(See Ref. 10.) These points are all on the top surface of the Brillouin zone, and it will be recalled that in a paramagnetic hcp metal, there is a twofold degeneracy all over this plane due to the presence of $\theta$, the operation of time inversion.

We may now summarize our conclusions. The inclusion of the antiunitary elements, which contain $\theta$, of the magnetic space group of a ferromagnetic fcc or bcc metal leads to no extra degeneracies in the electronic energy band structure. However, for ferromagnetic hcp metals, some extra degeneracies do occur, and the conclusions of the first paragraph of p. 507 of the article by Falicov and Ruvalds[1] would need to be amended. For hcp metals magnetized parallel to [0001], the sticking together of the bands all over the face *AHL* of the Brillouin zone is completely removed, except at the points *A* and *L and along the line R*. The line *R*, which in the paramagnetic structure is fourfold-degenerate (including spin) because of time-reversal symmetry, *splits into two twofold-degenerate levels*. For hcp metals magnetized parallel to [10$\bar{1}$0] or [11$\bar{2}$0], the twofold degeneracy, due to time-reversal symmetry, all over *AHL* is lifted in general, *but still survives at the points A and L and along the lines R, S, and S′.*

TABLE II. Magnetic space group of a ferromagnetic hcp metal.

| Direction of $\mathfrak{M}$ | Magnetic space group | Unitary subgroup | Antiunitary elements[a] |
|---|---|---|---|
| [0001] | $P6_3/mm'c'$ | $\{E\|0\}\{I\|\boldsymbol{\tau}\}$ | $\{C_{21}'\|0\}\{\sigma_{d1}\|\boldsymbol{\tau}\}$ |
| | | $\{C_3^+\|0\}\{S_6^-\|\boldsymbol{\tau}\}$ | $\{C_{22}'\|0\}\{\sigma_{d2}\|\boldsymbol{\tau}\}$ |
| | | $\{C_3^-\|0\}\{S_6^+\|\boldsymbol{\tau}\}$ | $\{C_{23}'\|0\}\{\sigma_{d3}\|\boldsymbol{\tau}\}$ |
| | | $\{\sigma_h\|0\}\{C_2\|\boldsymbol{\tau}\}$ | $\{\sigma_{v1}\|0\}\{C_{21}''\|\boldsymbol{\tau}\}$ |
| | | $\{S_3^+\|0\}\{C_6^-\|\boldsymbol{\tau}\}$ | $\{\sigma_{v2}\|0\}\{C_{22}''\|\boldsymbol{\tau}\}$ |
| | | $\{S_3^-\|0\}\{C_6^+\|\boldsymbol{\tau}\}$ | $\{\sigma_{v3}\|0\}\{C_{23}''\|\boldsymbol{\tau}\}$ |
| [10$\bar{1}$0] | $Cmc'm'$ | $\{E\|0\}\{I\|\boldsymbol{\tau}\}$ | $\{\sigma_h\|0\}\{C_2\|\boldsymbol{\tau}\}$ |
| | | $\{\sigma_{v3}\|0\}\{C_{23}''\|\boldsymbol{\tau}\}$ | $\{C_{23}'\|0\}\{\sigma_{d3}\|\boldsymbol{\tau}\}$ |
| [11$\bar{2}$0] | $Cm'cm'$ | $\{E\|0\}\{I\|\boldsymbol{\tau}\}$ | $\{\sigma_h\|0\}\{C_2\|\boldsymbol{\tau}\}$ |
| | | $\{C_{22}'\|0\}\{\sigma_{d2}\|\boldsymbol{\tau}\}$ | $\{\sigma_{v2}\|0\}\{C_{22}''\|\boldsymbol{\tau}\}$ |

[a] Each entry should be multiplied by $\theta$.

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[10] $H$ is no longer a special point and has the same symmetries and degeneracies as $S$ or $S'$. Also $K$ is no longer a special point.

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# Hyperfine Field Spectra of Binary Fe-Co Alloys: Nuclear and Magnetic Resonance of $^{57}$Fe and $^{59}$Co

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It is shown that a recent interpretation of $^{57}$Fe NMR data on dilute alloys of cobalt in iron is not consistent with certain results established by the Mössbauer effect.

In a recent publication,[1] Rubinstein offers new data and a reinterpretation of the $^{57}$Fe and $^{59}$Co NMR data of dilute alloys of cobalt in iron. His analysis is based on the assumption that the $^{57}$Fe satellite resonance ~1.4% above the main line is due to atoms with one cobalt nearest or next-nearest neighbor. It is shown here that the resulting interpretation is not consistent with certain results well established by Mössbauer-effect measurements on $^{57}$Fe in similar alloys.[2]

Table I of Ref. 1 provides numerical values for the change in the hyperfine field at an iron nucleus due to cobalt atoms in the four nearest-neighbor shells. The effect of more distant neighbors must be small, otherwise they would manifest themselves as a shift of the main resonance. It is also shown there that neighbor effects are additive. Although this has been verified only for small numbers of cobalt neighbors, only these are important in the dilute alloys under consideration. It is therefore possible to compute the average hyperfine field $\bar{H}$ as a function of cobalt concentration $c$:

$$\bar{H}=H_0+\sum_{i=1}^{\infty}\Delta H_i\sum_{n=0}^{N_i}np_{N_i}(n,c)\,, \tag{1}$$

where $H_0$ is the hyperfine field of iron without cobalt neighbors, $\Delta H_i$ is the change in field due to one neighbor in the $i$th coordination sphere, $N_i$ is the coordination number, $n$ is the number of cobalt atoms in a coordination sphere, and $p_{N_i}$ the probability of having $n$ impurities in the $i$th shell for concentration $c$. For a random solid solution,[3] the latter is given by

$$p_N(n,c)=\frac{N!}{n!(N-n)!}c^n(1-c)^{N-n}\,. \tag{2}$$

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[1] M. Rubinstein, Phys. Rev. **172**, 277 (1968).

[2] C. E. Johnson, M. S. Ridout, and T. E. Cranshaw, Proc. Phys. Soc. (London) **81**, 1079 (1963).

[3] The existence of a CsCl superlattice for Fe-Co near the equiatomic composition suggests that the formation of cobalt near-neighbor pairs is not energetically favorable. There may instead be a tendency for cobalt atoms to have iron near neighbors. In dilute alloys, the nonrandomness due to this effect is small. The sample preparation described in Ref. 2 should help to destroy any order which may form as the melt is cooled. The metallurgical history of the NMR samples is not given.

It is readily shown that

$$\sum_{n=0}^{N} np_N(n,c)=Nc, \tag{3}$$

so that Eq. (1) assumes the simple form

$$\bar{H}=H_0+c\sum_{i=1}^{\infty} N_i\Delta H_i. \tag{4}$$

Using the values from the table mentioned above and the well-known coordination number of the bcc structure (8, 6, 12, 24, 8, ...), Eq. (4) may be evaluated to the fourth term to yield

$$\bar{H}/H_0=1+0.278c. \tag{5}$$

It is clear from the data in Fig. 1 of Ref. 1 that additional terms cannot have a significant effect on the coefficient of $c$.

This change of the average hyperfine field with cobalt concentration has, however, also been directly obtained from room-temperature Mössbauer experiments,[2] yielding a linear increase in the range from 0–15 at.% which may be represented by the equation

$$\bar{H}/H_0=1+0.54c. \tag{6}$$

The discrepancy between the two results is almost a factor of 2.

The Mössbauer results of Ref. 2 are well substantiated by our own experiments,[4] which gave asymmetrically broadened lines.[5] In our earlier publications, these asymmetric lines were resolved into components ascribed to the two near-neighbor shells plus a concentration-dependent term representing the effect of more distant shells. When these are recombined to obtain the average field, we obtain

$$\bar{H}/H_0=1+0.51c, \tag{7}$$

in agreement with the results of Ref. 2. The same data were recently reanalyzed to obtain directly the average hyperfine fields, which were substantially in agreement with those of Ref. 2.[6]

The reliability of the resolution of the asymmetric line into components is not properly at issue here. The important point is that the directly determined change in the average field is much greater than can be accounted for by the lines resolved in the NMR experiments. This supports the earlier interpretation due to Mendis and Anderson[7] who assumed that iron atoms with nearest- or next-nearest-neighbor cobalt atoms are not observed in NMR because they are broadened by anisotropic hyperfine interactions. Their assignment of the dominant NMR satellite line to atoms with third-neighbor cobalts is also more satisfactory insofar as the intensity is concerned.

A better analysis of the contribution of the various coordination shells to the hfs field at iron could be obtained by combining the Mössbauer and NMR results.[7] As a step toward this goal, we are obtaining Mössbauer data at 4.2°K in order to have results directly comparable to those obtained by NMR. It may be anticipated that the inclusion of known contributions from the third and fourth shells will reduce the values of $\Delta H_1$ and $\Delta H_2$ in the analysis of the Mössbauer data.

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[4] G. K. Wertheim, V. Jaccarino, J. H. Wernick, and D. N. E. Buchanan, Phys. Rev. Letters **12**, 24 (1964).

[5] Contrary to the assertion in Ref. 1 we did not report resolved satellite structure for Fe-Co alloys. The existence of satellites and their positions was obtained by fitting asymmetrically broadened lines.

[6] The increase in the Mössbauer-effect linewidth reported in Ref. 2 also directly indicated that the hyperfine field spectra must extend further than the NMR spectrum. We find excess width above those of a comparable iron foil of 0.018, 0.023, and 0.027 cm/sec for 4-, 8-, and 12-at.% Co. These correspond to a range of hyperfine field of 10–15 kOe.

[7] E. F. Mendis and L. W. Anderson, Phys. Rev. Letters **19**, 1434 (1967).