BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1923—1928 (1973)

An Interstitial-Electron Model for the Structure of Metals and Alloys. IV. Magnetic Properties of Metals and Electronic Structures of Group VI—VIII Metals

Oliver JOHNSON*
Research Institute for Catalysis, Hokkaido University, Sapporo 060

(Received August 9, 1971)

The interstitial-electron model leads to localization of d-electrons on the metal ion cores starting with group 6 metals which would have all the tetrahedral and octahedral interstices occupied by itinerant electrons. In the model the itinerant electrons play the role of ligands and determine the degeneracy of the d-orbitals localized on the ion core. There are mutual accomodations as far as location of itinerant electrons in specific interstices and d-electrons in preferred orbitals. Consideration of metal properties, especially Hall Coefficients, leads to reasonable values for both localized and itinerant magnetic moments. The relatively large spatial extension of 3d-orbitals at low intermetallic distances accounts for the magnetic moments in Cr, Mn, Fe, Co, and Ni. A striking consequence of the application of the interstitial-electron model to Fe is that it reproduces in detail the regions of positive and negative magnetization (including the interlocking rings on edges and faces) observed in neutron diffraction studies by Shull and Mook.

This paper will treat the magnetic properties of metals and show how the interstitial-electron model[1] accounts for the very complex magnetic behavior of metals like Cr and Mn, the ferromagnetism of Fe, Co, and Ni and the lack of a magnetic moment for metals of 2nd and 3rd transition series.

The first paper in the series indicated that the model would require localization of d-electrons on the metal ion core at M^{6+} since 6 itinerant electrons would completely fill the 2 tetrahedral and 1 octahedral interstice with electron pairs. The problem then for the metals starting with chromium (Cr^{6+} ion core) is to decide how many d-electrons are localized. Since it is desirable to predict magnetic moments, the starting point will be to examine the metal properties to see if the number of itinerant electrons can be specified as they were in Group I—V metals. Properties such as electrical conductivity, electronic heat capacity and Hall Coefficient are indicative of number and kind of itinerant electrons.

Itinerant Electrons and d-Electrons in Metals

Just as for non-transition metals there will be a structure determined preference for electron occupancy of octahedral or tetrahedral interstice, but extension of d-orbitals into each type of interstice can influence the distribution of itinerant electrons. A localization of itinerant electron density in binding regions (interstices) has been described in detail.[1] The alternate "instantaneous" description of electrons in interstices is the unique new feature of the interstitial-electron model. These electrons or $(\bar{e})_2$ can be treated as ligands in determining the degeneracy of the localized d-orbitals on the metal ion cores. This differs from the use of ligand field theory in metals by both Trost[2] (orbital constructions) and Goodenough.[3] It is believed that the objection made by Brooks to the use of ligand field theory in metals does not hold for this model, since his objections were directed toward the use of d-orbitals on other ion cores as ligand fields. Elliot[4] also discusses crystal fields in metal and suggests methods for their use.

Thus, ligand field theory can give the value of the magnetic moment on the ion core once the electronic structure with number of itinerant electrons and localized d-electrons and orientation of d-orbitals with respect to lattice axes is decided. In cases where there is unequal distribution of itinerant electrons among octahedral (↑) and tetrahedral interstices (↓), there can be a magnetic moment of itinerant electrons. The combination and interaction of these two kinds of moments can lead to ferromagnetism, antiferromagnetism and itinerant ferromagnetism.

---

* Present address: Institute of Physics, University of Uppsala, Uppsala, Sweden.

[1] O. Johnson, This Bulletin, **45**, 1599, 1607 (1972).

[2] W. R. Trost, *Can. J. Chem.*, **37**, 460 (1959).

[3] J. B. Goodenough, "Magnetism and the Chemical Bond," J. Wiley and Sons, N. Y, (1963).

[4] R. J. Elliot, *Comments Solid State Phys.*, **1**, 85 (1968).

The nature of interaction between itinerant electrons and d-electrons has not been specified. The simple picture of ion cores and itinerant electrons in binding regions (See Part I) no longer holds for metals with localized d-electrons. It is assumed that the extension of 3d-orbitals at least is such that itinerant electrons in the interstice involved would have an electron spin *opposite* to that of the d-electron. This also assumes that the two electron energies are about equal which is a reasonable assumption and consistent with the band theory of metals. This description of the interaction of ē and d-electrons is essentially the "indirect exchange" used by Zener[5] but with antiparallel spin allignment as proposed by Vonsovsky and Vlasov[6] and Mott and Stevens.[7]

Trost[2] has argued for a strong interaction of adjacent 3d-orbitals on adjoining metal ion cores. He points out that the ratio of size of the (n−1) shell to the n shell has the smallest value for the first transition period. The two factors involved are the decreasing separation of ns, np, and (n−1) d atomic orbital energy and the increasing relative size of the (n−1) d-orbitals as n increases. This implies that the (n−1) d-orbitals become more important for binding and explains the increase in mp, bp, in transition metals as n increases (it decreases for non-transition metals). This effect of size and separation of d-orbitals reaches its maximum around Mn, Fe, and Co. It is believed that Trost's analysis is an even stronger argument for interaction of 3d electrons with itinerant electrons than his proposed interactions of 3d-3d on adjacent ion cores. In the present paper it is assumed that there are potential interactions between itinerant ē and d-electrons of all 3 transition series, but that the very low intermetallic distances for the 1st transition series is crucial for determining magnetic properties.

In a metal lattice the ion cores can have an orientation such that its d-orbital axes are identical to the crystal axes or they may be at an appropriate angle, *e.g.* 45°. This orientation will be determined by the magnitude of repulsive interactions between itinerant electrons and d-electrons as compared to interactions between d-electrons on two adjacent ion cores. It is assumed that the onset of magnetic properties corresponds to the condition where the d-electron interactions determine the orientation, and empirically this occurs for metals with interatomic distances of 2.6 Å or less. This can now be compared directly to the treatment of magnetic properties by Goodenough.[3] Goodenough assumes a critical separation of $R_c = 2.9 \pm 0.1$ Å, below which there is localization of d-electrons on ion cores and above which the d-electrons are considered itinerant. The treatment by the interstitial-electron model proposed the localization of d-electrons to occur after M^{5+} and at M^{6+} (the intermetallic distances here are close to R_c above). The additional criterion is that at $R \leq 2.6$ Å, the $M^{n+}(d)-M^{n+}(d)$ interactions become more important than the $M^{n+}(d)-\bar{e}$ interactions in determining the orientation of the axes of the d-orbitals on the ion core.

The above principles will now be used in formulating interstitial-electron structures, and thus magnetic properties, for metals of Groups VI—VIII.

Interstitial-Electron Structures for Group VI Metals

Chromium metal has many unusual properties such as a very high positive Hall Coefficient, low electronic heat capacity (γ) for a transition metal, high work function, low electric conductivity and small amplitude of lattice displacement. It is also likely that the Cr structure differs from that of Mo and W since it exhibits a complex antiferromagnetism and the latter two are paramagnetic. To assign a valence to Cr, and thus an ion core charge and the number of localized d-electrons, it is pertinent to note that Cr has the BCC structure as does V^{5+} and Ti^{4+} (at high temperatures). The relatively low value of γ, comparable to that of Ti, suggests an ion core charge of 4. The very high positive Hall Coefficient (+36) suggests at least 4 as the number of itinerant electrons to account for a large number of ($\bar{e}_2$) (or filled interstices) in the structure. Tentatively, the structure will be taken as:

$$\left|\begin{array}{l} Cr^{6+}(d^2),\ 4\bar{e} \\ \qquad\quad \text{tet rings} \end{array}\right|_{\text{BCC}}$$

It is inherent in the BCC crystal structure that the corner and body center ion cores are not equivalent. However, for an equal distribution of itinerant electron in the face tetrahedral and edge tetrahedral rings (See Part I) there is the same degeneracy of d-orbitals on both corner and body center ion cores. The degeneracy given below is based on ē in tet rings as ligands with equal ē density on all faces and d-orbital axes 45° to crystal axes:

$\overline{\text{xz}}\quad\overline{\text{yz}}$ (directed to Cr)

$\overline{\text{xy}}\quad\overline{z^2}$ (directed to edges)

$\overset{\uparrow\downarrow}{\overline{x^2-y^2}}$ (directed to face center)

Corner or Body Center $Cr^{6+}(d^2)$

This degeneracy is based on usual crystal field theory considerations. The 45° orientation is chosen since it conforms to the observed magnetic properties and has no occupied d-orbitals directed to Cr.

The degeneracy of d levels is such that the d^2 configuration of the Cr ion core leads to pairing of these localized d-electrons, and spatially they extend from corner ion cores (atoms) diagonally along horizontal faces and from body center ion cores perpendicular to the vertical face centers. The proposed structure for chromium has the following instantaneous distribution (See Part I[1]) of itinerant electrons in tetrahedral rings: 3 ē in each tet ring on 4 faces of the Cr unit cell (xz, yz planes) and 2 ē in each tet ring on two faces (xy plane). This is a total of 16 ē on faces, 8 ē per unit cell or 4 per Cr ion core. The e in tet rings on the 2 horizontal faces will be paired and the remain-

---

[5] C. Zener, *Phys. Rev.*, **81**, 440 (1951); *Rev. Mod. Phys.*, **25**, 191 (1953).

[6] S. V. Vonsovski and K. B. Vlasov, *Zh. Eksp. Teor. Fiz.*, **25**, 327 (1953).

[7] N. F. Mott and K. W. H. Stevens, *Phil. Mag.*, **2**, 1364 (1957).

ing 6 ē do not have any spin allignment except that adjacent ē in tet rings will have opposite spins. Thus, there can be 1 ē on each of 4 faces with undetermined spin, and this can lead to 0,1 or 2 ē with the same spin per unit cell or 0, 1/2 or 1 unpaired spin per Cr. This lies within the observed magnetic moment for Cr of 0.54 μ_B per Cr.

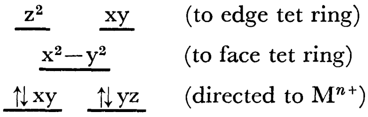
The model proposes that any itinerant moment is to be distributed among the 4 vertical faces of the unit cell. The theoretical prediction of an helical spin state as the ground state for magnetic systems,[8] and consideration of linear spin density waves for Cr makes it reasonable that the undetermined spin above leads to an itinerant moment on Cr of approximately 0.5 μ_B per Cr.

Neutron diffraction studies show that below 312K Chromium exhibits a complex antiferromagnetic behavior. There are not the usual two sublattices associated with antiferromagnetism but a sinusoidal modulation of moment over at least 21 unit cells *i.e.* the total moment varies with position. The model gives a physical picture of this complex behavior in terms of electrons with free spins in each of the 4 vertical faces of the Cr unit cell. It is understandable that this could easily revert to a paramagnetic state as temperature is increased and as is observed above 312K.

The smaller Hall Coefficient and greater electrical conductivity suggest fewer itinerant electrons for *Mo and W* than for Cr. This leads to the proposal of a d^4 localization of d electrons on Mo and W. A different localization is expected as well on the basis of the non-magnetic properties of Mo and W. The proposed itinerant-electron structure for Mo and W is:

$$\left| \begin{array}{l} M^{6+}(d^4),\ 2\bar{e} \\ \qquad\quad \text{tet rings} \end{array} \right|_{\text{BCC}}$$

The intermetallic distance for Mo and W (1.39 and 0.41 Å) places it in the group of metals where the interaction of localized d-electrons is expected to be larger than between ē and localized d-orbitals on adjacent ion cores. A 45° orientation of the axes of d-orbitals in respect to the crystal axis gives the minimum ē-d interaction, and the degeneracy of d levels is as follows:



This degeneracy leads to complete pairing of d-electrons for d^4 and accounts for the normal metallic paramagnetism of metallic Mo and W. The degeneracy is based on distribution of itinerant electrons as 1 ē per tet ring on each of 2 horizontal faces (xy plane) and 1 ē per tet ring on each of 4 edges (z^2 and xy of d-orbital axes). In such an arrangement electron spins can be random as in the cases of Ba metal (also BCC). Each ē has 4 interstitial locations and different spins in adjoining interstices. This contrasts with the greater restriction of ē spin in Cr. No itinerant moment (or SDW) have been observed in neutron diffraction studies of Mo or W.

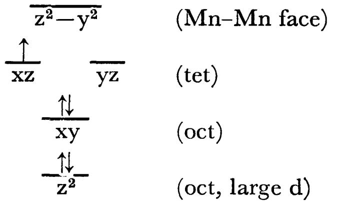
Interstitial-Electronic Structures for Group VII Metals

α-Manganese, the form of manganese metal stable from ordinary temperature to 710°C, has more than one type of Mn ion core in the structure. β-Manganese is paramagnetic and stable from 710—1079°C. It has 20 atoms per unit cell of which 8 are of higher valence (smaller size) than the remaining 12. A structure similar to those proposed for β-phases which have the same structure[9] is the following:

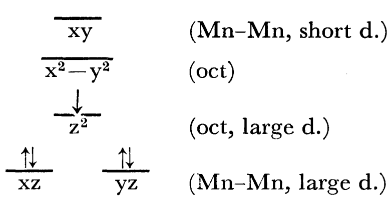
$$\left| 8Mn^{7+}(d^4),\ 12Mn^{7+}(d^6),\ 36\bar{e} \right|_{\beta\text{-Mn}}$$

This gives a number of itinerant electrons per unit cell which is close to the *e*/*a* ratio of 3/2 observed in β-phases. The structure has interstices which are not homogeneous in terms of ion cores around an interstitial electron. This is discussed in detail in Part V,[9] and in the case of Mn it leads to localization of ē in the structure as electron pairs and is associated with the hardness and brittleness of β-Mn.

γ-Manganese, stable in the temperature range 1079—1143°C, has a face-centered tetragonal structure when stabilized at room temperature and is CCP in its normal state. The room temperature modification has been observed to be antiferromagnetic[7] with a magnetic moment of 2.4 μ_B. The only data available to help establish the ion core charge is the relatively low atomic volume of 12.7 Å³. This is reasonable for a divalent ion core, $Mn^{7+}(d^5)$, also indicated by magnetic properties. In the antiferromagnetic face-centered tetragonal structure, Mn has 8 neighbors at 2.58 Å and 4 neighbors at 2.67 Å. It is proposed that in a distorted structure like this, the Mn ion cores in the top and bottom faces (short distances) have a 45° orientation of d-orbital axes which minimizes Mn–Mn interactions, and the face center Mn on vertical faces (larger distance) have a 90° orientation of d-orbital axes with respect to the tetragonal cell. This leads to the following degeneracy for $|Mn^{7+}(d^5),\ 2\bar{e}|$ FCTetr.



Mn ion cores on top and bottom face



Mn ion cores on Vert. Face Centers

---

[8] A. W. Overhauser and A. Arrott, *Phys. Rev. Lett.*, **4**, 226 (1960).

[9] O. Johnson, This Bulletin, **46**, 1929 (1973).

This degeneracy leads to one unpaired $\bar{e}$ localized on the Mn ion cores of the top and bottom faces of a tetragonal unit cell and one unpaired $\bar{e}$ on the Mn ion cores on centers of vertical faces. The former are directed into tet interstices and the latter into oct interstices so they will have opposite spins, and the total moment difference corresponds to 2 μ_B. In addition there is the chance of considerable imbalance in the itinerant electron spins since there is much more $\bar{e}$ density from d-electrons directed into oct interstices. A distribution, *e.g.* of 1/2 $\bar{e}$ in oct and 1 1/2 $\bar{e}$ in tet would lead to an itinerant moment of 1 ↑/unit cell or 0.25 ↑ per Mn ion core.

Tc and Re both form HCP lattices with c/a values close to normal. Little data is available on Tc, but Re has a high Hall Coefficient and moderate electronic heat capacity; both metals have low conductivity. The structure proposed below with 3 itinerant electrons is reasonable for these properties:

$$\left| M^{7+}(d^4),\ 3\bar{e} \right|_{HCP}$$

The degeneracy of d levels, discussed in detail for Co, leads to pairing of localized d-electrons and thus normal paramagnetism for these metals.

Interstitial-Electron Structures for Fe, Ru, and Os

The Hall Coefficient for metallic iron is positive but not as high as that of Cr. It also has a high electronic heat capacity for a group 8 metal. These properties suggest an electronic structure with at least 4 itinerant electrons as follows:

$$\left| Fe^{8+}(d^4),\ 4\bar{e} \right|_{BCC}$$

A d^2 structure as proposed by Lomer and Marshall[10] is not compatible with the interstitial electron model since it would have 6 itinerant electrons, postulated not to give metallic properties.

In deriving the degeneracy of d-orbitals it is assumed that the 4 $\bar{e}$ are distributed evenly among the tet rings on faces and edges of the BCC unit cell. An orientation of d-orbital axes of the Fe ion cores at 45° to the crystal axes leads both to the expected localized moment on the Fe ion cores and to the location of the magnetic lobes according to neutron diffraction studies.[11] The following degeneracy holds for both body-center and corner ion cores:

$\overline{xz}$ $\overline{yz}$ (directed to Fe)

$\underset{z^2}{\underline{\uparrow}}$ $\underset{xy}{\underline{\uparrow}}$ (along edges or to face centers)

$\underset{x^2-y^2}{\underline{\uparrow\downarrow}}$ (directed diagonally to tet rings)

The above electronic structure and degeneracy of d levels leads to d^2-orbitals along horizontal faces and directed to vertical edges from the body-centered ion cores. Unpaired d-electrons extend along all edges and from the body center Fe ion core to centers of all faces. The 4 itinerant electrons (or 8 $\bar{e}$ per unit cell) on an instantaneous picture can be pictured as occupying 4 face tet with 3 $\bar{e}$ each and the remaining 2 face tet per unit cell with 2 $\bar{e}$ each. Thus, the small negative magnetization (0.2 μ_B) is associated with the interlocking tet rings. It is striking that the model proposed here reproduces in detail the spatial arrangement of localized moments on Fe ion cores as well as the itinerant moment found by Shull and Mook,[11] in neutron diffraction studies of Fe.

The difference in magnetic properties of Fe and Cr requires comment. The lack of a localized moment in Cr is accounted for on the basis of its d^2 configuration. The two metals in BCC have the same number of itinerant electrons according to the proposed structures. The unpaired d-electrons in Fe must greatly restrict the location of itinerant electrons in tet ring interstices. This restriction of $\bar{e}$ in Fe is in keeping with the normal value of magnetic entropy ($k \ln 3$) observed for Fe and the very low magnetic entropy in the case of Cr.[11]

Os and Ru have HCP structures with c/a values of 1.57 and 1.59 and are expected to have 1 oct interstice and 1 Bipyramidal interstice per M^{n+}. This accounts for the very high Hall Coefficient of Ru if it has a d^4 structure (like Fe). The lower Hall Coefficient and electronic heat capacity suggest the following d^6 structure for Os:

$$\left| Os^{8+}(d^6),\ \bar{e}_{oct},\ \bar{e}_{BP} \right|_{HCP}$$

The degeneracy in HCP (see discussion, Part II[1]) leads to complete pairing of electrons for both Ru and Os, and the structure accounts for the normal paramagnetism of these metals.

Interstitial-Electron Structures for Co, Rh, and Ir

The Hall Coefficient is strongly negative for cobalt metal, an indication of lower electron occupancy of interstices and much less liklihood for presence of electron pairs in interstices. The electrical conductivity is higher than for iron, an indication of lower interstice occupancy than iron or of less interference in the conduction process by d-electrons.

These properties suggest a low ion core charge for Co relative to Fe, and the stability of Co^{2+} makes it a reasonable choice. The ion core structure below has the high d localizations as has been used by Lomer and Marshall[10] and others and applies to paramagnetic Co.

$$\left| Co^{9+}(d^7),\ 2\bar{e} \right|_{HCP}$$

The axes of the d-orbitals are placed so the z-axis corresponds to the c-axis of the hexagonal cobalt structure, the x-axis is placed along a line connecting 2 cobalt ion cores and the y-axis then passes 1/2 way between two other cobalt ion cores. This gives rise

---

10) W. M. Lomer and W. Marshall, *Phil. Mag.*, **3**, 185 (1958).

11) G. G. Shull and H. A. Mook, *Phys. Rev. Lett.*, **16**, 14 (1966); *Phys. Rev.*, **136**, A195 (1964); *ibid.*, **148**, 495 (1966).

to the following degeneracy for ferromagnetic Co:

$$\begin{array}{ccl} \multicolumn{2}{c}{\overline{\mathrm{x^2-y^2}}} & (\text{to } \mathrm{M}^+) \\ \underline{\uparrow(\downarrow)_{0.2}} & \underline{\uparrow} & \\ \mathrm{yz} & \mathrm{z^2} & (\mathrm{M}^+, \text{oct})\ (\text{tet}) \\ \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} & \\ \mathrm{xz} & \mathrm{xy} & (\text{no } \bar{\mathrm{e}} \text{ or ion cores}) \end{array}$$

The above degeneracy of d levels for $\mathrm{Co}^{9+}(\mathrm{d}^7)$ leads to unpaired d-electrons extending into tet interstices and 0.8 unpaired d-electrons extending near oct and another ion core. It is not likely that other orientations of the d-axes would lead to more favorable d-electron distribution as far as ion core interactions are concerned.

The spin requirements of oct interstices[1] in HCP leads to only 0.4↑ occupancy since an unpaired d-electron from the Co ion core directed to oct requires an opposite itinerant electron spin. This gives the following interstitial-electron structure for cobalt metal:

$$\left|\mathrm{Co}^{9+}(\mathrm{d}^{6.2}),\ \bar{\mathrm{e}}_{0.4}(\bar{\mathrm{e}}_2)_{0.6\,\mathrm{oct}},\ \bar{\mathrm{e}}_{1.2\,\mathrm{tet}}\right|_{\mathrm{HCP}}$$

This placement of additional ē in tet is also in keeping with the preference for tet occupancy in HCP lattices below 2 ē and accounts for a negative moment on ē.

The proposed structure has a magnetic moment corresponding to 1.8↑ on each Co ion core with spins alligned *via* tet electrons. The oct ē (0.4 ē) have all one spin and the ē in tet interstices can have a range of unpaired spins. Depending on whether these spins cancel or add, there could be no itinerant moment in Co or a maximum of 0.4↑. The observed moment of 1.7 μ_B lies within the range allowed by the above structure. The model would not give structures which would have more than 2 unpaired electrons localized on Co.

Rhodium and Iridium have a small positive Hall Coefficient so higher occupancy of interstices by electrons is indicated. The normal valence of 3 is thus indicated for the CCP structures of Rh and Ir.

$$\left|\mathrm{Rh}^{9+}(\mathrm{d}^6),\ \bar{\mathrm{e}}_{\mathrm{oct}},\ \bar{\mathrm{e}}_{\mathrm{tet}},\ (\bar{\mathrm{e}}_2)_{1/2\,\mathrm{tet}}\right|_{\mathrm{CCP}}$$

The distribution of electrons in interstices is that normally required in the CCP lattice to give balanced spins and preference for tet occupancy. The degeneracy for the d-electrons in this structure and the comparable Ir structure is:

$$\begin{array}{cccl} & \overline{} & \overline{} & \\ & \mathrm{z^2} & \mathrm{x^2-y^2} & (\text{directed to edges}) \\ \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} & \\ \mathrm{xy} & \mathrm{xz} & \mathrm{yz} & (\text{directed to } \mathrm{M}^{n+}) \end{array}$$

The degeneracy given above is for placement of axes of d-orbitals coincident with crystal axes. This leads to non-magnetic properties for Rh and Ir.

Interstitial-Electron Structures for Ni, Pd, and Pt

Mook[11] has shown by neutron diffraction for Ni a ferromagnetic moment of 0.71 μ_B (0.656, 3d and 0.055, orbital) is localized around the ion core with a negative magnetization of 0.105 μ_B. It has also been maintained that the moment is itinerant[12,13] for Ni. In the following a structure is proposed which attempts to resolve these conflicting interpretations.

As with cobalt metal, the negative Hall Coefficient, relatively low electronic heat capacity and moderate electrical conductivity make it reasonable that Nickel has a Ni^{2+} ion core. The following ion core structure is proposed:

$$\left|\mathrm{Ni}^{10+}(\mathrm{d}^8),\ 2\bar{\mathrm{e}}\right|_{\mathrm{CCP}}$$

To determine the d level degeneracy, the d-orbital axis is placed at 45° to the crystal axis since this gives the minimum extension of d-orbitals toward other Ni ion cores (R=2.5 Å). The degeneracy is as follows:

$$\begin{array}{ccl} \multicolumn{2}{c}{\overline{\mathrm{x^2-y^2}}} & (\text{toward Ni}) \\ \underline{\uparrow\downarrow} & \underline{\uparrow(\downarrow)_{0.3}} & \\ \mathrm{xz} & \mathrm{yz} & (\text{toward tet}) \\ \underline{\uparrow\downarrow} & \underline{\uparrow\downarrow} & \\ \mathrm{xy} & \mathrm{z^2} & (\text{toward oct}) \end{array}$$

The degeneracy has occupied d-orbitals extending into both oct and tet interstices. The resultant repulsive interaction between d^2 electrons and itinerant electrons could lead to a shift of ē from tet to oct (greater distance from ion core) or to a transfer of some d-electrons to tet interstices as itinerant electrons. The former requires ē pairing so the latter is considered more likely. Assuming a transfer of 0.7 ē from a localized d-orbital to tet interstice, the following structure results:

$$\left|\mathrm{Ni}^{10+}(\mathrm{d}^{7.3}),\ \bar{\mathrm{e}}_{\mathrm{oct}},\ (\bar{\mathrm{e}}_2)_{0.3}\bar{\mathrm{e}}_{1.1\,\mathrm{tet}}\right|_{\mathrm{CCP}} \quad (\text{Ferromagnetic Ni})$$

This electronic structure accounts for the observed moment around the Ni ion core observed by Mook and also its itinerant character. The equilibrium state can be looked on as having an occupied d-orbital extending into a tet interstitial region with a d-electron of one spin near the ion core and a d-electron of the opposite spin (and now indistinguishable from an itinerant electron) near the centre of a tet interstice. On an instantaneous basis there will be 30% regions of $\mathrm{Ni}^{10+}(\mathrm{d}^8)$, 1 $\bar{\mathrm{e}}_{\mathrm{tet}}$ (no magnetic moment) and 70% regions of $\mathrm{Ni}^{10+}(\mathrm{d}^7)$, 2 ē (with 1 unpaired electron). Above 700° where Ni shows paramagnetism a small additional shift of electrons can give the following structure with no coupling of spins:

$$\left|\mathrm{Ni}^{10+}(\mathrm{d}^7),\ \bar{\mathrm{e}}_{\mathrm{oct}},\ \bar{\mathrm{e}}_{\mathrm{tet}},\ (\bar{\mathrm{e}}_2)_{1/2\,\mathrm{tet}}\right|_{\mathrm{CCP}} \quad (\text{Paramagnetic Ni})$$

A similar equilibrium between d^2 electrons localized on Co ($\mathrm{d}^{4.2}$) and tet itinerant electrons can explain the total localized moment and form factor for Co.

Palladium and Platinum have higher electronic heat capacities and lower electrical conductivities than expected for these group 8 metals. This suggests more itinerant electrons than ferromagnetic Ni. An ion core structure with M^{3+} can account for the above properties and the paramagnetism of these metals.

$$\left|\mathrm{M}^{10+}(\mathrm{d}^7),\ \bar{\mathrm{e}}_{\mathrm{oct}},\ \bar{\mathrm{e}}_{\mathrm{tet}},\ (\bar{\mathrm{e}}_2)_{1/2\,\mathrm{tet}}\right|_{\mathrm{CCP}}$$

---

[12] A. Arrott, "Magnetism," Vol. 2B, Ed. by G.T. Rado and H. Suhl, Acad. Press, New York (1966), Chap. 4.

[13] C. Herring, "Magnetism," Vol. 4, Ed. by G. T. Rado, H. Suhl, Acad. Press, New York (1966).

This structure is the same as that proposed for paramagnetic Ni. This proposed structure has the same degeneracy as shown for Rh and Ir and leads to d^2 electrons directed toward other M^{n+} and an unpaired electron directed toward 1/2 of the oct interstices. No coupling of spins is expected.

Discussion

The interstitial-electron model has been used to formulate structures for the magnetic and non-magnetic metals of groups VI—VIII. Ion core charges were established by comparison of properties of these metals (Hall Coefficient, electronic heat capacity and electrical conductivity) with metals of known ion core charge. The view is taken that when d-orbitals of the ion core extend into interstices, electrons occupying these two positions will have anti-parallel spins. The placing of the axes of the d-orbitals of the ion cores is based on empirical choice of an intermetallic distance of 2.6 Å above which interactions between d-electrons on adjacent ion cores becomes less important than interactions between these d-electrons and itinerant electrons in metal interstices. The itinerant electrons are treated as ligands to establish the d level degeneracy for d-electrons localized on the ion cores. The more complex splitting of d-levels than the usual e_g-t_{3g} splitting provides a new basis for discussing magnetic form factor.

The model leads to a magnetic structure of iron which has 2 unpaired electrons localized on the ion core, and a small additional moment associated with itinerant electrons. The magnetic entropy value and the spherical form factor found in neutron diffraction studies support this structure. The model proposes a magnetic moment originating on the itinerant electrons for nickel. This is supported by the observation that for Ni and Co metals, orbital magnetic moments are completely quenched (g value approx 2) and by the anisotropic form factor observed in neutron diffraction. For cobalt the model leads to 1.8 unpaired electron localized on the ion core and an additional moment on itinerant electrons. There have been unsuccessful attempts to locate itinerant electron spin density waves in Ni and Co. The experiments appear to have been scans in the 1, 1, 1 direction. The model indicates, *e.g.*, for Ni that unpaired electrons would be in tet interstices which are not centered on the 1, 1, 1 plane. The interpretation of the antiferromagnetism of Chromium offers a useful physical picture of the unusual itinerant magnetism (spin density waves). The model suggests that the antiferromagnetism of γ-Manganese is like that of an oxide system with itinerant electrons providing the antiferromagnetic allignment of spins.

The scheme of localization of electrons in interstices has provided a basis for explaining the complex magnetic properties of group VI—VIII metals. The electron distributions formulated for metals in this paper have been the result of mutual accomodations of localized d-electrons and itinerant electrons as is inherent in ligand field theory. This resultant more uniform electron density is an important property of the transition metals, and it is anticipated that it will give valuable insight into metal properties.