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An Interstitial-Electron Model for the Structure of Metals and Alloys. VI. Interpretation of Superconductivity

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A physical interpretation of the superconducting state based on the interstitial-electron model for metals is given within the framework of the BCS theory. The following conditions for itinerant electrons ($\bar{e}$) and metal ion cores (M^{n+}) are postulated as necessary for superconductivity: (1) There must be a matching of $\bar{e}$ energies (velocity) and binding strength of M^{n+} so $\bar{e}$ initiation of a lattice vibration is possible. (2) Movement of $\bar{e}$ and M^{n+} must be synchronized so there is enhancement of $\bar{e}$-phonon coupling. (3) There must be $\bar{e}$ of one spin available to enter such $\bar{e}$-phonon "chains". The model leads to $\bar{e}$ of opposite spin in phonon chains 500—5000 Å apart. It gives physical interpretations of the thermodynamic properties of superconductors and clearly shows that type of lattice influences superconductivity. It shows the basis for the new correlation observed between superconductivity and a positive Hall Coefficient. Since the model can incorporate the presence of anions as well as $\bar{e}$, it provides a related explanation for superconductivity in non-metals.

The phenomenon of superconductivity has been known since 1911[1] and major efforts have been expended to discover superconducting materials with the highest possible T_c. The range of T_c for materials now known is from a fraction of a degree K to the region of 20K. The major advances have been achieved by Matthias and coworkers[2] whose experiments were based on very careful considerations of the periodic relationships involved. There are several different types of superconductors, and the BCS theory[3] does not explain all of them.[4] It was therefore of great interest to see what additional information and insight the interstitial-electron model[5] might offer for the understanding of superconductivity. It was anticipated that the spatial location of electrons as well as the inherently chemical approach would supplement the correlations of Matthias.[2,4]

Theoretical discussions on superconductivity have emphasized that it is a quantum phenomenon not to be understood on a classical basis. The interpretation presented in this paper is largely in classical terms, but the interstitial-electron model does incorporate all of the essential elements of quantum chemistry and indicates how a microscopic quantum state arises. This is possible because the model introduces spin correlation of electrons in its fundamental postulate of localization of $\bar{e}$ density in interstitial positions (or binding regions).[5] If this approximation of $\bar{e}$ density is reasonably accurate it should lead to the same interpretations of metal properties as the approximations of band theory using wave mechanical calculations involving overlap and exchange terms for atomic wave functions. The viewpoint in this paper follows from the ideas of Föhlich,[6] London[7] Pippard,[8] and Matthias[4] and it contains the essential energy gap[9] of the BCS theory.[3]

Description of the Superconducting State

The basis idea of an electron-phonon interaction,[6] which was incorporated into the BCS theory,[3] will be

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1) H. K. Onnes, *Leiden. Commun*, **1201**, 1226 (1911).

2) B. T. Matthias, T. H. Geballe, and V. B. Compton, *Rev. Mod. Phys.*, **35**, 1 (1963).

3) J. Bardeen, L. N. Cooper, and J. R. Schrieffer, *Phys. Rev.*, **108**, 1175 (1957).

4) B. T. Matthias, "Superconductivity," Vol. I, ed. by P. R. Wallace, Gordon and Breach, Sc. Pub., New York (1969).

5) O. Johnson, This Bulletin, **45**, 1599, 1607 (1972); *ibid.*, **46**, 1923 (1973).

6) H. Fröhlich, Reports on Prog. in Physics, XXIV, 1 (1961).

7) F. London, "Superfluids," Vol. I, Wiley, New York (1950).

8) A. B. Pippard, *Prov. Roy. Soc. Ser. A*, **216**, 547 (1953).

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

used in the physical picture for superconductivity according to the Interstitial-Electron Model. The treatment of metal properties in Parts I—V of this series of papers emphasized an instantaneous picture of a small degree of localization of electron density as "electrons-in-interstices". The Hellmann-Feynman Theorem was used to justify the electrostatic treatment of the quantum-mechanical electron distribution, and the interstitial electrons were pictured as moving between octahedral (oct) and tetrahedral (tet) binding regions separated by a triangle of 3 M^{n+} (positive ion cores). To treat the phenomenon of superconductivity the dynamic movement of electrons and ion cores must be included. In the normal metal, dynamic movement of $\bar{e}$ throughout the lattice is seen as part of a continuous reestablishment of equilibrium as $\bar{e}$ move to new positions in response to lattice vibrations. All of the properties of $\bar{e}$, including interstice preference and spin correlation are postulated to persist in the dynamic picture.

The concept of an electron initiating a lattice vibration[3,6] is used in qualitative discussions of superconductivity, but the details have not been explored beyond the postulate that upon movement of 2 M^{n+} closer together a second electron will be attracted to this region. At the critical temperature for superconductivity (T_c) the conditions must be such that electron motion can influence lattice vibrations. The Interstitial-Electron Model requires that the following conditions be fulfilled for superconductivity:

(1) There must be a matching of energy of electrons (velocity) and binding strength of M^{n+} for initiation of lattice vibrations. Taking a fixed electron velocity at T_c, when the amplitude of lattice vibrations is larger than optimum (low binding strength of M^{n+}) the lattice will not be significantly modified by motions of $\bar{e}$ in the vicinity of M^{n+}; when the amplitude is smaller than optimum (high binding strength), lattice vibrations cannot be initiated.

(2) The movement of $\bar{e}$ and M^{n+} must be synchronized so an $\bar{e}$ passes between $2M^{n+}$ at the precise time to give enhancement of lattice vibration. This condition includes the requirement of availability of a sufficient number of $\bar{e}$ at such critical positions and thus has a geometric component. This condition also implies that electrons not involved in the superconduction process do not scatter the phonons. This condition is in keeping with the treatment of superconductivity as a many body problem.[6]

(3) There must be a sufficient number of electrons of 1 spin in the above positions to sustain an electron-phonon chain. The detailed way in which these conditions lead to superconductivity can best be described by the interpretation of the persistent current and diamagnetism of the superconducting state.

The existence of the *persistent current* is the most spectacular consequence of the postulated electron-phonon coupling. The situation before application of an electric field is that there is relatively small amplitude of lattice vibration and random movement of $\bar{e}$. When electrons are set into motion by the electric field they will move from oct to tet between 2 (or 3) ion cores. Under conditions favorable for superconductivity the $\bar{e}$ will attract the ion cores toward each other and initiate or enhance a lattice vibration at that point. The initial moving electron, now moving faster than thermal velocity, continues on its path while a second electron is attracted to the region where the ion cores have moved even closer together. Thus, there is a phonon induced by the electron movement, and it has been proposed above that each phonon involves electrons of one spin type. This follows from the association of electron spin with an interstice type in the interstitial-electron model.[5] Thus, the second electron moving into the interstice vacated by the first moving electron must have the same spin. The same is true of subsequent electrons which are attracted. Along with the phonon, then, there is a group of $\bar{e}$ of the same spin moving through the lattice, and this has been termed an $\bar{e}$-phonon chain.

When the lattice vibration induced by the first moving electron is at minimum displacement (1/2 way through the vibration cycle), it will begin to move closer to metal ion cores in the adjoining layer in the lattice and thus attract an electron there, this time an electron of the opposite spin since it involves an adjoining interstice separated by an ion core. A new phonon chain is induced by the movement of electrons of spin opposite to the initial phonon chain and follows it by 1/2 of a vibration cycle, and a second group of $\bar{e}$ of opposite spin move in the same direction as the first group. If the vibration frequency induced is 10^{13} sec^{-1}, and the velocity of the electrons 10^8 cm/sec, the spacing of the two groups of $\bar{e}$ will be about 500 Å. For electrons of 10^9 cm/sec, the distance between these groups of $\bar{e}$ of opposite spin would be 5000 Å. These electron groups of opposite spins, in a sense bound together by induced phonons, are the counterpart to "Cooper Pairs" in the interstitial-electron model. It is easily seen that in a lattice like those of metals there is mutual reinforcement of all the phonons and consequently a persistent current in the superconducting state. It is also obvious that a metal surface as well as interstice vacancies or impurities will modify this effect, and this will be discussed in the next section. The range of distances of Cooper Pairs would represent a minimum since the lattice vibration in the adjoining layer may not always initiate a phonon.

Since lattice vibrations are a sensitive function of temperature it is reasonable that at a sufficiently low temperature (T_c for superconductivity), the optimum conditions for initiation of a phonon by an $\bar{e}$ would be reached. At T_c it becomes energetically more favorable for $\bar{e}$ of one spin to move in groups through the lattice as parts of a phonon chain than for $\bar{e}$ to move *via* the normal means of consecutive occupancy of vacant lattice interstices (energy gap). Since the new path has zero resistance there is a sharp drop in resistance over a small temperature interval as the electron transport shifts more and more to the new pathway.

The postulated $\bar{e}$-phonon chains with alternating spins associated with the moving itinerant electrons in a superconductor means that the superconducting metal

will exhibit *perfect diamagnetism* (Meissner Effect[10]). The interstitial-electron model gives a picture of the superconducting metal as a giant diamagnetic molecule which is a macroscopic manifestation[11] of the quantization of electrons (Pauli Principle). The diamagnetism of a superconductor is probable its most important property.

Properties of the Superconducting State

The model leads to a unique interpretation of the influence of crystal lattice on superconductivity and also to a new correlation with positive Hall Coefficient. These will be presented in detail, and then some major properties of the superconducting state will be briefly listed and commented on.

It has been observed that with few exceptions *superconducting metals have positive Hall Coefficients*. This appears to be an important correlation which has not been reported previously (See Paper III in Series). The interstitial-electron model for metals has interpreted a positive Hall Coefficient as indicative of electron pairs in the interstices of the metal in question. The presence of electron pairs goes along with high occupancy of interstices, large field of the metal ion core and fewer spin restrictions to the arrangement of electrons, all properties which favor the transition to a superconducting state. A small Hall Coefficient indicates nearly equal numbers of $\bar{e}$ and $\bar{e}_2$ in the interstices of the metal lattice, and metals with small Hall Coefficients are also expected to be potential superconductors. Another possibility is that the remaining $\bar{e}$ in the structure are more restricted (less phonon scattering) by the surrounding $(e)_2$ than in metals without these electron pairs. The $(e)_2$ also provide a source of $\bar{e}$ for the phonon interaction. Somewhat the same restriction may obtain in superconducting compounds such as NbN or MoC. The C^{4-} and N^{3-} anions in the structure restrict the movement of $\bar{e}$ which are present in the metallic structure and at the same time provide a source of additional $\bar{e}$ to propagate the phonon (*via* dissociation of electrons from the relatively unstable anion). The absence of a Hall Effect in the superconducting state provides confirmation of the proposed mechanism of superconductivity. A movement of chains of electrons of alternating spin with $\bar{e}_2$ as a major source of these electrons would not be affected by a magnetic field.

The type of crystal lattice is also expected to influence

Properties of Superconductor (S) Compared to Normal Metal (M)	Comments
1) There is an energy gap of approximately $3.5\,kT_c$ between S and M.	The $\bar{e}$-phonon chains give a pathway of lower potential energy; $\bar{e}$ kinetic energy may be higher.[12]
2) S has lower thermal conductivity than M.	Lattice vibrations are enhanced in S; this scatters $\bar{e}$ and there is lower dissipation of thermal energy.
3) At T_c, the electronic heat capacity (ν) increases for S.	In S, electrons require greater energy for excitation and more electrons are available. (See Text, Sect IV)
4) Penetration Depth for S is observed to be approximately 500 Å.	The 10—30% greater amplitude of lattice vibrations at the surface can disrupt phonon chains; proposed reinforcement at 1/2 of a vibration will be out of phase, effect is expected to extend at least 500 Å below the surface.
5) Coherence length (ε) of Pippard[8] (or correlation distance of BCS Theory) has been calculated[13] from the relation, $\varepsilon = 0.18\hbar V_f/kT_c$ to be (in Å) 830 for Pb, 2300 for Sn, 3800 for Nb, 7600 for Cd and 16000 for Al.	This is the spatial definition of the superconducting electron and is proposed to be in the range 500—5000 Å by the model. Gradation appears consistent with frequency of vibration expected for different M^{n+}.
6) For non-transition metals $T_c \propto m^{-1/2}$. For transition metals, no mass dependence or small dependence.	This isotope effect was the first demonstration of a relation between lattice vibration (frequency $\propto m^{-1/2}$) and S. Model suggests interaction of $\bar{e}$ and localized d-electrons in transition metals may provide a source of $\bar{e}$ of 1 spin and thus a modified mechanism of S.
7) Ferromagnetic or anti-ferromagnetic materials are not S.	The allignment of $\bar{e}$ with spin of d-electrons localized on ion cores interferes with $\bar{e}$-phonon chains.
8) S can be quenched by passing a critical transport current (Silsbee effect).	The greater number of moving $\bar{e}$ can disrupt $\bar{e}$-phonon chains.

10) W. Meissner and R. Ochenfeld, *Naturwissenschaften*, **21**, 787 (1933).
11) J. E. Mercereau, "Superconductivity", Vol. I, ed. by R. D. Parks, Marcel Dekker, Inc., New York (1966), Chap. 8, p. 174.
12) R. J. Weiss, "Solid State Physics for Metallurgists," Pergammon, Oxford (1963).
13) Ref. 11, Chap. 3, Vol. I by R. Meservey and B. B. Schwartz.

the possibility of superconductivity both by its determining influence on phonon paths but also by its indirect affect on localization of electrons in interstices. The cubic close-packed lattice (CCP) is expected to offer favorable pathways for $\bar{e}$ of one spin through the lattice because it has the largest number of interconnected oct and tet interstices. Of the various hexagonal close-packed lattices (HCP), the La structure (ABACAB arrangement of layers) is more favorable than normal HCP or HCP with c/a greater than 1.632. The HCP structure with c/a less than 1.632 is less favorable because with bipyramidal interstices occupied by $\bar{e}$ the oct interstices can be only 1/2 occupied with $\bar{e}$. This restriction is removed, however, when $\bar{e}_2$ occupy these interstices. The details of the symmetry of interstices was given in paper I.[5] In the BCC structure the $\bar{e}$ are well dispersed in interlocking tet rings and would be favorable for superconductivity only for high occupancy of interstices. Tendency for superconductivity is expected to decrease in the order CCP>HCP-(La)>HCP($c/a \geq 1.632$)>HCP($c/a < 1.632$)>BCC.

TABLE 1. SUPERCONDUCTING TRANSITION TEMPERATURE AND LATTICE TYPE

CCP	HCP (La)	HCP ($c/a>1.632$)		HCP ($c/a<1.632$)	BCC	
La 6.3	La 4.9	Ti 0.4	Zn 0.9	Be 8.0	V	5.0
Al 1.2		Zr 0.6	Cd 0.5	(as thin film	Nb	9.1
Ir 0.14		Hf 0.2		only)	Ta	4.5
Pb 7.2		Tc 9.3	Tl 2.4		Mo	0.9
Th 1.4		Re 1.7			W	0.9
		Ru 0.5				
		Os 0.65				

Several examples with values for T_c (in K) are tabulated below. In general these expectations agree with the observations of Matthias[2,4] as far as frequency of superconductors of various lattice types. Superconductors with high T_c values do occur for all types of metal lattices. It is the frequency of occurrence of superconductivity in many alloy systems and compounds which is the criterion for the gradations with lattice type. Matthias[4] mentions that the β-tungsten structure is particularly favorable and that it has strings of transition metal ions which do not intersect. This observation is in keeping with the postulation of phonon chains as one of the requirements of superconductivity.

Correlation of Physical Properties with T_c

The three interrelated conditions postulated for superconductivity in a metal can be best related to the transition temperature (T_c) through well-known metal properties. The onset of superconductivity must represent a very delicate balance of electron energies since the lowering of energy in the superconducting state is very small.

Electron velocity can be estimated from band width (X-ray spectra), but the data is sometimes controversial. *Lattice energy* will also reflect electron velocity, and Fig. 1 shows that there is a rough correlation of T_c and lattice energy. Lattice energy should be a good correlating parameter since it is a measure of $\bar{e}$-lattice interaction. The deviations in Fig. 1 may indicate some optimum favorable lattice energy.

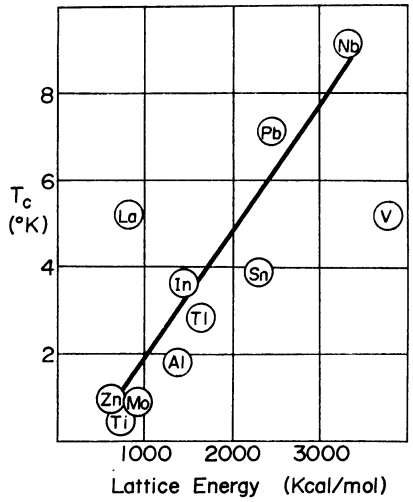

Fig. 1. Dependence of T_c on lattice energy of metal.

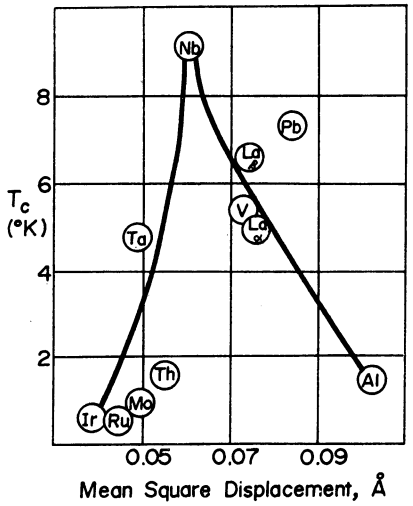

Fig. 2. Dependence of T_c on lattice displacement in thermal vibration.

Lattice displacement is directly related to ion core repulsion, and there is expected an increase in T_c as lattice displacement decreases followed by a decrease in T_c for ion core repulsions beyond the optimum for superconductivity. The data in Fig. 2 can be interpreted as showing such an optimum. The optimum may well be different for ion cores with completed d-shells. The relations in Fig. 2 show that T_c is inversely proportional to lattice displacement above values of 0.06 and directly proportional to $\sqrt{\bar{u}_0^2}$ for values below 0.06. The optimum may be 0.08 for d^{10} metals. In connection with the suggested optimum in Hall Coefficient it should be mentioned that although $\bar{e}_2$ are proposed to exist in the lattices of all superconducting metals, these $\bar{e}_2$ are not the "Cooper pairs" referred to above. The unusual gradation of T_c for group V metals (Nb>V≥Ta), not previously explained, appears to be due to an optimum lattice

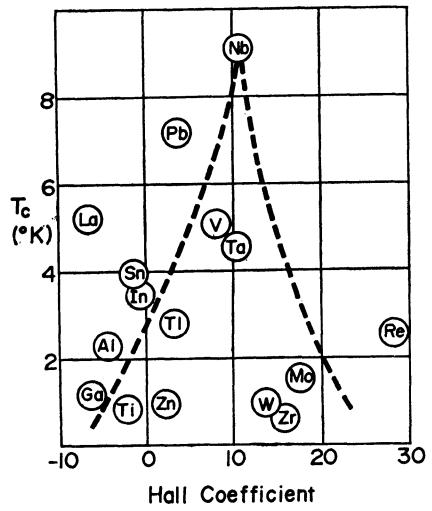

Fig. 3. Suggested dependence of T_c on Hall coefficient.

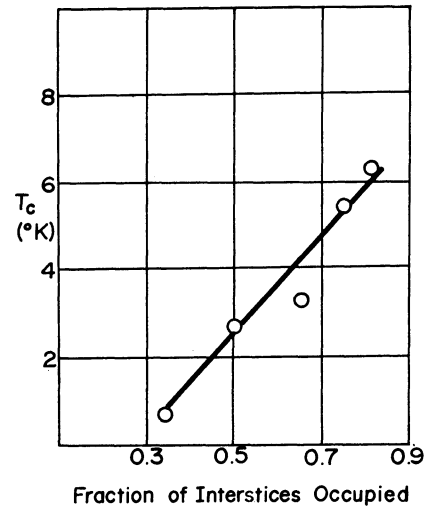

Fig. 4. Dependence of T_c on occupancy of metal interstices (average values)

displacement for Nb, less than optimum for Ta and more than optimum for V. The high T_c observed for La (as seen in Figs. 1 and 3) is due to the high favorability for superconductivity of the La-type packing in the lattice according to the interstitial-electron model.

The correlation with electron occupancy is shown in Fig. 4 and is based on values of electron occupancy of interstices given in Part II.[5] This appears to be a good correlation as expected. The largest deviations from the average line in Fig. 3 are for metals where other factors have a strong effect, *e.g.* for Pb (T_c= 7.2) and Ti, Zr, and Hf (0.2—0.6K) with 2/3 occupancy of interstices and for La (T_c=6.3) and Ir (0.14) both with 1/2 occupancy of interstices. The correlation with *Hall Coefficient* is shown in Fig. 3, where a maximum is suggested. This is a rough correlation and is given for illustration purposes. The interstitial-electron model clarifies the partial relation between *electronic heat capacity* (γ) and T_c. Qualitatively T_c and γ correlate[14] for M^{4+} to M^{6+} metals. There are opposite trends for M^{3+} (Sc, Y, and La) and for M^{7+}-M^{10+} ion cores. The lack of correlation for M^{3+} results from special $\bar{e}$ distribution due to lattice distortion in these metals (see Part II).[5] In groups 7 and 8 the localized d-electrons influence γ and no correlation with T_c is expected. These conclusions are related to the findings of Ishikawa and Totts[15] that a superconducting electron-phonon interaction parameter has a different behavior for d^{10} metals and transition metals. These authors use a correlation of T_c with a parameter combining γ and θ_D (Debye temperature).

The correlations given above offer a means of relating metal properties to the onset of superconductivity. It may be possible as well to relate these factors to superconductivity in non-metal materials. Factors which are more specific are the effects of type of lattice (sect. III) and effect of d-electrons localized on the ion core. Partially filled d-shells may lead to an interference with superconductivity due to asymmetry of ion core fields. For the ion cores with completed d-shells (Zn, Cd, Ga, In, Tl, Sn, Pb) the high positive field which results from the poor screening by d-electrons increases the chances of superconductivity. The greater $\bar{e}$ penetrability of the d^{10} ion cores also increases the chances of e-phonon interaction. Matthias[4] has pointed out the greater ease of preparing this group of superconductors.

Discussion

The interstitial-electron model for metals gives a detailed interpretation of the superconducting state as based on phonons induced by $\bar{e}$, very much as the general suggestions made by Fohlich[6] and Bardeen.[17] It also gives a qualitative physical interpretation of the energy gap which is the essential element of the BCS Theory. The model makes it possible to relate metal properties such as lattice energy, electron velocity, lattice displacement, type of metal lattice, and electron occupancy of interstices to the critical temperature(T_c) for superconductivity. These correlations can be the basis for further explorations for superconducting metals.

On the basis of the model all metals are not expected to become superconductors even at the lowest temperatures attainable. It is believed that the alkali metals and Cu, Ag, and Au have too many vacant interstices to allow superconductivity. In addition, certain intermetallic compounds with strong localization of $\bar{e}$ and $\bar{e}_2$ (inhomogeneous interstices, see Part IV) are not expected to allow superconductivity. The model does suggest that compounds with unstable anions (dissociable electrons) such as O^{2-}, S^{2-}, Se^{2-}, Te^{2-}, N^{3-}, P^{3-}, and C^{4-} are all possible superconductors when in metal-like compounds. (High pressure CS is superconducting.)

The present model gives a different interpretation from that of Matthias[18] for the gradations of T_c across

14) Ref. 11, Chap. 13, Vol. II by G. Gladstone, M. A. Jensen, and J. R. Schrieffer.

15) M. Ishikawa and L.E. Totts, *Solid State Commun.*, **9**, 799 (1971).
16) B. W. Roberts, "Progress in Cryogenics," Vol. IV, ed. by K. Mendelsohn, Academic Press (1964).,
17) J. Bardeen, *Rev. Mod. Phys.*, **23**, 261 (1951).
18) B. T. Matthias, "Progress in Low Temperature Physics," Vol. II, Interscience, New York (1955).

the rows in the periodic table. The maximum at Group V and VII and for Group IVB are considered to be the result of optima in lattice displacements and only indirectly a function of place in the periodic table. For example, the decreases from Nb to Mo followed by an increase to T_c are taken as due to changes in lattice displacement which reflect the different localization of d-electrons on the ion cores for Mo and T_c whereas Nb has no localized d-electrons. As mentioned earlier the maximum in T_c for Nb (and Pb) at a lattice displacement of approximately 0.06 Å (0.08 for Pb) represents the point at which strong ion core repulsion leads to low amplitude of lattice vibration but is not sufficiently strong to prevent initiation of phonons by $\bar{e}$. In the d^{10} group the inherently stronger forces lead to a larger optimum displacement and also lead to distorted structures and non-metallic properties beyond Group IV.

There are many superconductors not discussed in this paper. A detailed analysis of data on superconducting alloys would be needed to determine the effect of more than one ion core on superconductivity. It is anticipated for alloys with transition metals that the way the model allows ligand field theory to be used would be helpful in interpreting the effect of localized d-electrons in alloys on superconductivity.

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