, even if there were some small iron impurity in the aluminum target (say, 0.02%) and if half of that (for instance) were present in the form of  $\text{Fe}_4\text{Al}_{13}$ , then only about 0.03% of the total volume of the target would be the  $\text{Fe}_4\text{Al}_{13}$  phase, and all the rest would be the solid-solution phase. Therefore the probability that a recoil-implanted  $^{57}\text{Fe}$  atom would come to rest in the  $\text{Fe}_4\text{Al}_{13}$  instead of in the solid solution would be about 0.0003, which is too small to make an observable contribution to the Mössbauer spectrum. (Of course, this argument about the relative volumes of the solid solution and  $\text{Fe}_4\text{Al}_{13}$  phases does not apply to absorber experiments in which, under the same assumptions, the important consideration is that half of the iron capable of absorbing an incoming  $\gamma$  ray would be in one phase and half in the other.)

A further argument against assigning part of the recoil-implantation spectrum to  $\text{Fe}_4\text{Al}_{13}$  is that it is not possible to get a good fit by using the positions of the three lines that we use to simulate the  $\text{Fe}_4\text{Al}_{13}$  spectrum as given in Table I. Of course, the statistics of this spectrum are such that no fit to it is likely to be convincing, but a better fit can, in fact, be obtained by assuming that only two lines are present, each with the same width but with independent intensities and positions. The parameters of this fit are given in Table II, and the reliability of the fit may be judged from the solid curve drawn through the recoil-implantation data of Fig. 6. The linewidths required for this fit are 2.5 times the natural width, and it is apparent from the gentle slope of the sides of the dip that it would be impossible to fit this spectrum with only a few lines, each with the natural width. This means that the implanted iron atoms occupy a wide range of environments, each producing a somewhat different spectrum, and is probably related to the fact that each implanted iron atom tends to produce considerable damage in the aluminum lattice in the vicin-

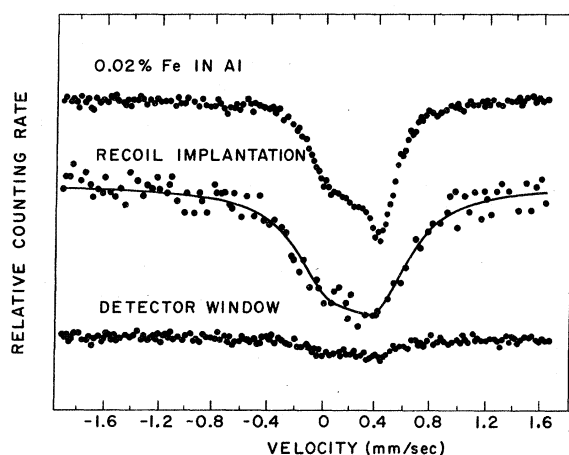


FIG. 6. Mössbauer spectra for 0.02% iron in aluminum, for recoil-implanted excited  $^{57}\text{Fe}$  in aluminum, and for natural iron impurities in “high-purity” aluminum. The original recoil-implantation source spectrum has been reversed horizontally to simulate an absorber spectrum. All velocities are relative to metallic iron at room temperature.

TABLE II. Results of fitting the recoil-implantation data of Sprouse and Latshaw (Ref. 16) to two lines with equal widths and independent intensities. This is an extreme oversimplification of a complicated spectrum, but the results demonstrate that part of the spectrum is very much like a broadened solid-solution line, while the rest is very dissimilar to the  $\text{Fe}_4\text{Al}_{13}$  spectrum (see Table I).

Component	Line position (mm/sec relative to iron metal at room temperature)		Linewidth (mm/sec)	Fraction of total intensity	Constraints used in fitting
"Solid solution"	$0.42 \pm 0.01$	$0.55 \pm 0.03$		0.65	Same width for both lines
Extra component	$-0.01 \pm 0.03$	$0.55 \pm 0.03$		0.35	

ity of its own final equilibrium position.

There has been much experimental and theoretical investigation of the damage done by heavy particles traveling through crystal lattices.<sup>17</sup> This work has led to the view that as a primary particle (such as an iron atom) slows down in aluminum, it can produce a branching cascade of atomic collisions within the lattice – the immediate result being that a large number of normally filled lattice sites are left vacant, while an equal number of atoms originally at lattice sites now reside in interstitial locations. In the vicinity of the place where the iron atom finally stops, there is a region of damage that may extend over hundreds or thousands of lattice sites. The tendency is for interstitials to be more numerous than vacancies near the boundaries of the damaged region, and for vacancies to be more numerous than interstitials in the center of the damaged region where the stopped iron atom is also likely to be. Both the vacancies and the interstitials immediately begin to diffuse through the lattice. Since the lifetime of the excited nuclear state in  $^{57}\text{Fe}$  is  $10^{-7}$  sec, the Mössbauer spectrum will depend on what happens in the vicinity of the iron atom during the  $10^{-6}$  sec right after its implantation.

A lattice defect diffuses by jumping at an average rate of about  $10^{13} \times e^{-E/kT}$  jumps per second, where  $E$  is the activation energy for defect motion.<sup>18</sup> For vacancies in aluminum the activation energy is about 0.6 eV,<sup>19</sup> while for free interstitials the value is probably about 0.1 eV, as it is for copper and nickel<sup>19</sup> (both also fcc). From these values of the activation energy we conclude that at room temperature each vacancy jumps about  $10^3$  times per second, while each interstitial jumps about  $10^{12}$  times per second. During the first  $10^{-6}$  sec, which is all we need to consider, the vacancies are therefore practically immobile, while the interstitials make many jumps. As a consequence of the rapid jump

rate for interstitials we expect that the implanted iron atom, if it were not already on a lattice site, would migrate rapidly to a vacant site and remain there. For an interstitial aluminum atom there are several possible fates<sup>19</sup>: It may diffuse away from the damaged region entirely; it may jump into a vacant lattice site (interstitial-vacancy recombination); it may come close enough to another interstitial that both of them are effectively immobilized (interstitial cluster formation); it may, as has been suggested, be converted to a new type of interstitial with a very low mobility (interstitial conversion); or, finally, it may become trapped in the vicinity of the implanted iron atom (impurity trapping). In any case its rapid, free migration in the vicinity of the iron atom certainly comes to an end on a time scale very short compared with  $10^{-6}$  sec. In all but one of these cases its subsequent jumping rate at room temperature is so low that thereafter it is effectively immobile during the remainder of the first  $10^{-6}$  sec. The exceptional case is that of trapping of the interstitial by the implanted iron atom. The activation energy for an interstitial trapped by an impurity in aluminum is unknown. It could well be such that it would jump, but not very often during the rest of the first  $10^{-6}$  sec.

Thus we arrive at a picture of an excited  $^{57}\text{Fe}$  atom coming to rest and decaying very nearly as it would if it had always been on a lattice site. There will be some effectively immobile vacancies left in the vicinity because many of the interstitials will have suffered fates other than recombination. There may also be immobile interstitial clusters in the vicinity, and there may even be a somewhat insecurely bound interstitial atom next to the iron atom. With this picture in mind we can give a qualitative explanation of the recoil-implantation Mössbauer spectrum. First, regardless of the details of the cascade process and the subsequent migration of interstitials, we expect that some fraction of the iron atoms will be surrounded by just a full complement of 12 nearest-neighbor aluminum atoms. These iron atoms should contribute a component to the Mössbauer spectrum which is simply the regular solid-solution line, except that it may be broadened by variations in the configuration of vacancies and interstitial clusters at greater distances. The apparent presence in the recoil-implantation spectrum of a broad line centered about the normal location of the solid-solution line (Table II) seems to fulfill this expectation.

The most likely sources of the remainder of the spectrum are iron atoms which have one or more nearest-neighbor vacancies or interstitials, again with additional blurring due to variations in the environment at greater distances. An estimate of the relative importance of these contributions to the spectrum is impossible without detailed knowledge

of the initial state of the damaged region as well as of the subsequent behavior of the migrating interstitials. However, it does seem that it would be difficult for an interstitial atom to penetrate the region of high vacancy concentration surrounding the implanted atom without recombining. Therefore the trapping of an interstitial by the implanted atom may be a relatively rare event. If so, the Mössbauer spectrum would then be basically a composite of the spectra for solid-solution iron with 0, 1, 2, ... nearest-neighbor vacancies, each of these basic spectra being blurred by variations in the arrangement of vacancies and interstitial clusters at greater distances.

We are planning some measurements on quenched samples and radiation-damaged samples of dilute

alloys of Fe in aluminum, hoping to learn how to distinguish between nearest-neighbor vacancies and nearest-neighbor interstitials by their effects on the Mössbauer spectrum.

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