An Interstitial-Electron Model for the Structure of Metals and Alloys. III. Interpretation and Correlation of Properties of Group I—V Metals

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The interstitial-electron model for metals supplements the concepts of band theory to give a detailed interpretation of the properties of metals. The instantaneous picture of vacant and electron-occupied interstices given by the model clarifies the complex gradations in electrical conductivity which are not explained by an electron per unit volume term. The consideration of polarization of the itinerant electron cloud by ion cores with high positive fields and of interpenetration of the more deformable ion cores by itinerant electrons is another new feature of the model. The interstitial-electron model leads to the expectation of parallel gradations for electronic heat capacity and magnetic susceptibility and an inverse relation of both of these properties with electrical conductivity. The presence of ($\bar{e}_2$) in the metal structure is associated with a positive Hall Coefficient for a metal, and a new correlation between positive Hall Coefficient and superconductivity for a metal is pointed out.

The interstitial-electron model for metals postulates an interstitial localization of electron density in close-packed metal structures.[1] The different interstice distances, the degree to which an $\bar{e}$ in an interstice is screened by ion cores, and requirement of alternating electron spin in adjoining interstices leads to variations in occupation of octahedral and tetrahedral interstices in metals. It was shown[2] that electron occupancy of interstices could be specified quite closely for metals of Group I—V. The definition of an electron in an interstice as an itinerant electron moving predominantly in a binding region provides a rigorous basis for handling interactions of $\bar{e}$ and ion cores on an electrostatic basis.[1]

The difference in the present interpretation with those of the band theory of metals is illustrated by the lack of a "density of states" term in the present paper. This arises because band theory uses energy and momentum coordinates while the interstitial model uses space coordinates. Band theory has given quantitative accounting of many properties of lower valent metal and much work is currently published on more complex metals.[3]

Electrical Conductivity of Metals

The four major factors which determine electrical conductivity of metals are (1) the number of electrons moving under the influence of the electric field, (2) the velocity of these electrons, (3) the scattering of electrons by metal ion cores due to their displacement during lattice vibrations, and (4) the degree of interpenetration of the ion cores by itinerant electrons. From the interstitial-electron model it is obvious that the number of electrons which can move under the influence of the electric field is directly proportional to the number of vacant interstices in the metal structure. The velocity of electrons will depend on electron energy, and the maximum electron velocities are for electrons at the Fermi Surface. The relative velocities of electrons in two metals can be compared from estimates of Fermi energies.[4] Electrons moving with maximum velocity will dominate the conduction process. The spin requirements of the lattice must be obeyed in relation to both factors (1) and (2). The greater the amplitude of lattice vibration, the greater the scattering of itinerant electrons by ion cores, and thus lowering of electrical conductivity. Lattice displacements are known experimentally.[5] Interpenetration of ion cores will reduce conductivity and, as discussed in part II, is expected to be largest for ion cores containing d-electrons (non-rare gas shells).

Conductivity Trends in Metals. The new concept in the interstitial-electron model is the presence of vacant interstices, and it is of interest to demonstrate the role of vacant interstices in the conductivity process. Electrical conductivity will be discussed in this paper in terms of molar conductivity (specific conductivity × atomic volume).

The molar conductivity for alkali metals increases from Li to K and then declines to Rb and Cs. See Fig. 1. The interstitial-electronic structures are the

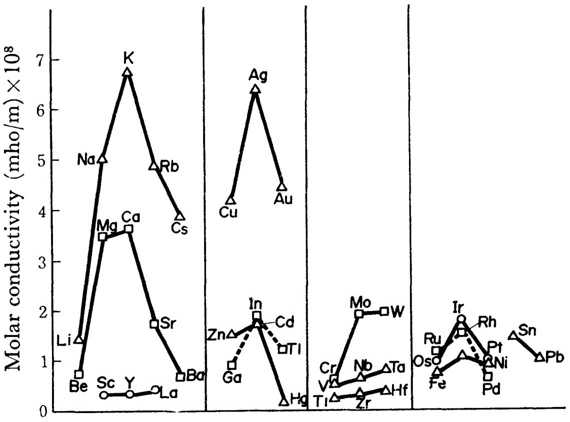

Fig. 1. Variations in molar conductivity for groups of metals.

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[1] O. Johnson, Part I of Series, This Bulletin, **45**, 1599 (1972).

[2] O. Johnson, Part II, of Series *ibid.*, **45**, 1607 (1972).

[3] W. M. Lomer, *Prog. Materials Sci.*, **14**, 99 (1969).

[4] R. A. Smith, "Wave Mechanics of Crystalline Solids," Chapman and Hall, Ltd., London (1969).

[5] G. V. Samsonov, "Handbook of Physicochemical Properties of the Elements," Plenum, New York (1968).

same for all the alkali metals, and the number of vacant interstices is the same. Electron velocities are expected to increase monotonically from Li to Cs, with the decrease in positive field of the ion core with increase in size. The amplitude of lattice vibrations also increases monotonically from Li to Cs, but this is expected to lead to the opposite effect, a decrease in conductivity. The combination of these two opposing factors leads to the maximum at K (See Fig. 1) with decreasing conductivity for Rb and Cs due to larger effect of lattice vibrations. These same two factors account for the maximum at Ca in the series Be to Ba (See Fig. 1). For the latter series changes in crystal structure modify the trends of Mg to Ca as shown in Fig. 1. The maximum for Ag in the series Cu, Ag, Au cannot have the same explanation since the lattice displacements are very nearly the same for Ag and Au. There is an unusually high positive field in case of Au,[6] leading to lower electron velocity and lower conductivity. These are all manifestations of greater interpenetration of the Au^{25+} ($4f^{14}$, $5d^{10}$) ion core by itinerant electrons.

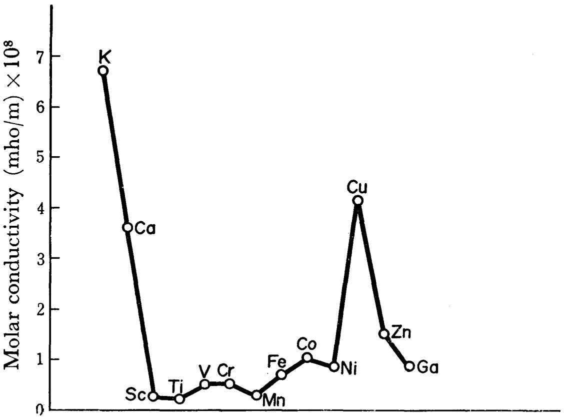

Fig. 2. Gradations in molar conductivity for metals.

It is of interest to note the relatively few metals with high molar conductance in Figs. 1 and 2. Those with values above 3.5 are Na, K, Rb, Cs, Cu, Ag, Au, Mg, Ca, and Al. All of the other metals including many not shown in Figs. 1 and 2 have molar conductivities below 2. Since there is a large variation in both E_f and amplitude of lattice vibration in both groups, the preponderance of metals with high conductivity which have large number of vacancies is a strong support for emphasis of this property of metals.

The sharp decrease in the order K, Ca, Sc, in Fig. 2 has not been explained previously. It will be noted that conductivities remain low for the series of 1st row transition metals until Cu is reached. For the series K, Ca, Sc the lattice displacements decrease so this factor should lead to increased conductivity. There is an increase in positive field, and this factor could cause a small decrease in conductivity (perhaps 2-fold). However, the 20-fold drop in conductivity is unexpected and must be connected with the decline in number of vacant interstices. There are 5 vacant interstices per metal ion core in K, 4 in Ca and only 1 in Sc (See Part 1). The series Cu, Zn, Ga represents a similar series, but the non-close packed structure of Ga may have influence here.

The gradations in conductivity Na>Cu and Mg>Zn show the effect of d-shell ion cores in lowering electron velocities due to the interpenetration of the d-shell by itinerant electrons.[2] The similar conductivities of Mg and Al are in sharp contrast to the sharp decline from Ca to Sc. In the above example there is a change from HCP to CCP for Mg to Al and from CCP to HCP for Ca to Sc. Due to pairing in the Al structure (See Part 1) there are a larger than normal number of vacant interstices. The especially low conductivities of Sc, Y, and La can all be traced to the distortion of the HCP lattice for these metals which reduces the number of tetrahedral interstices from 2 to 1 (bipyramical interstice) and thus reduces the total number of interstice vacancies. Vacancies listed above are based on 6 $\bar{e}$ (or 3 $\bar{e}_2$) in the normal 2 tet and 1 oct interstice per ion cores. A 1-electron vacancy and a 2-electron vacancy could be distinguished.

The interstitial-electron model also leads to the expectation of a dependence of conductivity on lattice structure. It is especially clear from the geometry that the pathways for itinerant electrons are more direct in HCP than CCP for non-distorted lattices (See Part I and II). This can explain the low position of Ca (CCP) in Fig. 1 as compared to Mg (HCP). A greater conductivity would be expected in normal HCP metals parallel to the c-axis than perpendicular to the axis. This is as observed for HCP magnesium.

Comparison of Interpretations of Conductivity. Band theory has accounted for the major effects observed experimentally for electrical conductivity, and it is generally assumed that it gives a quantitative interpretation. This is the case for Na and K metals, but with Li, Rb, and Cs there are 2—4 fold differences between calculated electrical conductivity and observed values, similar discrepancies for noble metals and poor results for higher valent metals.[7] From the interpretations of the interstitial-electron model it would appear that two factors have not been taken into account in the band theory treatment of conductivity. One is the concept of vacant interstices (on an instantaneous picture) although a term for $\bar{e}$ per unit volume partially takes care of this. The second factor is the polarization of the itinerant electron cloud by ion cores of strong positive field and interpenetration of deformable ion cores by itinerant electrons. The latter factor explains the very low conductivities for Li and Be and the trends for the noble metals.

The marked advantage of the Interstitial-Electron Model over previous attempts to account for gradations in electrical conductivity is demonstrated in Table 1. The first comparison is Bardeen's[7] Band Theory calculation where only Na and K show calculated values within 20% of the experimental conductivity. The second comparison is that of Ziman's[8] reduced re-

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[6] O. Johnson, *J. Chem. Educ.*, **47**, 43, (1970).

[7] W. Bardeen, *J. Appl. Phys.*, **11**, 88 (1940).

[8] J. M. Ziman, "Electrons and Phonons," Oxford, Clarendon Press (1968).

TABLE 1. COMPARISON OF THREE APPROACHES TO EXPLANATION OF GRADATIONS IN ELECTRICAL CONDUCTIVITY

Band theory calculations (Bardeen[7])

	Li	Na	K	Rb	Cu	Ag	Au
Obsd	11.8	23.4	16.4	8.6	64	66	49
Calcd	28	23	20	5.3	174	143	142

Ziman[8] $\left(\text{Reduced Resistivity} = \frac{4e^2 M\alpha\theta^2}{n^2h^3n^{-1/2}Q_D T}\rho(T)\right)$

	Li	1.63	Be	3.76	Al	1.98	Zn	3.94
	Na	1.04	Mg	2.36	Ca	3.12	Cd	4.42
	K	2.08	Ca	2.30	In	4.26	Hg	7.76
	Rb	2.62	Sr	11.3	Tl	5.76		
Theory		1		1.6		2		1.6

Interstitial-Electron model[a]

	Conductivity	$(\text{Vac})^2$	$\frac{\text{Cond.}}{(\text{Vac})^2}$		Conductivity	$(\text{Vac})^2$	$\frac{\text{Cond.}}{(\text{Vac})^2}$
K	6.75	25	0.27	Cu	4.17	25	0.16
Ca	3.6	16	0.23	Zn	1.50	16	0.09
Sc	0.28	1	0.28	Mg	3.5	16	0.22
Be	0.75	4	0.19	Li	1.39	25	0.06
Mg	3.5	16	0.22	Be	0.75	4	0.19
Ca	3.6	16	0.23				
Al	3.82	9	0.42	Na	5.06	25	0.20
Sc	0.18	1	0.28	Mg	3.5	16	0.22

a) (Vac) = Vacant interstices

sistivity values where Na and Al give the only close correlation with the theoretical values. A correlation of electrical conductivity and *square* of number of vacancies is given for the interstitial-electron model. The reason for using (vac)^2 involves the direct dependence of conductivity on vacancies *via* number of electrons moving and an indirect dependence since the velocity of electrons is also directly dependent on the number of vacancies. In the table the deviations of the ratios of cond/(vac)^2 from the mean value of about 0.23 are all within 20% except for Li, Zn, and Al. This is a rather remarkable correlation when it is considered that a single parameter is used and that effects of lattice vibrations have not been directly included. The latter become important *e.g.* in extending the comparisons to Rb, Cs.

Thermal Conductivity of Metals

The same factors responsible for the gradations in electrical conductivity influence thermal conductivity: (1) the number of electrons moving as a result of the temperature gradient is directly proportional to the number of vacant interstices, (2) the velocity of electrons which move depend on the Fermi Energy, and those at the Fermi Level dominate the thermal conduction, (3) lattice vibration and (4) ion core interpenetration reduces thermal conductivity. In addition there is an influence of temperature since the number of electrons involved in heat conduction is a function of kT.

Electronic Heat Capacity of Metals

The interstitial-electron model accounts for the abnormally low value of the electronic heat capacity of metals in the same way as does band theory. While the movement of electrons which accounted for electrical conductivity did not depend on an excitation of electrons, the heat absorption by electrons does depend on excitation of electrons to a higher energy level. The electronic heat capacity, γ, depends also on the number of electrons at the Fermi Level which can be excited (absorb heat). Since kT is very small (0.02 eV at room temperature) relatively few electrons will be excited, and the expected electronic heat capacity will be a small fraction of 3/2 k. Because kT is small, the number of electrons at E_f is expected to be the decisive factor in determining electronic heat capacities of metals. From the interstitial model the number of electrons is directly proportional to the occupied interstices (and inversely proportional to the number of vacancies). This leads to the expectation of an inverse relation between electrical conductivity and electronic heat capacity since the conductivity is directly proportional to the number of vacancies. The influence of energy of excitation will be expected to show up in series of metals with the same number of vacancies (*e.g.* alkali metals).

The interstitial-electron model accounts for the major trends in γ for the metals as follows: (1) The small increase in γ in the order Na–Cs, metals which all have the same number of $\bar{e}$ at E_f is due to a decrease in the energy of excitation of $\bar{e}$. This is expected for the larger ion cores and indicated by band widths, but the larger value of Li than Na is due to an unexpectedly weak field of Li$^+$. This comes about by polarization of the $\bar{e}$ cloud and has been commented on in part II. (2) There is a monotonic increase from Be to Sr followed by a drop in γ at Ba. The first increase parallels the increase observed for the alkalis. The low value for Ba is associated with the change to BCC structure with a greater energy for excitation of $\bar{e}$ as compared to HCP. (3) The noble metals have γ values about 4 times smaller than the corresponding alkali metals and there also is lower electronic heat capacity for Zn, Cd, and Hg than the alkaline earths. This also is due to the larger excitation energy resulting from the 18-shell ion cores of the noble metals and Zn, Cd, and Hg. (4) In group 3 metals there is a large increase in γ from Al to Sc, Y, and La. In this case the distorted HCP lattice of the latter three metals leads to high occupancy of the fewer interstices. The larger number of $\bar{e}$ at E_f leads to the higher γ values. (5) The relatively high values of γ for group IV and group V metals also reflects the high occupancy of interstices in these metals. It is believed that across a row in the periodic table the increase Ca to Sc and Zr to V represents the normal trend of increased interstice occupancy, and the very high values for Sc, Y, and La are abnormal and due to restricted number of interstices in the distorted HCP lattice. (6) In general γ increases from M$^+$ to M^{2+} to M^{3+}, *etc.*, in proportion to the occupancy of interstices even though excitation energy increases in that order. The close proximity of tet interstices in HCP leads to the expectation of higher electronic heat capacity for HCP than BCC or FCC at least for high occupancy of interstices. This is the observation for Ti and Zr.[9] The γ values for BCC Fe and Mn are higher than for FCC structures.

The discussion of electronic heat capacity has considered the number of ē at E_f (occupied interstices) as well as the difference in energy of electron energy levels. These are usually considered as "density of states" in band theory. The density of states which is defined as the number of electron energy levels per ev is a theoretically derived concept and not an experimental number. There does appear to be a direct relation of the intensity of X-ray spectra to density of states.

Magnetic Susceptibility of Metals

The reason for weak paramagnetism in many metals is that only the ē near E_f can have the spins reversed by the applied magnetic field. The gradations in paramagnetic susceptibility as for γ will depend primarily on the number of ē at E_f but also on the energy required to reallign the electron spin. Thus, magnetic susceptibility should parallel the gradations in γ with the additional effect that electron pairs among the itinerant electrons can reduce the paramagnetism of the metal. Figure 3 shows the expected parallel behavior of γ and χ.

The diamagnetism of Be is an example of a divergence of magnetic properties from the observed gradation of γ. The diamagnetism of Be is undoubtedly the result of greater electron pairing of ē in the distorted HCP structure ($c/a=1.567$) of Be (See Part II). There is a minimum in magnetic susceptibility at Na for the alkali metals which reflects the abnormally high value for Li. This is due to polarization of the itinerant electron cloud by the high field of Li^+. It can be looked on as the result of an increase in electron density around the Li^+ core. The trends in magnetic susceptibility for the heavier metals are difficult to interpret because of the large correction for the diamagnetism of the ion core. The χ values in Fig. 3 are not corrected for core diamagnetism.

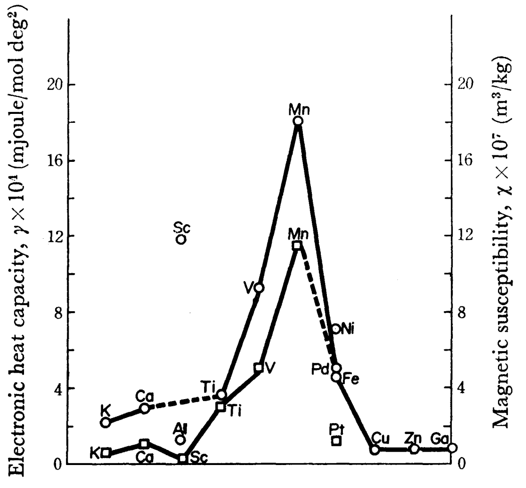

Fig. 3. Electronic heat capacity and magnetic susceptibility of metals.
(○: Electronic heat capacity, □: Magnetic susceptibility)

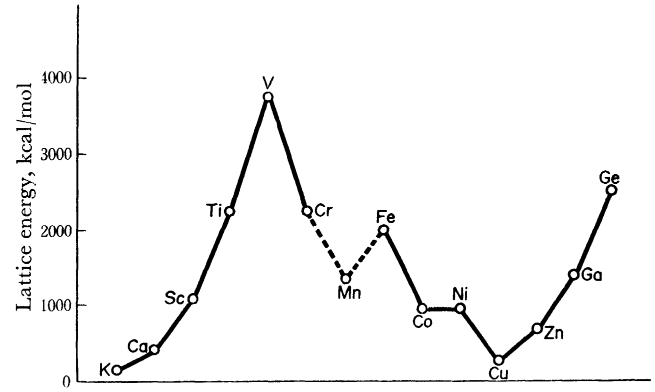

Fig. 4. Variation in lattice energy with group in periodic table.

Hall Coefficients of Metals

When a magnetic field is applied to a metal through which an electric current is passing, there is a drift of electrons in the direction of the magnetic field. The derived Hall Coefficients of metals have been taken as a measure of whether there are + or − carriers of electric current.

The alkali metals, noble metals, Mg, Ca, Al, and several other metals have −Hall Coefficients, while Be, Zn, Cd, V, Cr, Mn, Fe, and a number of other metals have +Hall Coefficients.[9] The explanation has been given tha tthe metals with +Hall Coefficient have positive hole conduction. The interstitial-electron model gives the following different interpretation. It is noticeable that the metals with +Hall Coefficients are those which contain electron pairs in their structure. It is proposed that in the conduction process an ē dissociates from an $(\bar{e})_2$ and moves to an adjacent interstice. Then an ē from a neighboring $(\bar{e})_2$ takes the place of the first ē. This process can continue and the resulting chain is equivalent to the movement of an ē in the direction opposite to the movement of the first ē. This parallels the hole conduction explanation, but there are additional consequences of $(\bar{e})_2$ in metal lattices which are completely different from those of "holes" and which have been discussed in connection with other metal properties.

It is of great interest that with very few exceptions the metals with +Hall Coefficients are superconducting metals. The exceptions, *i.e.* superconductors which have −Hall Coefficients are La, Ga, In, Sn, all of which have unusual or distorted lattices. Th and Ti, also exceptions, have very low Hall Coefficients. This correlation between superconductivity and +Hall Coefficient has not been pointed out previously, and the role of $(\bar{e})_2$ in the superconducting state will be discussed in detail in Part VI of this series of papers.

Physical Properties of Metals

Only some general comments will be made relating to the very extensive area of physical and metallurgical properties of metals. The greater the degree of localiza-

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[9] R. J. Weiss, "Solid State Physics for Metallurgists," Pergamon, Oxford (1963).

tion of ē density in a metal structure, the more brittle and hard the metal or alloy. This shows up in some of the metal alloys with large number of $(\bar{e})_2$ postulated for their structures and will be discussed in Part V for intermetallic phases. The localization of ē density can also come *via* electron preference for occupancy of one type of interstice, or by asymmetry in ē density in an interstice. The greater ductility of CCP metals as compared to HCP or BCC is probably connected to with the greater symmetry of ē distribution in CCP.