Comments and Addenda

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Time-Reversal Degeneracies in the Band Structure of a Ferromagnetic Metal

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(Received 25 April 1969)

Symmetry of a single domain of a ferromagnetic metal should be described by the appropriate magnetic (Shubnikov) space group **M**. Previous workers have used only the unitary subgroup of **M**. It is shown here that the inclusion of the antiunitary elements of **M** may lead to some degeneracies, beyond those noted previously, in the electronic band structure for a hexagonal close-packed metal, but not for a cubic metal.

THE essential degeneracies that may arise in the electronic band structure of a magnetic metal have been investigated by Falicov and Ruvalds.[1] The appearance of a spontaneous magnetic moment $\mathfrak{M}$ when a metal becomes ferromagnetically ordered causes a considerable reduction in the symmetry, and consequently many degeneracies that were present in the band structure of the nonmagnetic metal become lifted. In particular, the presence of a net magnetic moment $\mathfrak{M}$ in a ferromagnetic metal destroys the operation of time reversal θ as a symmetry operation of the crystal. Falicov and Ruvalds, however, appear to ignore the fact that the operation of time reversal, while not present on its own, may still occur in combination with some point-group or space-group operation as a symmetry operation of the crystal. That is, it is important to consider the magnetic space group of the crystal and not only the unitary subgroup of this magnetic group. The consideration of the antiunitary elements may lead to the discovery of some extra degeneracies not predicted by Falicov and Ruvalds.[1]

In recent years considerable work has been done on the theory of magnetic groups and their corepresentations[2,3]; the theory of the corepresentations of magnetic groups, which was originally developed by Wigner, has been applied to the study of several antiferromagnetic crystals.[4]

The symmetry properties and the essential degeneracies of the electronic band structure of a ferromagnetic metal will be determined by the group of the wave vector $\mathbf{k}$ in the Brillouin zone of the magnetic metal. The magnetic little group $\mathbf{M}^{\mathbf{k}}$ consists of[3] (i) those unitary elements of the magnetic space group that send $\mathbf{k}$ into $+\mathbf{k}+\mathbf{K}_0$, $(\mathbf{G}^{\mathbf{k}})$ and (ii) those antiunitary elements of the magnetic space group that send $\mathbf{k}$ into $-\mathbf{k}+\mathbf{K}_0$, $(\theta\mathbf{G}_I{}^{\mathbf{k}})$, where $\mathbf{K}_0$ is a vector of the reciprocal lattice. That is, we may write

$$\mathbf{M}^{\mathbf{k}}=\mathbf{G}^{\mathbf{k}}+\theta\mathbf{G}_I{}^{\mathbf{k}}. \tag{1}$$

The symmetries of the spin-wave dispersion curves or of the electronic band structure of a ferromagnetic metal are properly described by the corepresentations of $\mathbf{M}^{\mathbf{k}}$, and these corepresentations can all be determined from the representations of $\mathbf{G}^{\mathbf{k}}$. Let us suppose that Γ_i is one of the irreducible representations ("reps") of $\mathbf{G}^{\mathbf{k}}$; then one of three possibilities will arise: (i) The irreducible corepresentation ("corep") of $\mathbf{M}^{\mathbf{k}}$ derived from the rep Γ_i, which we shall call $D\Gamma_i$, will belong to case (a),[3,4] and there will be no extra degeneracy due to the presence of the antiunitary elements. (ii) $D\Gamma_i$ will belong to case (b) and will be of dimension equal to twice the dimension of Γ_i; that is, two energy levels belonging to the same rep Γ_i will stick together because of the antiunitary elements. (iii) $D\Gamma_i$ will belong to case (c) and will be of dimension equal to twice that of Γ_i; that is, two energy levels belonging to two inequivalent reps Γ_i and Γ_j of $\mathbf{G}^{\mathbf{k}}$ stick together. The existence of case-(b) coreps is quite rare, but case-(c) coreps occur commonly, so that the presence of the antiunitary elements can be important.

[1] L. M. Falicov and J. Ruvalds, Phys. Rev. **172**, 498 (1968).
[2] R. R. Birss, *Symmetry and Magnetism* (North-Holland Publishing Co., Amsterdam, 1964); A. P. Cracknell, Contemp. Phys. 8, 459 (1967); W. Opechowski and R. Guccione, in *Magnetism*, edited by G. T. Rado and H. Suhl (Academic Press, Inc., New York, 1965), Vol. IIA, p. 105.
[3] C. J. Bradley and B. L. Davies, Rev. Mod. Phys. **40**, 359 (1968).
[4] M. R. Daniel and A. P. Cracknell, Phys. Rev. **177**, 932 (1969); J. O. Dimmock and R. G. Wheeler, *ibid.* **127**, 391 (1962); S. J. Joshua and A. P. Cracknell, J. Phys. C 2, 24 (1969).

TABLE I. Magnetic point group of a ferromagnetic cubic metal.

Direction of $\mathfrak{M}$	Magnetic point group	Unitary subgroup		Antiunitary elements[a]
[001]	$4/mm'm'$	$4/m$	$E, C_{4z}^{+}, C_{2z}, C_{4z}^{-}, I, S_{4z}^{-}, \sigma_z, S_{4z}^{+}$	$C_{2x}, C_{2y}, C_{2a}, C_{2b}$ $\sigma_x, \sigma_y, \sigma_{da}, \sigma_{db}$
[111]	$\bar{3}m'$	$\bar{3}$	$E, C_{31}^{+}, C_{31}^{-}, I, S_{61}^{-}, S_{61}^{+}$	C_{2b}, C_{2e}, C_{2f}, $\sigma_{db}, \sigma_{de}, \sigma_{df}$
[110]	$m'm'm$	$2/m$	$E, C_{2a}, I, \sigma_{da}$	C_{2b}, C_{2z} σ_{db}, σ_z

[a] Each entry should be multiplied by θ.

If the magnetic moment $\mathfrak{M}$ of a domain of a ferromagnetic cubic metal is in some specified direction relative to the crystallographic axes, then the point group of the symmetry of the domain will be the intersection of the point group $m3m1'$ with the noncrystallographic black-and-white point group ∞/mm', which is the group of the symmetry operations of an isolated magnetic moment $\mathfrak{M}$ and comprises all rotations about the axis of $\mathfrak{M}$, together with all operations compounded of θ and a rotation through π about any axis normal to $\mathfrak{M}$; it also contains the product of I, the operation of space inversion, with each of the above operations. If $\mathfrak{M}$ is parallel to [001], the magnetic point group of the ferromagnetic metal is $4/mm'm'$. The elements of this magnetic point group are identified in Table I, where the notation is that of Altmann and Cracknell.[5] If $\mathfrak{M}$ is parallel to [111], the magnetic point group of the ferromagnetic cubic metal is the trigonal point group $\bar{3}m'$, and if $\mathfrak{M}$ is parallel to [110], the magnetic point group of the metal is the orthorhombic point group $m'm'm$; the elements of these magnetic point groups are also identified in Table I.

It is then possible to identify $\mathbf{G}^{\mathbf{k}}$ and $\mathbf{M}^{\mathbf{k}}$ for each of the special points in the Brillouin zone; for a ferromagnetic fcc or bcc metal magnetized parallel to [001], [111], or [110], $\mathbf{G}^{\mathbf{k}}$ is identified in Tables X–XV of Ref. 1. Because $Fm3m$ is a symmorphic space group, the unitary elements that form $\mathbf{G}^{\mathbf{k}}$ must form one of the crystallographic point groups, whose irreducible representations are tabulated, for instance, by Koster, Dimmock, Wheeler, and Statz.[6] Each of the magnetic little groups $\mathbf{M}^{\mathbf{k}}$ is then also isomorphic with one or another of the 58 black-and-white magnetic point groups, and therefore the corepresentations of each magnetic little group $\mathbf{M}^{\mathbf{k}}$ are then immediately available.[7] The presence of the antiunitary elements will lead to an extra degeneracy, at $\mathbf{k}$, in the electronic band structure for any bands that belong to a double-valued rep of $\mathbf{G}^{\mathbf{k}}$, which leads to a case-(b) or a case-(c) corep of $\mathbf{M}^{\mathbf{k}}$. However, inspection shows that for each of the double-valued coreps of each magnetic point group that occurs for each structure and each magnetization direction, only case-(a) coreps actually occur; lack of space prevents us from presenting a complete identification of $\mathbf{M}^{\mathbf{k}}$ and the coreps of $\mathbf{M}^{\mathbf{k}}$ here, but a complete account has been submitted elsewhere.[8] Therefore, the antiunitary elements of the magnetic space group fortuitously cause no extra degeneracies, beyond those noted in Ref. 1, in the electronic band structure of a ferromagnetic fcc or bcc metal with $\mathfrak{M}$ parallel to [001], [111], or [110].

We now turn to the consideration of the hcp structure. The space group of the paramagnetic state of a hexagonal close-packed metal is a nonsymmorphic group, and therefore $\mathbf{G}^{\mathbf{k}}$ is not necessarily isomorphic with one of the 32 point groups, nor is $\mathbf{M}^{\mathbf{k}}$ necessarily isomorphic with one of the 58 magnetic point groups. The space group of the paramagnetic hcp metal is $P6_3/mmc1'$, and the magnetic space group of a ferromagnetic hcp metal with $\mathfrak{M}$ parallel to [0001], [10$\bar{1}$0], or [11$\bar{2}$0] is identified in Table II, where the notation is that of Altmann and Bradley.[9] For each of these three magnetization directions of a ferromagnetic hcp metal, it is then possible to identify $\mathbf{G}^{\mathbf{k}}$ and $\mathbf{M}^{\mathbf{k}}$. The reps of $\mathbf{G}^{\mathbf{k}}$ and their character tables are identified in Tables XVI–XVIII of Ref. 1. It is then possible, by using the test given in Eq. (2.40) of Ref. 3, to determine when the corep $D\Gamma_i$ of $\mathbf{M}^{\mathbf{k}}$ derived from the rep Γ_i of $\mathbf{G}^{\mathbf{k}}$ belongs to case (a), case (b), or case (c). When this test was applied for $\mathfrak{M}$ parallel to [0001], it was found that the coreps of $\mathbf{M}^{\mathbf{k}}$ all belong to case (a), except at R, when they belong to case (c); once again, there is no space here to include complete tables of $\mathbf{M}^{\mathbf{k}}$, but a full account submitted elsewhere.[8] There is therefore an extra double degeneracy, beyond those noted in Ref. 1, along the line R, due to the presence of the antiunitary elements. When the test was applied for ferromagnetic hcp metals magnetized parallel to [10$\bar{1}$0] or [11$\bar{2}$0], case-(b) and case-(c) coreps appeared for several wave vectors, so that there are several extra double degeneracies due to the presence of the antiunitary elements. Specifically, the points involved are

$\mathfrak{M}\|[10\bar{1}0]$:

$L\{(0, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$ or $(\frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2})\}$, R, S, and S'

and

$\mathfrak{M}\|[11\bar{2}0]$:

$A, L\{(\frac{1}{2}, 0, -\frac{1}{2}, \frac{1}{2}), (0, \frac{1}{2}, -\frac{1}{2}, \frac{1}{2})$, and $(\frac{1}{2}, -\frac{1}{2}, 0, \frac{1}{2})\}$, R, S, and S'.

[5] S. L. Altmann and A. P. Cracknell, Rev. Mod. Phys. **37**, 19 (1965).

[6] G. F. Koster, J. O. Dimmock, R. G. Wheeler, and H. Statz, *Properties of the Thirty-two Point Groups* (MIT Press, Cambridge, Mass., 1963).

[7] A. P. Cracknell, Progr. Theoret. Phys. (Kyoto) **35**, 196 (1966); A. P. Cracknell and K. C. Wong, Australian J. Phys. **20**, 173 (1967); J. O. Dimmock and R. G. Wheeler, J. Phys. Chem. Solids **23**, 729 (1962).

[8] A. P. Cracknell, J. Phys. C **2**, 1425 (1969).

[9] S. L. Altmann and C. J. Bradley, Rev. Mod. Phys. **37**, 33 (1965).

(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 θ, the operation of time inversion.

We may now summarize our conclusions. The inclusion of the antiunitary elements, which contain θ, 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'.

[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.

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

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

[a] Each entry should be multiplied by θ.

PHYSICAL REVIEW B VOLUME 1, NUMBER 3 1 FEBRUARY 1970

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 $\sim$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, ΔH_i is the change in field due to one neighbor in the ith 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 ith shell for concentration c. For a random solid solution,[3] the latter is given by

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

[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 nea ıthe 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.