

Within the framework of Eq. (1), we seem to have to conclude that alloying appreciably affects the mean electron-electron interaction  $V$ .<sup>31</sup> It is interesting to note the effect of algebraically subtracting the dashed lines in Fig. 4 from the appropriate solid curves. The curve of  $\Delta T_c$  vs (residual resistance ratio) for the (InSb) alloys remains unchanged, and the shape of the curve for the Bi alloys is little altered, being pushed toward increasing values of  $T_c$  at the higher concentrations. The form of the curve for the In alloys is changed, however, and closely resembles that for bismuth, with a minimum and a subsequent upward trend. Thus our specific heat results lead to very similar curves for the alloying effect on  $T_c$  of tin, once the effect of changes in  $\gamma$  and  $\Theta$  has been taken into account. This conclusion is already implicit in the work of Seraphim *et al.*<sup>7</sup> It would appear, therefore, that in tin alloys (and by inference in indium and aluminum alloys as well) the effect of alloying on  $V$  is such as to result in an increasing  $T_c$  once the electronic mean free

path becomes less than the range of coherence. To determine this residual effect on  $V$  one must subtract small quantities of comparable magnitude. Unfortunately, the accuracy of our present data does not permit us to determine whether  $V$  depends only on electronic mean free path, or whether there is a residual dependence on valence.

In conclusion, it may be useful to emphasize that the solute concentrations used and the resulting changes in  $T_c$  are much smaller than those considered in various recent surveys of binary and ternary compounds.<sup>32,33</sup> Consequently our conclusions concerning small changes in  $V$  do not directly affect the question of the relative insensitivity of  $V$  to large-scale variations in composition.

#### ACKNOWLEDGMENTS

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<sup>32</sup> B. B. Goodman, J. Hillairet, J. J. Veyssié, and L. Weil, reference 3, p. 350.

<sup>33</sup> J. K. Hulm and R. D. Blaugher, Phys. Rev. **123**, 1569 (1961).

<sup>31</sup> According to P. Morel, J. Phys. Chem. Solids **10**, 277 (1959), a change in  $V$  is expected to arise from variations in lattice spacing. However, the changes in lattice parameters for these alloys are so small<sup>28</sup> that even the largest resulting change in  $V$  is about an order of magnitude smaller than the total alloying effect which we observe.

## Mössbauer Study of Hyperfine Fields and Isomer Shifts in $\text{Fe}_4\text{N}$ and $(\text{Fe,Ni})_4\text{N}$

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Mössbauer measurements of  $\text{Fe}^{57}$  were made on ferromagnetic  $\text{Fe}_4\text{N}$ , which has a face-centered cubic arrangement of iron atoms with nitrogen at the body-center position. The hyperfine fields are 345 koe for the corner Fe and 215 koe for the three face-center Fe, approximately proportional to their magnetic moments,  $3\mu_B$  and  $2\mu_B$ . The isomer shifts, measured against a stainless steel source, are 0.30 mm/sec for the corner Fe and 0.45 mm/sec for the face-center Fe. These values are in line with their proposed electronic configurations of  $3d^7 4s$  and  $3d^8 4s$ , which are derived on the assumption that the nitrogen at the body-center position acts as an electron "donor" to the face-center Fe. The Mössbauer spectra of  $(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$  and  $(\text{Fe}_3\text{Ni})\text{N}$  are consistent with their ordered structures in which Ni replaces the corner Fe preferentially.

#### INTRODUCTION

THE magnetic properties of  $\text{Fe}_4\text{N}$  have been the subject of several investigations in recent years, since its simple structure offers an ideal case for the study of the effects of local environment on electronic configuration and magnetic moments. The crystal structure may best be visualized as a face-center  $\gamma$  iron lattice with nitrogen at the body-center position<sup>1</sup> (see Table I). The corner Fe atom, Fe I, is surrounded by 12 Fe nearest neighbors at 2.96 Å, while the face-center Fe atom, Fe II, has two nitrogens at 1.90 Å as the nearest

neighbors. The body-center nitrogen is surrounded by an Fe II octahedron.

Guillaud and Creveaux<sup>2</sup> have reported a saturation moment of 2.2 Bohr magneton per Fe atom for  $\text{Fe}_4\text{N}$  approximately  $9\mu_B$  for the formula unit. Wiener and Berger<sup>3</sup> have proposed a magnetic structure, in which  $3\mu_B$  and  $2\mu_B$  are assigned to Fe I and Fe II, respectively. This model was based on the assumption that nitrogen acts as a "donor" of electrons, giving one electron to each of the three nearest Fe II atoms. This gives electronic configurations of  $3d^7 4s$  for Fe I and  $3d^8 4s$  for

<sup>1</sup> K. H. Jack, Proc. Roy. Soc. (London) **A195**, 34 (1948).

<sup>2</sup> C. Guillaud and H. Creveaux, Compt. rend. **222**, 1170 (1946).

<sup>3</sup> G. W. Wiener and J. A. Berger, J. Metals **7**, 360 (1955).

TABLE I. Magnetic structure of  $\text{Fe}_4\text{N}$ .  
Nitrogen is located at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

	Position	Outer electrons	Moment
Fe I	(0,0,0)	$3d^7 4s$	$3\mu_B$
3 Fe II	$(\frac{1}{2}, \frac{1}{2}, 0)$ etc.	$3d^8 4s$	$2\mu_B$

Fe II (see Table I). In this way, it was possible to account for the observed moments of  $\text{Fe}_4\text{N}$ ,  $(\text{Fe}_3\text{Ni})\text{N}$ , and  $(\text{Fe}_3\text{Pt})\text{N}$ . Frazer<sup>4</sup> has confirmed this magnetic structure of  $\text{Fe}_4\text{N}$  by neutron diffraction measurements. Later, Goodenough *et al.*<sup>5</sup> proposed a further splitting of  $d$  bands due to the crystalline fields in  $(\text{Fe}, \text{Ni})_4\text{N}$ .

Recently, the recoil-free absorption of 14.4-keV gamma rays of  $\text{Fe}^{57}$ , first discovered by Mössbauer,<sup>6</sup> became available as an important tool for the study of the magnetic properties of solids. This method can yield, among others, two important quantities: the hyperfine field,  $H_i$ , and the isomer shift,  $\Delta E$ . Experimentally, the absorption spectra of  $\text{Fe}^{57}$  in a ferromagnetic spin arrangement shows six symmetrical peaks as a function of the relative velocity of source and absorber. The spreading of these peaks is proportional to the hyperfine field and the shift of the center of this group from zero velocity is defined as the isomer shift.<sup>7</sup>

Although the proportionality of the hyperfine fields of Fe metal to its magnetic moment was established by changing the temperature,<sup>8</sup> the relation between  $H_i$  and the electronic structure of Fe atoms in different environments is not yet well understood. The isomer shift is caused by the difference in the  $s$ -electron densities at the nuclei of the source and the absorber. The theoretical consideration of this problem by Walker, Wertheim, and Jaccarino<sup>7</sup> has shed considerable light on the interpretation of the isomer shift. Utilizing calculated wave functions, they have calibrated the observed isomer shifts as a function of the number of  $3d$  and  $4s$  electrons.

$\text{Fe}_4\text{N}$  offers an interesting problem for Mössbauer study since Fe I and Fe II are considered to be in the  $3d^7 4s$  and  $3d^8 4s$  states, respectively, and the latter configuration has never been investigated by Mössbauer

TABLE II. Magnetic data for  $(\text{Fe}, \text{Ni})_4\text{N}$ .  $\sigma$  and  $\sigma_0$  are the saturation moments in Bohr magnetons per formula unit at 300°K and 0°K, respectively.

		$\text{Fe}_4\text{N}$	$(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$	$(\text{Fe}_3\text{Ni})\text{N}$
$a_0$	( $\pm 0.002\text{\AA}$ )	3.797	3.788	3.786
$T_c$	( $\pm 10^\circ\text{K}$ )	767	695	640
$\sigma$	( $\pm 0.2\mu_B$ )	9.1	8.0	6.9
$\sigma/\sigma_0$	( $\pm 0.01$ )	0.92	0.88	0.86

<sup>4</sup> B. C. Frazer, Phys. Rev. **112**, 751 (1958).

<sup>5</sup> J. B. Goodenough, A. Wold, and R. J. Arnott, J. Appl. Phys. **31**, 342S (1960).

<sup>6</sup> R. L. Mössbauer, Z. Physik **151**, 124 (1958).

<sup>7</sup> L. R. Walker, G. K. Wertheim, and V. Jaccarino, Phys. Rev. Letters **6**, 98 (1961).

<sup>8</sup> D. E. Nagle, H. Frauenfelder, R. D. Taylor, D. R. F. Cochran, and B. T. Matthias, Phys. Rev. Letters **5**, 364 (1960).

absorption. In addition to  $\text{Fe}_4\text{N}$ , measurements were made on  $(\text{Fe}_{4-x}\text{Ni}_x)\text{N}$  with  $x=0.4$  and 1.0. In this solid solution system, Ni substitutes preferentially for Fe I at the corner, as was shown by the x-ray studies of Wiener and Berger<sup>3</sup> and Arnott and Wold.<sup>9</sup> In  $\text{Fe}_3\text{NiN}$ , therefore, all Fe atoms are equivalent, namely, Fe II. These compounds were selected not only to study the possible effect of Ni substitution on the Fe moment, but to eliminate any ambiguity which might possibly exist in an interpretation of the Mössbauer data of pure  $\text{Fe}_4\text{N}$ , where the spectra were expected to be a superposition of two "6 fingers."

### EXPERIMENTAL

The nitride samples were prepared following the procedure of Arnott and Wold.<sup>9</sup> Iron and nickel oxides were obtained by coprecipitation of the oxalates which were then ignited. These oxides were reduced to the metals in a finely divided state by heating in hydrogen. Heating

TABLE III. Mössbauer absorption of  $(\text{Fe}, \text{Ni})_4\text{N}$  at room temperature (mm/sec). Fe was used as a standard to calibrate the velocity scale, by using  $H_i=333$  koe. Errors of line positions were estimated from the results of several runs.

	$\text{Fe}_4\text{N}$ ( $\pm 0.08$ )	$(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$ ( $\pm 0.14$ )	$(\text{Fe}_3\text{Ni})\text{N}$ ( $\pm 0.14$ )	Fe ( $\pm 0.06$ )
1	-5.20	-5.5		
2	-3.00	-3.1	-2.8	-5.20
3	-1.65	-1.5	-1.5	-2.95
4	-0.30	-0.2	0.0	-0.70
5	1.05	1.0	1.1	0.96
6	2.30	2.3	2.2	3.22
7	3.90	3.9	3.7	5.47
8	5.80	6.1		

this metal powder in an ammonia and hydrogen stream produced the nitrides. The x-ray examination of the samples has shown that they are single phase and no trace of free Fe was observed. The chemical analysis indicated a slight deficiency of nitrogen content of 8% in the Ni-containing samples and less than 3% in  $\text{Fe}_4\text{N}$ . The lattice parameters and the magnetic properties of these compositions are in reasonably good agreement with the previous work<sup>2,3,9</sup> (see Table II).

Mössbauer data were obtained by using a multi-channel analyzer coupled with an instantaneous velocity measurement of the stainless steel source.<sup>10</sup> The thickness of the samples was adjusted to give 20 mg/cm<sup>2</sup> of natural Fe. The data presented in this paper give the Mössbauer absorption as a percentage of the nonresonant absorption. The background due to 120-keV gamma rays was determined with a  $\frac{1}{16}$ -in. Al sheet and was subtracted from the data. The velocity scale was

<sup>9</sup> R. J. Arnott and A. Wold, J. Phys. Chem. Solids **15**, 152 (1960).

<sup>10</sup> S. L. Ruby and D. E. Bolef, Phys. Rev. Letters **5**, 5 (1960).

TABLE IV. Hyperfine field,  $H_i$  (koe), and isomer shift,  $\Delta E$  (mm/sec), of  $(\text{Fe}, \text{Ni})_4\text{N}$  at 300°K.  $\Delta E$  referred to the stainless steel source.

		$\text{Fe}_4\text{N}$	$(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$	$(\text{Fe}_3\text{Ni})\text{N}$	Fe
Fe I	$H_i$	$345 \pm 10$	$363 \pm 15$		$333 \pm 8$
	$\Delta E$	$0.30 \pm 0.08$	$0.30 \pm 0.14$		$0.10 \pm 0.05$
Fe II	$H_i$	$215 \pm 10$	$220 \pm 15$	$205 \pm 15$	
	$\Delta E$	$0.45 \pm 0.06$	$0.40 \pm 0.10$	$0.45 \pm 0.10$	

calibrated by using Fe metal as a standard<sup>11</sup> (see Table III).

### $\text{Fe}_4\text{N}$

The Mössbauer absorption data on this compound are shown in Fig. 1 and Table III. The observed curve should be a composite of two "6 fingers" with relative intensities of 3:1, corresponding to 3 Fe II:1 Fe I. Individual 6 fingers must approximate the 3:2:1 branches of an ideal thin absorber. An inspection of the eight resolved peaks immediately gives the following assignment: lines 2 to 7 form six fingers due to 3 Fe II and the lines 1 and 8 correspond to the outer two peaks of Fe I. The inner four peaks of Fe I are more or less hidden by lines 2 to 7, resulting in a slight modification of line shape and intensities of these lines.

The insert in Fig. 1 shows the line position and relative intensities of the 12 components. For this calculation, the pairs 1-8 and 2-7 were matched to the observed lines. There appears to be little doubt that our line indexing is a unique one. To further confirm this point, the composite absorption curve was calculated by superposing 12 lines with the theoretical intensity ratios. Each line was assumed to have a line shape,  $y = (1 + x/\Gamma)^{-1}$ , where  $\Gamma$ , the half-width at half-maximum, was assumed to be 0.27 mm/sec for all the lines. The calculated curve duplicates the observed one quite closely in both line shape and position, except for some deviations in relative intensities attributable to the finite sample thickness.

The hyperfine field,  $H_i$ , and the isomer shifts derived from these lines are listed in Table IV. The values for Fe I had to be derived from only two peaks, 1 and 8. For this reason, the measurements were repeated several times and the stability of the velocity scale was checked repeatedly against an iron standard.

TABLE V. Comparison of hyperfine fields (koe) in Fe metal and  $\text{Fe}_4\text{N}$ .  $\mu_0$  is the atomic moment extrapolated to 0°K.  $H_i$  and  $H_0$  are the hyperfine fields at 300°K and 0°K, respectively.

		$\mu_0$	$\sigma/\sigma_0$	$H_i$	$H_0$	$H_0/\mu_0$
Fe metal		$2.22 \pm 0.02$	0.982	333	$340 \pm 10$	$155 \pm 5$
$\text{Fe}_4\text{N}$	Fe I	$3.0 \pm 0.1$	0.92	345	$375 \pm 15$	$125 \pm 10$
	Fe II	$2.0 \pm 0.1$	0.92	215	$234 \pm 15$	$117 \pm 10$

<sup>11</sup> S. S. Hanna, J. Heberle, C. Littlejohn, G. J. Perlow, R. S. Preston, and D. H. Vincent, Phys. Rev. Letters 4, 177 (1960).

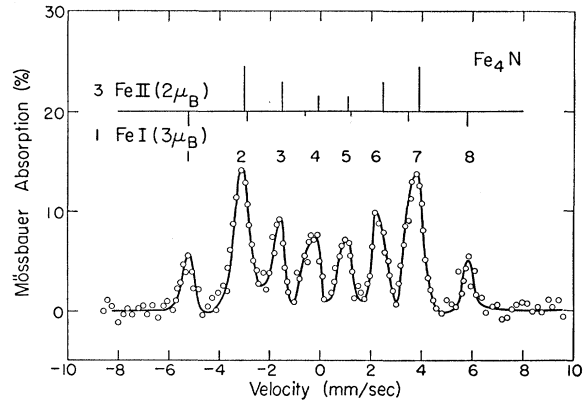


Fig. 1. Mössbauer absorption of  $\text{Fe}_4\text{N}$ . The positive velocities indicate a motion of source toward absorber.

The ratio of the observed hyperfine fields, 345 koe for Fe I and 215 koe for Fe II, is  $1.6 \pm 0.1$ , in good agreement with the ratio of their magnetic moments, 1.5. These internal fields are compared with the value in Fe metal in Table V. The room temperature hyperfine fields were extrapolated to 0°K by using  $\sigma/\sigma_0$ . The last column indicates that the ratio between the hyperfine field and saturation moment in Fe is somewhat different from the corresponding ratios in  $\text{Fe}_4\text{N}$ .

It is interesting to note that the observed isomer shift is definitely larger for Fe II (0.45 mm/sec) than for Fe I (0.30 mm/sec). This difference is in accordance with the expectation from their electronic structures since the isomer shift increases with increasing number of 3d electrons if the number of 4s electrons remains the same. This is the first measurement of the isomer shift of Fe in the  $3d^8 4s$  configuration.

Walker *et al.*<sup>7</sup> assigned a  $3d^7 4s$  configuration for Fe metal, which shows an isomer shift of 0.10–0.15 mm/sec.<sup>7,12</sup> The observed isomer shift for Fe I, which is assumed to have the same configuration, approximately, is somewhat larger than in Fe. This difference

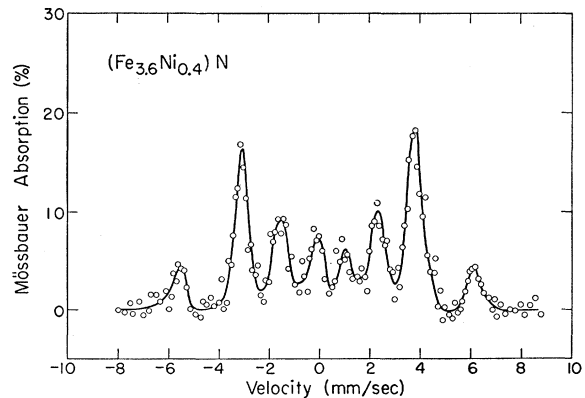
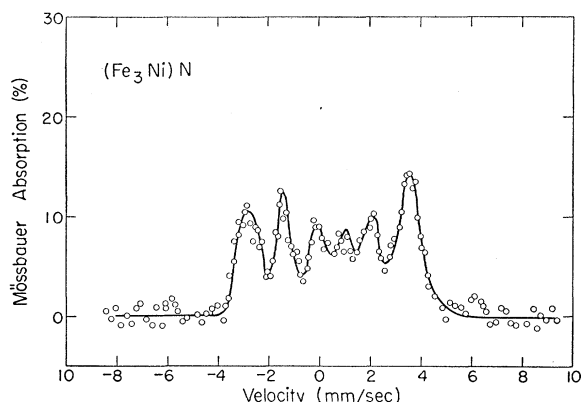


Fig. 2. Mössbauer absorption of  $(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$ .

<sup>12</sup> O. C. Kistner and A. W. Sunyar, Phys. Rev. Letters 4, 412 (1960).

FIG. 3. Mössbauer absorption of  $(\text{Fe}_3\text{Ni})\text{N}$ .

may be attributed to subtle differences of the electronic configurations of the two Fe atoms under comparison, as one may expect from the difference of their magnetic moments and the crystal structures. It should be pointed out that if we use the chart of Walker *et al.*, the observed isomer shift of Fe I corresponds to  $3d^7 4s^{0.95}$ , only a 5% difference in *s*-electron density.

During the course of our investigation, we were informed that Kocher, Mozer, and Nathans<sup>13</sup> of Brookhaven National Laboratory had carried out a Mössbauer measurement of a  $\text{Fe}_4\text{N}$  sample, containing some free Fe, which was previously used for the neutron diffraction study.<sup>4</sup> Their results are in reasonably good agreement with ours.

#### $(\text{Fe}, \text{Ni})_4\text{N}$

Mössbauer spectra of the  $(\text{Fe}, \text{Ni})_4\text{N}$  compounds are shown in Figs. 2 and 3. The outer two peaks of  $\text{Fe}_4\text{N}$ , namely 1 and 8 of Fig. 1, have decreased in intensity in  $(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$  and they have disappeared almost completely in  $(\text{Fe}_3\text{Ni})\text{N}$ , while the inner six lines remain essentially unchanged. This is in accordance with our line indexing of  $\text{Fe}_4\text{N}$  and an ordered structure of  $(\text{Fe}, \text{Ni})_4\text{N}$ , in which Ni replaces Fe I preferentially. The relative intensities of lines 1 and 8 in Fig. 2 are somewhat larger than the expected values for complete Ni ordering in  $(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$  and there appears to be some absorption remaining in  $(\text{Fe}_3\text{Ni})\text{N}$  at the positions corresponding to the lines 1 and 8. This may be a result of some Ni at the face-center positions. Though an accurate estimate of the order parameter from Mössbauer data is difficult, it may be safe to conclude that at least 80% of the Ni atoms are located at the corner position.

The hyperfine fields and the isomer shifts obtained for these two compositions are listed in Table IV. The

hyperfine field at the Fe II nuclei remains almost constant. The slight decrease observed with increasing concentration of Ni is not more than the amount attributable to the decrease of the Néel temperature (see Table I). The hyperfine field at Fe I, on the other hand, increases by 5% from  $\text{Fe}_4\text{N}$  to  $(\text{Fe}_{3.6}\text{Ni}_{0.4})\text{N}$ . A similar increase in  $H_i$  was observed in Fe-Ni alloys by Johnson *et al.*<sup>14</sup> It is not certain, at present, whether this change is directly related to a corresponding increase of the Fe I moment.

The observed isomer shifts of Ni-substituted compounds show little change from the corresponding values of  $\text{Fe}_4\text{N}$ . This implies that the electronic structures of the Fe's are not appreciably affected by Ni additions.

One peculiar anomaly was observed in the  $(\text{Fe}_3\text{Ni})\text{N}$  sample. In Fig. 3, line 2 (using the same line numbering as in Fig. 1) exhibits considerably more line broadening than other lines, although the integrated intensity of this line appear to be normal. This anomaly is evident if compared with line 7 which is supposedly equivalent to line 2. This anomaly cannot be explained by a simple inhomogeneity of isomer shift or a fluctuation of the hyperfine field. The former should give a uniform broadening for all the lines and the latter should result in the greatest line broadening at the outermost peaks.<sup>15</sup> It is conceivable, of course, that an inhomogeneous isomer shift, caused by a slight deficiency of nitrogen, is correlated to a hyperfine field fluctuation in such a way as to result in the observed effect.

The more likely source of this anomaly may be the quadrupole interaction. The local symmetry of the corner Fe I is cubic and no quadrupole effect is expected. The Fe II atoms at the face center position, on the other hand, may exhibit a quadrupole shift because the local symmetry is uniaxial, with the principal axis of the electrical field gradient tensor along the N-Fe II-N direction. The observed effect could be explained qualitatively by assuming a small negative  $e^2qQ$  and the spin direction along [110]. This speculation is by no means well founded and, moreover, there is no *a priori* reason why the quadrupole effect should be larger in  $(\text{Fe}_3\text{Ni})\text{N}$  than in the other nitrides.

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<sup>13</sup> C. W. Kocher, B. Mozer, and R. Nathans (private communication, June, 1961).

<sup>14</sup> C. E. Johnson, M. S. Ridout, T. E. Cranshaw, and P. E. Madsen, *Phys. Rev. Letters* **6**, 450 (1961).

<sup>15</sup> P. A. Flinn and S. L. Ruby, *Phys. Rev.* **124**, 34 (1961).