

## Crystal Structures of V-Fe Alloys as Determined by the Mössbauer Effect in Fe<sup>57</sup>†

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We have measured Mössbauer absorption by Fe<sup>57</sup> in vanadium-rich V-Fe alloys in the composition range from 0–50 at.% Fe and have interpreted our results in terms of structural features. The literature on the V-Fe system does not suggest the existence of ordering in samples quenched from high temperatures, and x-ray diffraction patterns for our own V-Fe samples include only the lines characteristic of a disordered (bcc) lattice. However, the Mössbauer results can be understood only if a CsCl-like ordering exists over the range of compositions from about 15 to 50 at.% Fe.

### I. INTRODUCTION

THE Mössbauer absorption by Fe<sup>57</sup> in V-Fe alloys has been measured by Kocher and Moser<sup>1</sup> over the concentration range from 1 to 20% Fe.<sup>2</sup> They found that the linewidth varies from a minimum at 1% iron to a plateau starting at 15%, and that the isomer shift changes very little over this concentration range. We have performed a similar series of measurements on alloys containing 1–50% Fe, and our observations agree with those of Kocher and Moser in the region of overlap.

Our measurements were made on alloy samples which had been quenched from high temperatures. Since the x-ray powder patterns were characteristic of the bcc structure with no superlattice lines, we assumed that the iron and vanadium atoms were randomly distributed on a body-centered-cubic space lattice. However, our results are inconsistent with simple qualitative predictions that follow from this assumption.

### II. EXPECTED DEPENDENCE OF THE MÖSSBAUER PATTERN ON IRON CONCENTRATION

The behavior of the Mössbauer pattern as a function of the iron concentration in V-Fe alloys can be predicted qualitatively by use of existing information on the crystallographic and magnetic properties of the V-Fe system in conjunction with the results of previous Mössbauer measurements on other iron alloys.

No detailed study of short- or long-range order in the vanadium-iron system has been reported, and the crystallographic situation has been unclear. X-ray measurements on V-Fe samples quenched from high

temperatures in the alpha phase region show that the lattice is body-centered cubic. Usually there is no evidence of atomic ordering. However, there are several experimental problems associated with the discernment of ordering in V-Fe alloys by x-ray measurements. First, the atomic scattering factors of vanadium and iron are very similar; superlattice lines will be faint even for chromium  $K\alpha$  radiation for which the difference in atomic scattering factors is maximum. Second, unless powder samples are annealed to remove the plastic deformation produced by filing or crushing, they give diffuse lines so that superlattice reflections, weak to begin with, are made even more difficult to distinguish from the background. At concentrations higher than 38% Fe it is possible to effect a transformation to the  $\sigma$  phase<sup>3</sup> by suitable heat treatment. The presence of the  $\sigma$  phase is, of course, readily detected by x-ray diffraction. It is only the observation of ordering *within* the bcc phase that is difficult.

In the region from 0 to 38% Fe, no x-ray evidence of any kind has been found for order in the alpha phase. Hanneman and Mariano<sup>4</sup> interpret their observation of negative deviations from Vegard's law in the region from 0–30% Fe as evidence that V-Fe bonds are stronger than V-V or Fe-Fe bonds. They do not report the presence of superlattice lines. However, their x-ray measurements were made with  $K\alpha$  radiation from Co, not Cr.

In the region from 38 to 60% Fe, there is some evidence for ordering. Nevitt and Aldred<sup>5</sup> report that in this range of compositions there are weak CsCl superlattice reflections of chromium  $K\alpha$  radiation after the samples are annealed for  $\frac{1}{2}$  h at 625°C. Longer annealing converts these samples to the  $\sigma$  phase. The

† Work performed under the auspices of the U. S. Atomic Energy Commission.

<sup>1</sup> C. W. Kocher and B. Moser, *Bull. Am. Phys. Soc.* **8**, 600 (1963).

<sup>2</sup> Concentrations are expressed in atomic percent.

<sup>3</sup> M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Company, Inc., New York, 1958), p. 729.

<sup>4</sup> R. E. Hanneman and A. N. Mariano, *Trans. AIME* **230**, 937 (1964).

<sup>5</sup> M. Nevitt and A. Aldred, *J. Appl. Phys.* **34**, 463 (1963).

strongest evidence for atomic order in the alpha phase exists at 50% Fe. Beck *et al.*<sup>6</sup> and Philip and Beck<sup>7</sup> report weak CsCl superlattice reflections of chromium  $K\alpha$  radiation from a 50% Fe sample quenched from a high temperature, and an enhancement of these reflections after the sample was annealed for a short period at 625°C.

We have measured the diffraction of chromium  $K\alpha$  radiation by samples in the range from 0 to 50% Fe. These samples were quenched from temperatures near 1200°C and then powdered by filing. The bcc reflections are diffuse and no superlattice lines are visible. No appreciable amount of the  $\sigma$  phase is present. After the powder samples are annealed for  $\frac{1}{2}$  h at 625°C, the diffraction pattern appears completely unchanged for 38% Fe; but for 45% Fe the diffraction pattern then becomes sharp and CsCl superlattice lines become clearly visible. The  $\sigma$  phase is still absent.

Taking into account our results and the earlier findings, we assumed that when V-Fe samples are quenched from high temperatures, those containing between 0 and about 40% Fe have the disordered bcc structure, while samples containing 40-50% Fe have some tendency to order with the CsCl structure, but remain primarily disordered unless they are annealed at the lower temperature. Our first series of Mössbauer measurements was made with samples that had not been annealed, so we assumed they were all in the disordered bcc phase.

There have been two studies of the magnetic properties of V-Fe alloys quenched from high temperatures in the  $\alpha$ -phase field. Nevitt and Aldred<sup>5</sup> measured the saturation magnetization in the range 30-100% Fe. Lam *et al.*<sup>8</sup> measured magnetic susceptibility in the range 0-30% Fe. These investigators found no ferromagnetic ordering at room temperature at concentrations below about 50% Fe, no ferromagnetic ordering at any temperature below 30% Fe, and no atomic magnetic moment below 23% Fe.

At room temperature, then, the Mössbauer spectra of the disordered vanadium-iron alloys should show no magnetic splitting except for concentrations near 50% Fe. On the other hand, electric-quadrupole and isomer-shift effects are likely at all concentrations. These effects are related to each other through the fact that they both depend on the distribution of electric charge in the lattice. The isomer shift reflects the density of electronic charge at the Fe<sup>57</sup> nucleus, while the total charge distribution in the lattice affects the gradient of the electric field at the Fe<sup>57</sup> nucleus by a net amount reflected by the quadrupole splitting.

The isomer shift has been measured for Fe<sup>57</sup> con-

tained as an impurity in all of the 3d metals.<sup>9</sup> As noted by Walker *et al.*,<sup>10</sup> by Goldansky,<sup>11</sup> and by Wertheim,<sup>9</sup> these isomer shifts (despite the differences among them) are all sufficiently similar to each other to indicate that the charge density at the Fe nuclei is almost independent of which of the 3d metals serves as the host lattice. High-pressure measurements by Pound *et al.*<sup>12</sup> and by Nicol and Jura<sup>13</sup> have shown that the isomer shift changes with volume. Pipkorn *et al.*<sup>14</sup> and Edge *et al.*<sup>15</sup> have studied this effect in detail and find that for Fe in iron and for Fe in vanadium as well as other lattices, the small but observable variation in isomer shift is proportional to the fractional change in volume. Similarly, Nevitt *et al.*<sup>16</sup> have found that the Fe<sup>57</sup> isomer shift for ordered XFe<sub>2</sub>-type Laves phases depends on the volume available to the iron atoms about as strongly as it depends on the nature of the X component. According to Sutton and Hume-Rothery,<sup>17</sup> the lattice parameter changes by 4% in the range from 0 to 50% Fe in V-Fe alloys. Therefore, variations of isomer shift with concentration are to be expected.

Wertheim and Wernick,<sup>18</sup> who measured the isomer shift for Fe<sup>57</sup> impurities in Cu-Ni alloys, observed a smooth variation in the mean isomer shift as the proportions of Cu and Ni were varied over the whole range from 0 to 100% Cu. This behavior is reasonable in view of the fact that both the average volume per Fe atom and the average electronic features of the lattice to which the Fe<sup>57</sup> isomer shift might respond are smoothly varying functions of the Cu-Ni ratio.

In more detailed studies involving ferromagnetic alloys of iron, a number of investigators<sup>19-25</sup> have observed that at a given concentration of iron, the isomer

<sup>9</sup> G. K. Wertheim, *Mössbauer Effect: Principles and Applications* (Academic Press Inc., New York, 1964), p. 57.

<sup>10</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, *Phys. Rev. Letters* **6**, 98 (1961).

<sup>11</sup> V. I. Goldansky, *At. Energy Rev.* **1**, 3 (1964).

<sup>12</sup> R. V. Pound, G. B. Benedek, and R. Drever, *Phys. Rev. Letters* **7**, 405 (1961).

<sup>13</sup> M. Nicol and G. Jura, *Science* **141**, 1035 (1963).

<sup>14</sup> D. N. Pipkorn, C. K. Edge, P. Debrunner, G. De Pasquali, H. G. Drickamer, and H. Frauenfelder, *Phys. Rev.* **135**, A1604 (1964).

<sup>15</sup> C. K. Edge, R. Ingalls, P. Debrunner, H. G. Drickamer, and H. Frauenfelder, *Phys. Rev.* **138**, A729 (1965).

<sup>16</sup> M. V. Nevitt, C. W. Kimball, and R. S. Preston, *Proceedings of the International Conference on Magnetism, Nottingham, 1964* (Institute of Physics and The Physical Society, London, 1965), p. 137.

<sup>17</sup> W. B. Pearson, *A Handbook of Lattice Spacings and Structures of Metals and Alloys* (Pergamon Press, Ltd., London, 1958), p. 663.

<sup>18</sup> G. K. Wertheim and J. H. Wernick, *Phys. Rev.* **123**, 755 (1961).

<sup>19</sup> P. A. Flinn and S. L. Ruby, *Phys. Rev.* **124**, 34 (1961).

<sup>20</sup> M. B. Sterns, *Phys. Rev.* **129**, 1136 (1963).

<sup>21</sup> G. Shirane, C. W. Chen, P. A. Flinn, and R. Nathans, *Phys. Rev.* **131**, 183 (1963).

<sup>22</sup> C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, *Proc. Phys. Soc. (London)* **81**, 1079 (1963).

<sup>23</sup> T. Cranshaw, *Rev. Mod. Phys.* **36**, 395 (1964).

<sup>24</sup> G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, *Phys. Rev. Letters* **12**, 24 (1964).

<sup>25</sup> Mary Beth Stearns and Stephen S. Wilson, *Phys. Rev. Letters* **13**, 313 (1964).

<sup>6</sup> P. A. Beck, J. B. Darby, Jr., and O. P. Arora, *Trans. AIME* **206**, 148 (1956).

<sup>7</sup> T. V. Philip and P. A. Beck, *Trans. AIME* **209**, 1269 (1957).

<sup>8</sup> D. J. Lam, D. O. Van Ostenburg, M. V. Nevitt, H. D. Trapp, and D. W. Pracht, *Phys. Rev.* **131**, 1428 (1963).

shift for a particular Fe<sup>57</sup> atom depends almost linearly on the number of iron atoms that occupy the nearest-neighbor sites. No cases have been reported for which there is an appreciable dependence on the number of Fe second-nearest neighbors. For small concentrations of V in Fe, the variation in isomer shift per nearest-neighbor iron atom has been found to be +0.06 mm/sec.<sup>24</sup>

When Fe<sup>57</sup> is in the cubic lattice of  $\alpha$  iron, or is present as a trace impurity in the cubic lattice of vanadium, no quadrupole effects can be observed because the distribution of charge about each iron site is approximately cubic and therefore the electric field gradients at these sites are vanishingly small. However, at other concentrations of iron in vanadium there will be observable quadrupole effects in spite of the fact that the lattice is nominally cubic. This is because the random placement of V and Fe at all the lattice sites will cause departures from exact cubic symmetry about the Fe atoms. An atom at a distant site can contribute to the quadrupole field at an Fe nucleus in a number of different ways, but for each type of contribution the effect will decrease with distance approximately as  $1/r^3$ . For example, if the atomic core of a distant atom can be represented by a point charge, its quadrupole effect will follow an exact  $1/r^3$  dependence.<sup>26</sup> If the distant ionic charge is screened by conduction electrons,<sup>27</sup> the screening charge produces a strongly enhanced quadrupole effect and the dependence on distance will become  $1/r^3$  multiplied by an oscillating function of  $r$ . (The finite value of this screening charge at neighboring nuclei may also be responsible for part of the effect that neighboring impurity atoms are observed to have on each other's isomer shifts.) Lattice distortions due to unequal atomic sizes can also contribute to the quadrupole field. The contribution to the quadrupole field tensor is proportional to the local strain tensor,<sup>26</sup> and the strain produced by a distant atom<sup>28</sup> varies approximately as  $1/r^3$ .

In an ordered lattice, distant atoms can contribute appreciably to the quadrupole field at a site of non-cubic symmetry because the  $1/r^3$  dependence is nearly balanced by the increase with distance in the number of contributing atoms. In a disordered cubic lattice, however, the quadrupole effects of distant atoms will tend to cancel each other, on the average, because of the random placement of the two types of atoms. Therefore, in estimating the quadrupole field at an Fe site we may,

<sup>26</sup> M. H. Cohen and F. Reif, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1957), Vol. 5, p. 321.

<sup>27</sup> J. Friedel, *Phil. Mag.* **43**, 153 (1952); J. S. Langer and S. H. Vosko, *J. Phys. Chem. Solids* **12**, 196 (1959); A. Blandin and J. Friedel, *J. Phys. Radium* **21**, 689 (1960); W. Kohn and S. H. Vosko, *Phys. Rev.* **119**, 912 (1960).

<sup>28</sup> J. D. Eshelby, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press Inc., New York, 1956), Vol. 3, p. 79. See especially Sec. 8.

to a good approximation, consider only the contributions of the nearer atoms.

### A. Broadening of the Spectrum

We assume that for any given configuration  $C$  of the surrounding V and Fe atoms, the tensor of the electric field gradient at any iron nucleus is the sum of the tensors calculated by considering each of the surrounding atoms acting separately.<sup>29</sup> For the present we restrict our attention to the eight nearest neighbors in the bcc lattice, and we assume that the isomer shift depends only on these neighbors and not on any additional concentration-dependent parameters such as lattice spacing, etc. If this lattice is considered to be basically vanadium with iron impurities, then only those neighboring sites occupied by Fe atoms contribute to the tensor of the electric field gradient at the Fe nucleus under consideration. For  $n$  Fe nearest neighbors ( $0 \leq n \leq 8$ ) in a given configuration  $C$ ,

$$V_{ij}(C) = \sum_{l=1}^n V_{ij}(l), \quad (1)$$

where  $V_{ij} = \partial^2 V / \partial x_i \partial x_j$ , and  $V_{ij}(l)$  is the contribution of the  $l$ th neighboring Fe impurity.

For any given number  $n$  of Fe nearest neighbors, there are  $m = 8! / [n!(8-n)!]$  distinguishable configurations  $C_k$ , where  $1 \leq k \leq m$ . The  $m$  different  $C_k$  are all equally likely to occur. Each configuration  $C_k$  produces a characteristic quadrupole field gradient at the body-center site, and therefore a characteristic Mössbauer absorption spectrum. In the case of Fe<sup>57</sup>, each spectrum is split into two equal components displaced by equal amounts on either side of the centroid.<sup>30</sup> For Fe atoms with  $n$  Fe nearest neighbors, the Mössbauer absorption as a function of velocity will be

$$A_n(v) = \frac{1}{m} \sum_{k=1}^m A_k(v), \quad (2)$$

where  $A_k(v)$  is the absorption spectrum characteristic of  $C_k$ . The spectrum  $A_n(v)$  is a superposition of symmetrically broadened or split lines, all of which have the same  $n$ . We assume that all the  $A_k(v)$  for a given  $n$  have the same isomer shift. Therefore each  $A_n(v)$  is itself symmetrical.

At any iron concentration  $c$ , the total Mössbauer absorption will be given by

$$A_c(v) = \sum_{n=0}^8 P(n,c) A_n(v), \quad (3)$$

where  $P(n,c)$  is the readily calculated probability that

<sup>29</sup> See Ref. 26, p. 368.

<sup>30</sup> We do not consider special cases in which the quadrupole-split pattern may be asymmetric.

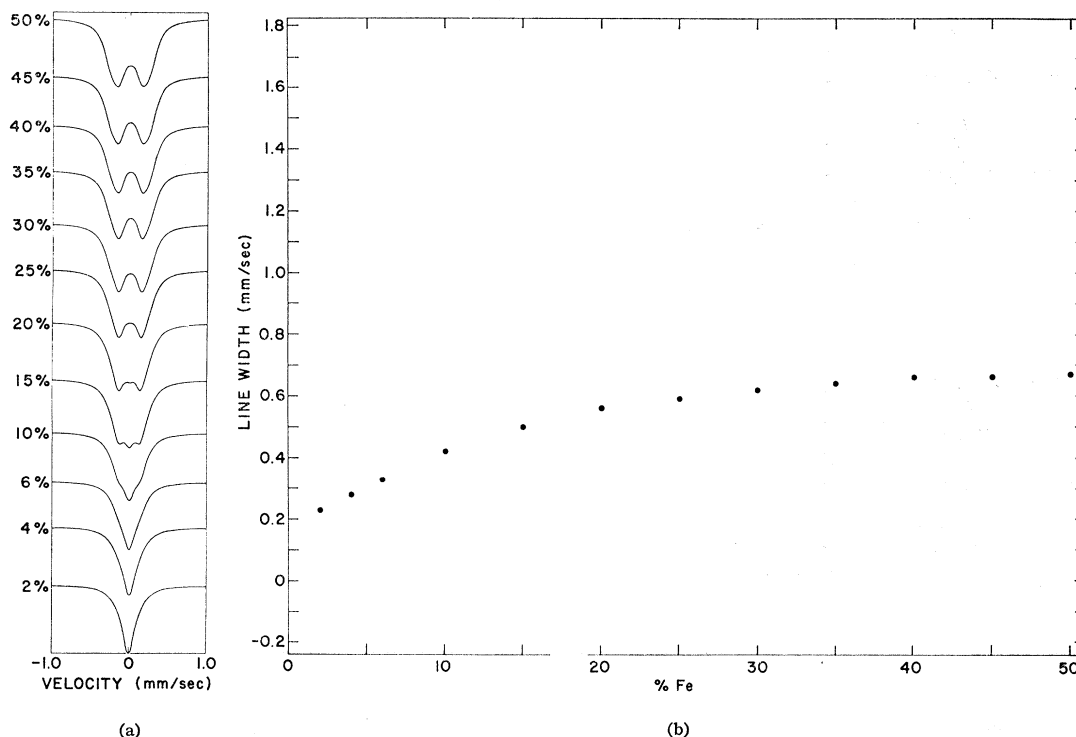


FIG. 1. Mössbauer absorption spectra calculated for various concentrations of iron in a bcc lattice: (a) calculated spectra, (b) linewidth plotted as a function of iron concentration. It has been assumed that the eight nearest neighbors are responsible for the quadrupole broadening, and that the isomer shift is independent of the surroundings.

at concentration  $c$  any Fe atom has  $n$  Fe nearest neighbors and

$$\sum_{n=0}^8 P(n,c) = 1$$

for every  $c$ . The absorption  $A_c(v)$  is a superposition of symmetrically-broadened or split-line spectra  $A_n(v)$ . If the isomer shifts for the different  $A_n(v)$  happened to be independent of  $n$ , then  $A_c(v)$  would also be symmetric about its centroid. Typically, however, the isomer shift of  $A_n(v)$  is a function of  $n$  (independent of  $c$  according to our present assumptions). Therefore, we may expect some asymmetry in the spectral shape, and a further contribution to the spectral width from the distribution of isomer shifts.

For a fixed absorber thickness, exponential absorption may contribute an additional broadening of the Mössbauer lines which increases with increasing iron concentration.

### B. Effective Isomer Shift

The shift of the centroid of the composite Mössbauer pattern (the average isomer shift) is given by

$$\bar{S}(c) = \sum_{n=0}^8 S(n)P(n,c) + \delta(c), \quad (4)$$

where  $S(n)$  is the shift characteristic of absorbing atoms

with  $n$  iron nearest neighbors, and  $\delta(c)$  represents any possible concentration-dependent shift that would shift all the  $A_k(v)$  equally. The existence of a nonzero  $\delta(c)$  would shift any spectrum  $A_c(v)$  calculated by Eq. (3), but would not alter its shape.

### C. Numerical Calculations

Using Eqs. (1)–(3), we have calculated the spectral shape as a function of concentration for two hypothetical cases. In Fig. 1(a) we show spectra calculated for the case in which the full width at half-minimum of the unsplit absorption line would be 0.20 mm/sec and the quadrupole field produced by a single Fe nearest neighbor would split the line into two minima separated by 0.28 mm/sec. This amount of quadrupole splitting was chosen because the calculated spectra are then similar in general appearance to the experimental spectra, as will be discussed below. Since  $n \leq 8$ , the number of  $A_k(v)$  that had to be calculated for use in Eq. (2) was large but manageable. We have taken  $S(n) = \text{const} = 0$ ; this is responsible for the bilaterally symmetric shapes of all the spectra. We have also taken  $\delta(c) = 0$ . The constancy of both  $S(n)$  and  $\delta(c)$  accounts for the constancy of the average isomer shift. We have not included any effects of exponential absorption on the spectral shapes. In Fig. 1(b), the linewidths of the calculated spectra are plotted as functions of iron concentration. We note that the broadening is minimum

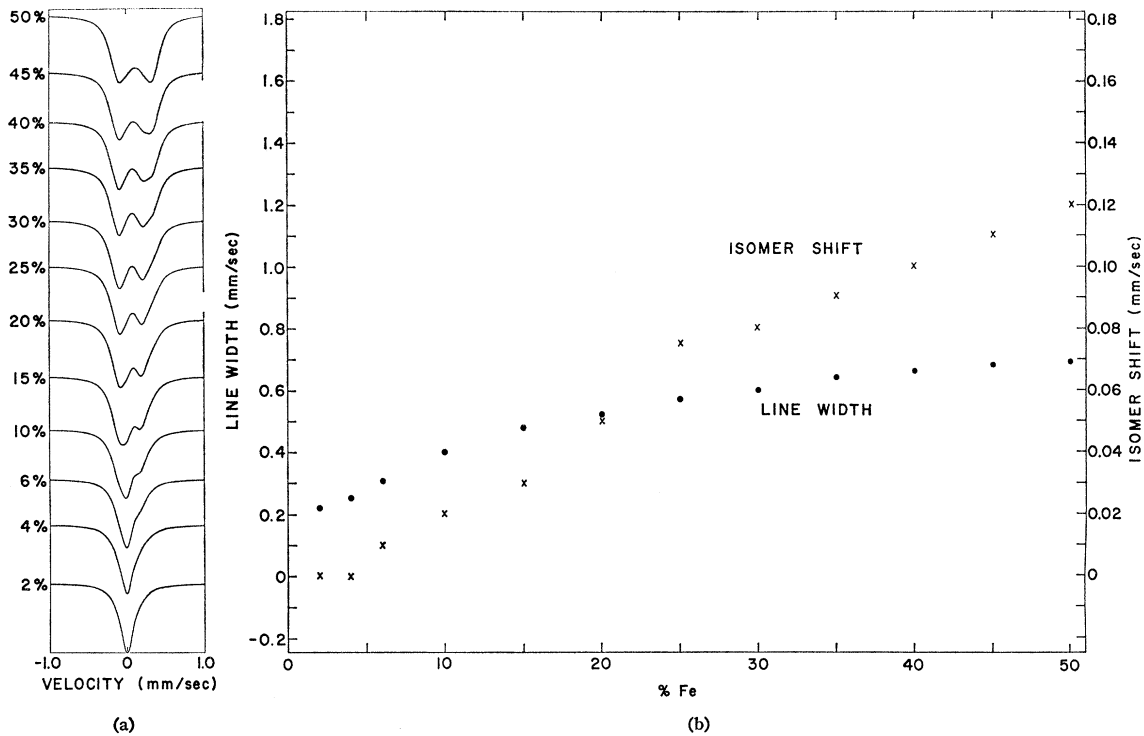


FIG. 2. Mössbauer spectra calculated for various concentrations of iron in a bcc lattice: (a) calculated spectra, (b) linewidth and isomer shift plotted as functions of iron concentration. It has been assumed that the eight nearest neighbors are responsible for the quadrupole broadening, and that the isomer shift is proportional to the number of iron nearest neighbors.

at low iron concentrations at which, in effect, every iron atom has only vanadium atoms as nearest neighbors, so the local symmetry at iron sites is cubic and there are no quadrupole fields. The broadening rises monotonically to a maximum at 50% Fe. In the absence of magnetic effects, the broadening would then fall to a minimum again at 100% Fe. And since it happens in this particular case that  $A_c(v) = A_{1-c}(v)$ , the curve of spectral width versus  $c$  would be symmetrical about  $c = 0.5$ .

A more realistic calculation would include some dependence of  $S(n)$  on the number of nearest neighbors. Wertheim *et al.*<sup>24</sup> report that the shift is  $\partial S(n)/\partial n = 0.06$  mm/sec for  $nn$  Fe atoms in iron-rich V-Fe alloys ( $n \approx 8$ ). Figure 2 summarizes the results of calculations in which, for illustrative purposes only, we have used  $S(n) = 0.03n$  mm/sec and  $\delta(c) = \text{const} = 0$ . The spectral shapes are not symmetrical, but again the linewidth is seen to rise monotonically between 0 and 50% Fe. In this case, in which  $S(n)$  is a linear function of  $n$ , the curve of linewidth versus concentration would again be symmetrical about  $c = 0.5$ .

### III. EXPERIMENT

The source,  $\text{Co}^{57}$  diffused into copper, gave a Mössbauer linewidth of 0.21 mm/sec when used with a thin iron absorber. Powdered absorbers were prepared by crushing or filing portions of the bulk samples used in

the previous studies of the magnetic properties of vanadium-iron. The only exception was the 50% Fe sample, which was rolled into a foil. In a few cases, to be described, the samples were given additional heat treatment after they had been powdered. Usually the powdered samples (400 mesh) were encapsulated in Lucite disks to insure rigidity. However, in cases in which the absorber had to be kept at a high temperature during the Mössbauer measurement, the powdered sample was dispersed in boron nitride powder. This mixture was then sandwiched between thin boron nitride disks for mounting in a vacuum oven.

### IV. RESULTS

The first series of Mössbauer measurements was made at room temperature with absorber samples which had received no heat treatment after they were powdered. Examples of these spectra are shown in Fig. 3(a). The linewidths and effective isomer shifts (relative to the centroid of the absorption spectrum of  $\text{Fe}^{57}$  in iron at 300°K) are plotted in Fig. 3(b). The spectrum of the 50% Fe foil is not shown because the width is too large for the scale of Fig. 3(a) and because fine structure of magnetic origin is present in the spectrum.

Certain features of our results (Fig. 3) disagree with our expectations (Fig. 2). First, although the 10% sample has an asymmetrical spectrum similar to the calculated 10% spectrum of Fig. 2, all the others are

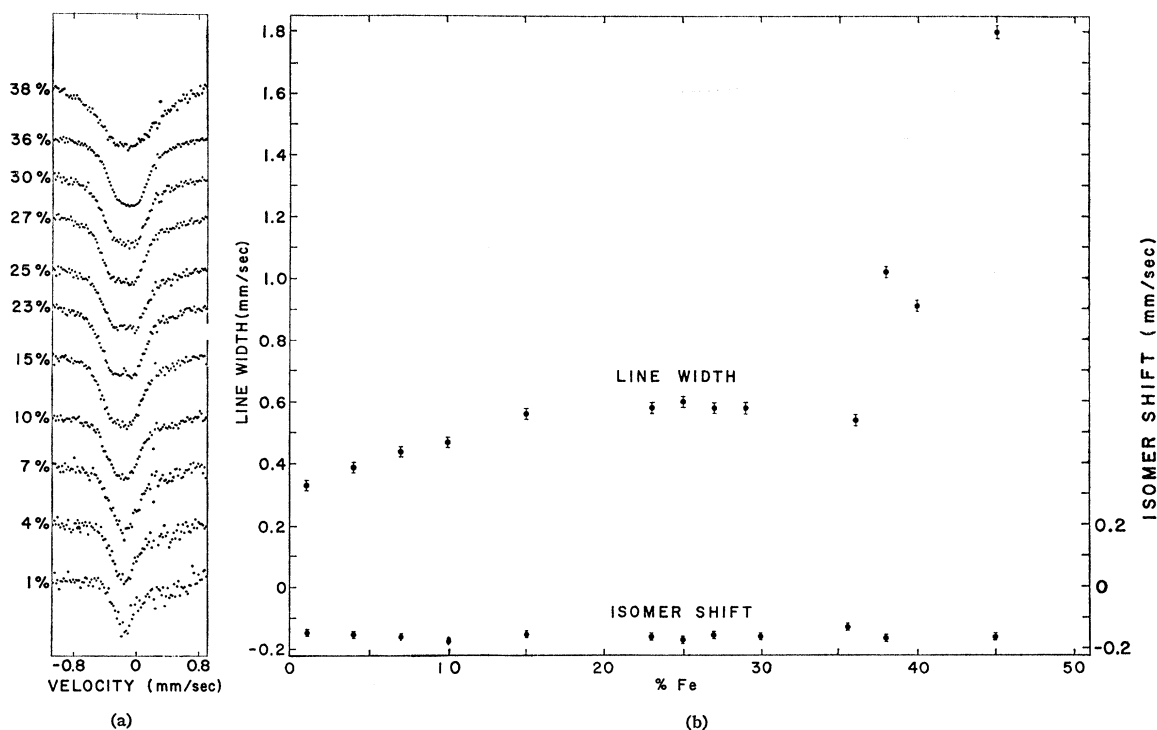


Fig. 3. Mössbauer absorption by  $Fe^{57}$  in V-Fe alloys. (a) Measured spectra, (b) linewidth and isomer shift (relative to the centroid of the absorption spectrum of  $Fe^{57}$  in iron at 300°K) as functions of iron concentration.

nearly symmetrical. If they are really completely symmetrical, then, according to our previous discussion, this could signify that  $S(n)$  is independent of  $n$  over the concentration range from about 15 to 50%. This is unlikely in view of the fact that  $\partial S(n)/\partial n = +0.06$  mm/sec near 100% Fe. Alternatively, according to Eq. (3), a symmetrical spectrum could mean that  $P(n,c)=1$  for a particular value of  $n$  and vanishes for all other values of  $n$ . This is likely, of course, at small concentrations for which we expect  $P(0,c)=1$ , so that the spectra will be symmetrical (as seen in Fig. 2), but it is not possible at higher concentrations if the disposition of V and Fe atoms on the lattice sites is random.

Second, the effective isomer shifts are practically independent of the concentration. According to Eq. (4), this implies that

$$\sum_{n=0}^8 S(n)P(n,c) = -\delta(c)$$

over the range from 0 to 50% Fe. If, as is suggested by the symmetry of the spectra,

$$\sum_{n=0}^8 S(n)P(n,c)$$

is independent of concentration for concentrations greater than 10% Fe, then we have  $\delta(c) = \text{const}$  over this range of concentrations. That is, there is no over-

all concentration-dependent isomer shift, in spite of the known variation of the electron-atom ratio and lattice parameter with concentration. We do not know the significance of this fact, but it is similar to the assumption we made for calculating the curves of Fig. 1. Indeed, with respect to both symmetry of the spectra and constancy of the isomer shift, the experimental data are more reminiscent of the curves of Fig. 1 than of Fig. 2.

A third discrepancy between Fig. 3 and Fig. 2 is that the widths of the experimental spectra, although they vary with concentration, do not increase monotonically in the range from 0 to 50% Fe. Instead, a plateau near 25% Fe is followed by a small but definite decrease in linewidth and then a sharp increase starting near 36% Fe. If the superposition principle expressed by Eq. (1) is approximately correct, then this departure from the expected monotonic behavior can only be interpreted as a departure from randomness. Even when the assumed value for the contribution to the quadrupole field tensor from one  $mn$  atom is taken so large or so small that there is little similarity between the calculated curves and the experimental data, the linewidth broadens monotonically between 0 and 50% Fe if the V and Fe atoms are distributed randomly. On the other hand, without a certain amount of disorder the linewidth and shape would not vary with concentration.

In interpreting these data, we seem to be faced with a contradiction. Certain features of our spectra can be

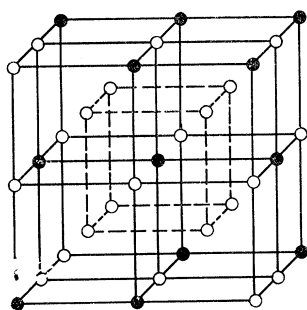


FIG. 4. Body-centered cubic lattice represented as two interlocking simple-cubic sublattices. One simple-cubic lattice consists entirely of vanadium. The other is a random mixture of vanadium and iron.  $\circ$ —vanadium;  $\bullet$ —iron.

understood only if a high degree of order exists within the crystal over most of the range of concentrations, while other features are intelligible only if the crystal is disordered. Nevertheless, there are several ways in which it is possible for a crystal to be sufficiently ordered for all the spectra to be very symmetrical, and yet sufficiently disordered for the broadening to vary with concentration and to be a maximum at 25% Fe. One way is illustrated in Fig. 5 in which a body-centered cubic lattice is represented as two interlocking simple-cubic sublattices. We have assumed that one of the simple-cubic sublattices is completely filled with vanadium at all concentrations from 0 to 50% Fe, while the other sublattice is assumed to contain a random mixture of vanadium and iron atoms. Thus one sublattice is ordered and the other disordered. Complete ordering of the one sublattice is unlikely, but this is the simplest case to consider.

One immediate consequence of this CsCl-type of

ordering is that for the purpose of calculating the isomer shift the lattice may be considered to be ordered. Each Fe atom is surrounded by eight nearest neighbors of vanadium (i.e.,  $n=0$ ) at every concentration from 0 to 50% Fe, and therefore we expect all of the spectra to be symmetric about their centroids—in agreement with our actual findings for >10% Fe. In the calculation of the quadrupole broadening, however, the pertinent lattice is completely disordered. In this model, the ordered sublattice of vanadium has cubic symmetry about every Fe atom and thus contributes nothing to the quadrupole broadening of the  $\text{Fe}^{57}$  spectra at any concentration from 0 to 50% Fe. The quadrupole broadening is, therefore, entirely a consequence of the random ordering of vanadium and iron in the disordered sublattice. We have already pointed out that for completely random placement of V and Fe atoms in a bcc lattice, the curve of linewidth versus concentration will be maximum at 50% and symmetric about 50%.

Without making detailed calculations it is easy to see that for the disordered simple-cubic sublattice we are now considering, the quadrupole broadening will also reach a maximum when 50% of the atoms in the sublattice are iron. This occurs when 25% of the whole lattice is iron. The curve of linewidth versus concentration in the range from 0 to 50% Fe will then be symmetric about 25% Fe. The results of a detailed calculation using only the six next-nearest neighbors in a bcc lattice are shown in Fig. 5.

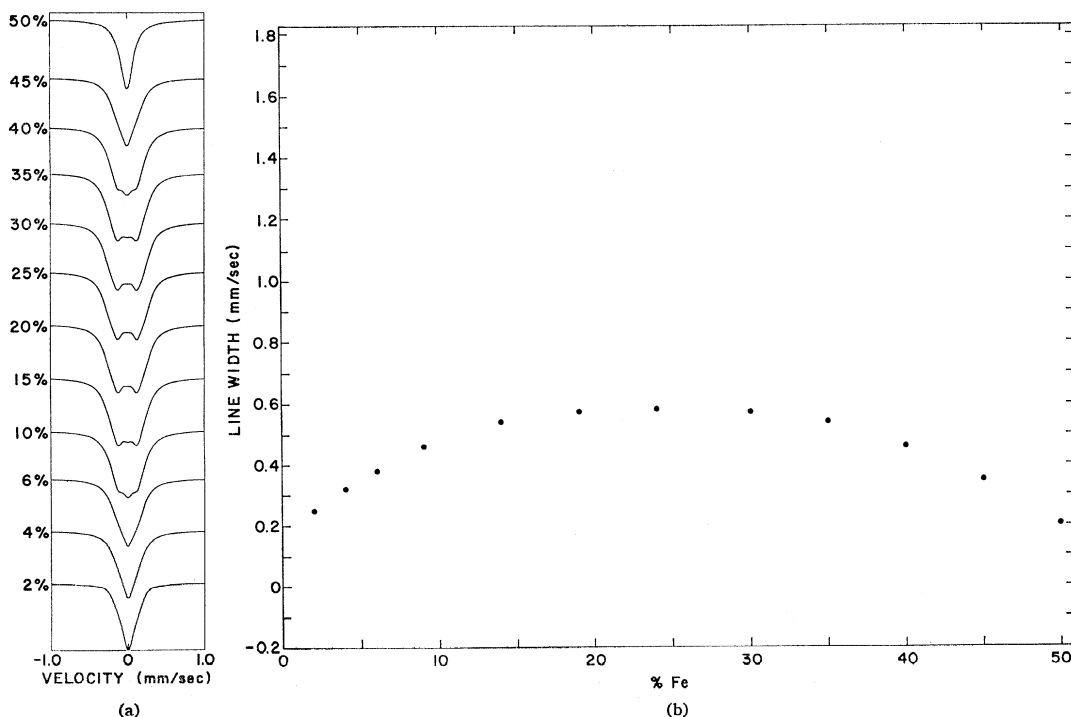


FIG. 5. Mössbauer spectra calculated for various concentrations of iron in a bcc lattice: (a) calculated spectra, (b) linewidth plotted as a function of iron concentration. It has been assumed that the six next-nearest neighbors are responsible for the quadrupole broadening, and that the isomer shift is independent of the surroundings.

A second type of ordering that would yield similar but not identical results is a short-range order that would occur if the otherwise random order were modified by a prohibition against Fe-Fe nearest-neighbor pairs. In this case also, the eight nearest neighbors surrounding an Fe atom would all be vanadium ( $n=0$ ) in the range from 0 to 50% Fe, so that the spectra would all be symmetric.

At low Fe concentrations long-range order, short-range order, and complete disorder are indistinguishable in Mössbauer spectra because all Fe atoms are well isolated from each other in any case. At 50% Fe, either of the two types of ordering produces long-range CsCl order and the Mössbauer spectra would be the same for both cases, but readily distinguishable from the broad spectra characteristic of disorder. An intermediate concentrations, both types of order would give the same nearest-neighbor environments for all Fe atoms ( $n=0$ ), but the distribution of next nearest-neighbor configurations would be different in the two cases.<sup>31</sup> Since the next nearest neighbors are responsible for the (quadrupole) broadening of the spectra if either type of order exists, the details of the spectral broadening would be slightly different in the two cases.

Although the observed linewidths do reach a local maximum near 25% Fe, beyond 34% Fe the behavior is not as predicted for either type of ordering. Either the order disappears above this concentration, or another (overriding) effect appears. Since the symmetry of the spectra still implies that  $n=0$ , and since we know of no evidence of a crystallographic change, we have no reason to assume that the order disappears. Rather, we are prompted to search for electronic effects that could mask the simple predictions based on ordering in the lattice. Since the constancy of the isomer shift argues against any radical changes in the distribution of electron density in the lattice, we must focus our attention on the spins of the electrons. As noted above, previous measurements have shown that ferromagnetic ordering at low temperatures begins to occur at Fe concentrations higher than 30%. This suggests the possibility that the unexpected line broadening at the higher iron concentrations may be magnetic in origin,

TABLE I. Linewidth as a function of temperature for a powdered sample of V 38% Fe. The sample was quenched from 1000°C, then filed to obtain a powder.

Run	Temperature (°C)	Linewidth (mm/sec)
1	20	1.02
2	100	0.50
3	200	0.50
4	20	0.96
5	430	0.46
6	20	0.54

<sup>31</sup> This small but real difference, as well as its consequences for the corresponding Mössbauer spectra, are clearly evident in the results of recent calculations by T. Cranshaw (private communication).

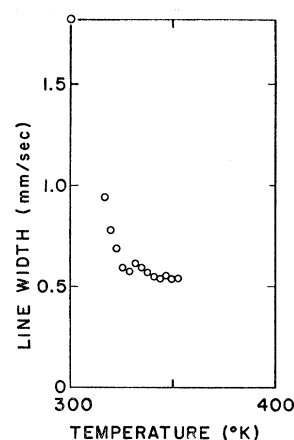


FIG. 6. Linewidth plotted as a function of temperature for a V-Fe absorber containing 45% Fe.

in spite of the fact that below 50% Fe there is supposedly no ferromagnetism at room temperature.

To test this possibility, we measured the Mössbauer absorption as a function of temperature for samples containing 38, 45, and 50% Fe. Table I shows the results of the measurements for the 38% sample. Runs 1-3 show that the linewidth decreases to a minimum of 0.50 mm/sec at some temperature below 100°C. Run 4 shows that when the temperature is returned to 20°C the linewidth increases again, as it should if the narrowing is associated with a magnetic transition. Runs 5 and 6 show that keeping the sample at 430°C for 24 h permanently removes the magnetic broadening at room temperature. This is an annealing effect which will be discussed later. The transition observed in the 45% Fe sample near 60°C is shown in more detail in Fig. 6. It is apparent that this is not an abrupt crystallographic transition, but instead follows the familiar pattern of a curve of magnetization versus temperature near the Curie point. A similar magnetic transition was also found between 300 and 350°C in the 50% Fe foil sample.

In Fig. 7 we have again plotted linewidth versus iron concentration, this time using the new high-temperature values for 38, 45, and 50% Fe. The symmetry of this curve is qualitatively consistent with the assumption of CsCl-like ordering over the whole range from 0 to 50% Fe. Although order cannot be distinguished from disorder in the Mössbauer spectra for the very lowest concentrations, the asymmetry of the spectrum for the 10% sample indicates that the order has disappeared at that concentration. Therefore, we conclude that CsCl-like order actually exists only from about 15 to at least 50% Fe. It should be noted that if there were any tendency toward further ordering of the type that would lead to the  $Fe_3Al$  structure at 25% Fe, the linewidth would be at a minimum rather than the observed maximum at 25%.

Analysis of the Mössbauer data cannot be pushed far enough to lead to a choice between short-range and long-range order, but there is one indication that the basic source of the observed order is a tendency toward



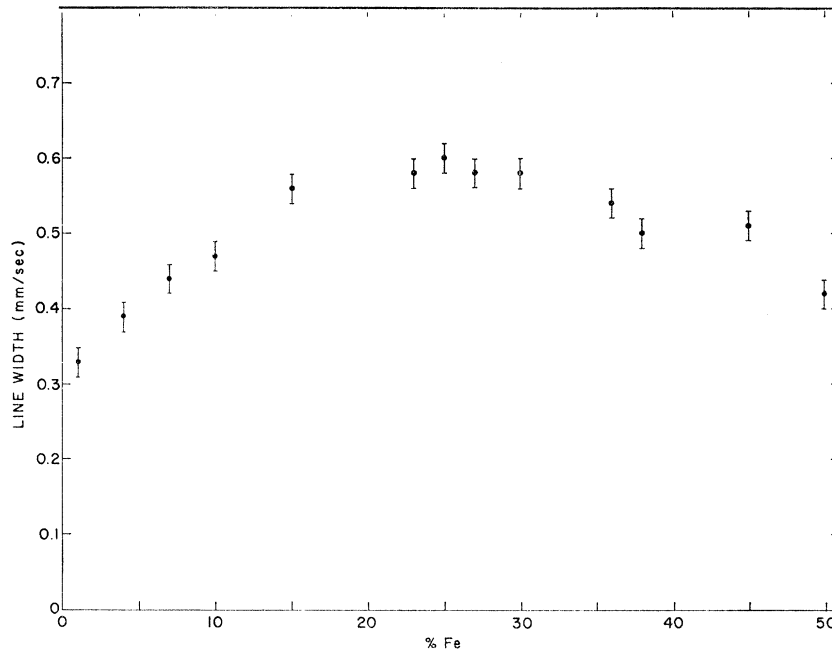


FIG. 7. Measured Mössbauer line-width plotted as a function of iron concentration for nonmagnetic V-Fe samples.

long-range order. This is the fact that the order becomes much weaker below 15%. If the order were simple short range, depending on a prohibition against Fe-Fe pairs, there would be no reason to expect the prohibition to be inoperative below some critical concentration. On the other hand, it is typical of long-range order that it exists only between well-defined concentration limits.

On the assumption that the order is basically long range, it is of interest to consider the completeness of the segregation of Fe atoms onto one of the simple-cubic sublattices of Fig. 4. If there were a tendency toward long-range CsCl order, and a countervailing tendency toward a short-range order that favored Fe-Fe pairs, then the segregation might not be complete. We can take account of possibilities of this sort by introducing a short-range order parameter into our calculations of theoretical Mössbauer spectra. The short-range order parameter  $\sigma$  is related to the probability  $p$  that both members of a nearest-neighbor pair chosen at random will be Fe. According to the usual definition of  $\sigma$ , this probability is given by  $p = c^2(1 - \sigma)$ , where  $c$  is the Fe concentration and  $1 \geq \sigma \geq 0$ . For  $\sigma = 0$ , this reduces to  $p = c^2$ , which is characteristic of complete disorder. For  $\sigma = 1$ , the expression becomes  $p = 0$ , which is characteristic of complete short-range order. We retain this definition of  $\sigma$ , but apply it to the case in which the two simple cubic sublattices are distinguished by the fact that they have different concentrations of iron for a given over-all value of iron concentration. In order to calculate Mössbauer spectra, it is necessary to know the probabilities  $P_V$  and  $P_{V-Fe}$  that arbitrarily chosen sites on the "vanadium" and "vanadium-iron" sublattices, respectively, are occupied by Fe atoms. Since  $p = P_V P_{V-Fe}$ , and since for a given departure from

random order the deficiency of Fe atoms on the "vanadium" sublattice must equal the excess of Fe atoms on the "vanadium-iron" sublattice, we find that  $P_V = c(1 - \sqrt{\sigma})$ ,  $P_{V-Fe} = c(1 + \sqrt{\sigma})$ .

Using these probabilities, we have performed Monte Carlo calculations to determine the expected composite Mössbauer spectra for various concentrations and various degrees of ordering. The parameters of each calculation were (1) the iron concentration, (2) the short-range-order parameter, (3) the shift per  $nn$  Fe atom, and (4) the quadrupole splitting produced by a single  $nn$  Fe atom (a  $1/r^3$  dependence was used to determine the relative contributions of  $nn$  and  $nnn$  Fe atoms to the quadrupole field). The composite spectra obtained from the calculation were actually combinations of two separate composites, one typical of Fe atoms on the "vanadium" sublattice and one typical of Fe atoms on the "vanadium-iron" sublattice. These two components were weighted by the factors  $P_V$  and  $P_{V-Fe}$  before they were added together. For every set of parameters, 5000 simple spectra were calculated for Fe atoms on each type of sublattice. For each simple spectrum, the Monte Carlo procedure was used to decide which of the fourteen nearest and next-nearest neighbor sites were occupied by V and which by Fe atoms, again with the appropriate use of  $P_V$  and  $P_{V-Fe}$ .

There is no reason to suppose that one particular value of  $\sigma$  would actually hold for all concentrations. Also the shift per  $nn$  Fe atom is unknown for this concentration range. Nevertheless, we can attempt to estimate a range of possible values for  $\sigma$  at particular concentrations from a comparison of the shapes of the experimental and calculated spectra.

Figure 8 shows some of the spectra for 10% and 25%

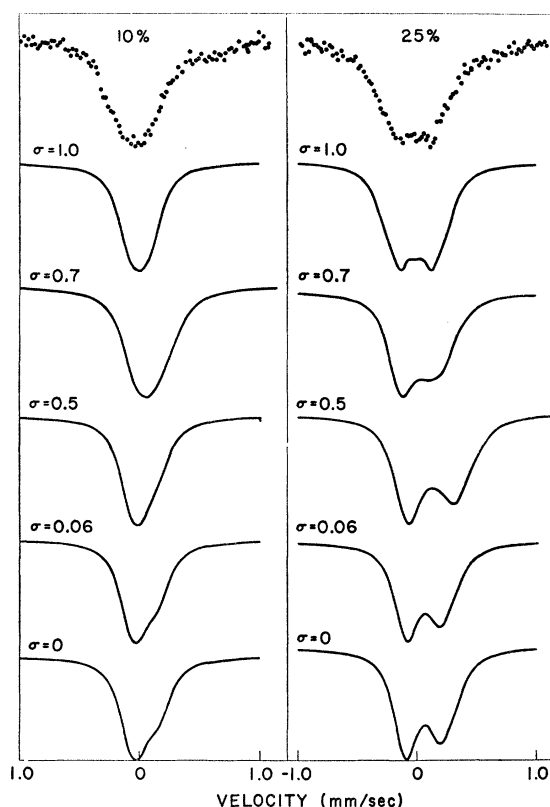


FIG. 8. Experimental Mössbauer spectra, and spectra calculated for various values of the short-range order parameter.

Fe calculated for various values of the short-range-order parameter  $\sigma$ , as well as the experimental spectra for these two concentrations (reproduced from Fig. 3). These theoretical spectra were all calculated with the shift per *nn* Fe atom taken to be 0.03 mm/sec. This is half the value observed near 100% Fe and is meant to be a conservative estimate. The quadrupole splitting per *nn* Fe atom was adjusted for each value of  $\sigma$  to give approximately the same linewidth as the experimental spectrum.

Judging from the apparent symmetry of the actual 25% spectrum as compared with the obvious asymmetry of most of the calculated 25% spectra, we might conclude that  $\sigma \approx 1$  for 25% Fe, provided that 0.03 mm/sec is a good estimate of the shift per *nn* Fe atom. For the 10% Fe sample, however, the asymmetry of the measured spectrum leads to an estimate of  $\sigma < 0.5$ , but only if the shift per *nn* Fe atom is changed from +0.03 mm/sec to -0.03 mm/sec. Because some asymmetry exists, it is obvious that there is some disorder. The fact that the shift per *nn* Fe atom has changed sign between 100% Fe and 10% means that our estimated shift of 0.03 mm/sec cannot be trusted at any intermediate concentration, and our estimate of  $\sigma \approx 1$  at 25% Fe may not be justified on the basis of symmetry alone.

At this point it is pertinent to inquire why, if long-range order exists, x-ray measurements do not reveal

its presence. The answer probably lies in the previously discussed experimental difficulties in detecting atomic ordering in this system. In addition, we note the possibility that the size of the ordered domains is too small to be detected by x-ray diffraction, but not too small to be seen in Mössbauer measurements.

We may also ask why the Mössbauer measurements indicate magnetic order at room temperature in the samples with the higher iron concentrations, although previous magnetic measurements did not. The answer seems to be that as a consequence of the cold working involved in crushing the samples to make Mössbauer absorbers, the samples with the higher iron concentrations unexpectedly became ferromagnetic at room temperature. As indicated by runs 4, 5, and 6 (Table I) with the 38% Fe sample, the room-temperature ferromagnetism of a powdered sample can be annealed out. Also, simple experiments show that a small permanent magnet attracts a bulk sample much more strongly after the specimen has suffered a single hammer blow.

In further experiments involving both Mössbauer measurements and a small magnet, we have confirmed the fact that a 38% Fe sample quenched from 1200°C has a Curie temperature below room temperature. If it is filed, the filings have a Curie temperature above room temperature. If these filings are then annealed for  $\frac{1}{2}h$  at 625°C, the Curie temperature is again lower than room temperature. Both before and after the annealing, only bcc lines are visible in the Cr  $K\alpha$  x-ray powder patterns; and in both cases the lines are diffuse. Thus, although plastic deformation is responsible for the rise in the Curie temperature, the subsequent lowering of the Curie temperature can be brought about by an amount of annealing insufficient to produce complete recrystallization.

## V. SUMMARY

The results of the Mössbauer measurements on V-Fe alloys quenched from the high-temperature region of the  $\alpha$  solid solution are consistent with a CsCl type of ordering over the concentration range from about 15 to 50% Fe. Plastic deformation of alloys with the higher iron concentrations can raise the magnetic ordering temperature without producing a significant change in the crystalline ordering as determined by the Mössbauer effect.

Recently Mueller and Heaton of this laboratory have used neutron diffraction to search for long-range order in some of our samples. They observe CsCl superlattice lines over a wide range of concentrations.<sup>32</sup>

## ACKNOWLEDGMENTS

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<sup>32</sup> M. H. Mueller and L. Heaton (private communication).