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Superconductivity in transition metals and compounds

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A qualitative account of the T_c systematics of transition metals and compounds is presented from a novel point of view. The suggestion is that the d density of states at the Fermi surface is zero near the center of the series. The idea unifies the T_c systematics with other physical properties, and includes the relationship betwen high T_c and lattice instability. The superconductivity of rare earths and neighboring elements is considered with special emphasis on the role of the $4f$ core.

I. INTRODUCTION

In a previous paper,[1] hereafter referred to as I, we outlined a coherent description of trends in superconductivity among the elements of the Periodic Table. We sought, in particular, to lay open the essential physical mechanisms which determine both the strength of the electron-phonon interaction and the phonon frequencies, assuming, as is now commonly accepted, that virtual phonon exchange is primarily responsible for the electron-electron attraction leading to superconductivity. Transition metals, defined as d-band metals with Fermi surface in the region of overlap of d bands and the conduction band, do not fit into the scheme in a simple way. We are therefore considering these metals apart.

In the transition series, the d electrons near the Fermi surface undergo virtual-phonon-exchange scattering, and participate in the BCS condensation, although too immobile for significance in normal-state conductivity. However, little is known of the behavior of d electrons, and therefore the trends in superconductivity are difficult to understand. The difficulty hinges on the strength of the d-electron–ion coupling and the d-electron mobility.

Most theories of T_c in transition metals (TM) have concentrated on understanding electron-phonon interaction[2-6]; characteristic phonon frequencies were introduced separately as known physical parameters. It turned out in this work that it is the phonon frequencies which largely determine T_c, but little was understood of their variation through the TM series. Some recent work, however, has now appeared on phonon frequencies.[7-10] It is to this problem also that we direct our attention mainly in the present paper. We shall adopt an unconventional point of view on the electronic structure of the TM and compounds which, reflected in the phonon frequencies, gives an account of both the systematics of T_c and other physical properties in a unified way.

Our viewpoint is expressed in Sec. II; it differs from the usual theories in the interpretation of the low density of states $g(E_F)$ observed at the center of the TM series. Instead of the commonly held assumption of stronger delocalization of d states at the center of the series, we shall present a case for adopting the opposite view, viz., that d electrons are *localized in covalent bonds* near the center of the TM series. Off the center, however, we are free to adopt any of the conventional theories. The outlook on the electronic structure of TM is related to the Engel-Brewer correlation,[11,12] for which it may provide a theoretical interpretation; its consequences for superconductivity leads to the application of Brout's suggestion[13] for noble metals to the center of the TM series. We are led to the concept of broken covalency as criterion favoring T_c. This unifies the discussion of the T_c systematics of transition and simple metals,[1] and of the relationship between high T_c and lattice instability.

In Sec. III A, we make some remarks on the far ends of the TM series, chiefly the late TM and compounds. In Sec. III B, we present our views on the rare earths and their neighboring elements.

II. LATTICE STABILITY AND T_c

Materials at the center of the transition series (elements and solid alloy solutions) exhibit various physical properties besides the drop in T_c, which distinguish them from the high T_c members. In the scheme to be proposed, the strong variations in T_c, $g(E_F)$ and the various other physical properties are all interrelated. Other TM systems are also included and will be considered in Sec. II D.

In the first place we direct our attention to the origin of the drop in $g(E_F)$. In tight-binding d-band calculations in the bcc structure, the low $g_d(E_F)$ at the half-filled d shell occurs as follows[14]: The fivefold-degenerate d shell is split into two narrow bonding bands, two narrow antibonding bands, and a broad band connecting them; at the center of the series the broad band is half-filled and $g_d(E_F)$ is low. The bands are hybridized with the overlapping nearly free sp band. Similar results are obtained in the augmented-plane-wave (APW) resonance model.[15] Conceptually these results are not easy to understand. We venture to suggest the following situation at the center of the TM series: that the Fermi surface has the low $g(E_F)$ of a nearly-free-electron gas, while the more localized states form covalent bonds. This effect could provide the unifying principle underlying the lattice structure, lattice dynamics, superconductivity, and other properties. First, we shall expound our interpretation of electronic structure in the TM series.

A. Electronic structure in the transition-metal series

We consider the two types of outer orbitals in the center and late transition atoms, viz., the s and d orbitals, as analogous to the outer orbitals of nontransition atoms in the low- and high-valency groups, respectively. We describe the cohesion of TM in terms of an interplay of the two cohesive mechanisms which act respectively in these two regions of the Periodic Table. Let us review these mechanisms. The natural description for the covalent bonding of the highly polyvalent nontransition elements is in terms of valence-bond theory; for the metallic bonding in lower valency groups, it is the molecular-orbital theory, i.e., band theory, which is more appropriate. It is useful, however, for acquiring insight, to move between both descriptions.

Beginning with the highly polyvalent nontransition elements, we recall that covalent open structures, with a few neighbors close in relative to mean lattice spacing, R_a, give the maximum stability. In the valence-bond description, the unpaired atomic orbitals of the free atom form bonds with neighbors. These paired bonds, together with the paired outer atomic orbitals, prevent symmetrical close packing by their directional Pauli repulsion, since the atomic promotion energies are so high that other states would not be available for occupation, if the paired bonds and orbitals were to be strongly overlapping in close-packed metallic structures. If this were reexpressed in the language of band theory,[16] then the lattice spacing R_a, in first approximation, is that with minimum energy for a uniform electron gas in the pseudopotential; the high-valency gas, resisting the compression of a symmetric close-packed structure, keeps R_a well away from the core diameter $2R_c$. The strong scattering by the pseudopotential $W(\tau)$, outside second-order perturbation, then favors a less symmetrical crystal structure, which encloses the Fermi surface with Brillouin-zone boundaries. We recall that in real space the electrons are well localized at the ionic sites; the higher the valency and the smaller R_c, the more atomiclike is the electronic structure at the sites.

On moving left towards group IVB, the atomic $s \to p$ promotion energy, $E(s \to p)$, becomes weak enough for the closed atomic s orbitals to be broken up by the nearest-neighbor approach R_{nn}, which can now lie closer to the larger $2R_c$; thus the Pauli repulsion of the s orbitals is overcome to form more bonds. In group IVB, the low-temperature normal pressure phases of Si, Ge, and Sn form four equal covalent sp^3 bonds in a diamond structure; the bonds are nearly independent and localized. In the lower-valency groups, R_{nn} and $2R_c$ continue to approach each other, as R_c grows and $E(s \to p)$ diminishes. Moreover, since atomic promotion energies have now become small, the Pauli repulsion between closed localized bonds can easily be overcome, to form symmetric close-packed structures, $R_a \sim R_{\text{nn}} \sim 2R_c$, in which other than closed bonds are occupied. While R_c increases on proceeding from right to left along a series, R_a stays relatively constant. The strongly coupled bonds then have fluctuating occupation (resonance), which constitutes the electron gas with a Fermi surface. Here the band-theory description becomes more natural: The close-packed array, $R_a \approx 2R_c$, favored by the low-valency electron gas, has a smooth pseudopotential in which the electrons are nearly free.

Turning now to the TM, we shall interpret their electronic structure as a competition between the above two mechanisms. Leftwards from the noble-metal group, the d electrons become less tightly bound to the ions as their charge decreases, and d occupation falls from the inert-gas core configuration. We may compare to the nontransition elements on the left of the inert gases. In both cases, the cohesive energies increase on moving left along a series towards the center, since, as atomic orbitals become available, more bonding states are formed. We suggest that in the TM the requirements for lattice stability of the d-d bonds, the sp-sp bonds, and the sp-d hybridization will not in general coincide, and that where they are in conflict the d-d bonds's preference is overridden. The labels d and sp refer to the dominating atomic orbitals of the respective hybridized wave functions in the solid, and we are considering their occupation as in the solid. We suggest that d-d bonds, i.e., bonds between mainly d orbitals hybridized with some sp, would tend to prefer localized covalent bonding, as do the p-p or sp-sp bonds in the higher groups of nontransition elements. The crystal structure would ensure only weak sp hybridization with the d, and keep the bonds nearly independent. Instead, the crystal structure chosen by the *sp*-electron gas couples the *d*-*d* bonds together (including paired *d* orbitals or antibonds) to give a fluctuating charge, which is equivalent to a partially occupied *d* band (generally split into subbands) with high $g_d(E_F)$. Similar considerations would apply to the earlier TM (except for the beginning of the series where the *d* potential is not so strong); thus *d*-*d* bonding, there, would also prefer covalency but for the *sp* electrons, in analogy perhaps to the *sp* states of boron with its small core. The usual band structure, we maintain therefore, carries a high $g_d(E_F)$ because *d*-*d* covalent bonds have been broken. The breaking mechanism is the *sp* orbitals, which determines the crystal structure.

We now come to the main point of this section. At the center of the TM series, the number of *d*-*d* bonds is maximum and the cohesive energy is at its highest. Moreover, by Hund's rule, all the five *d* orbitals are unpaired in the free atom and available for *d*-*d* bonding, thereby furthering the cohesion, unlike, incidentally, their maximally bonded counterpart in the non-TM, viz., group IV*B*. One might therefore have good reason to expect that *d*-*d* bonding rivals other considerations at the center of the series. We propose, therefore, that at the center the *d*-*d* bonds are indeed preferentially localized. Support for this idea comes from the following considerations. The sharp drop in $g(E_F)$, observed at the center, indicates either a strong delocalization of *d* electrons into nearly free electrons, or, on the contrary, a strong localization, depressing the *d* bands below the Fermi surface. While the former result is indicated by the band calculations, it is not easy to understand conceptually, nor to link it with other physical properties. On the other hand, the sharp rise in melting point, accompanied by the brittleness and hardness of these metals and alloys all point to directional covalent bonding. Other evidence is the failure to absorb hydrogen, in marked contrast to the other TM, especially those with high $g_d(E_F)$, where the *d* band absorbs the electron of each hydrogen atom; and the electrical resistivity,[17] exhibiting T dependence T^5, like simple metals, in the center TM, instead of the T^3 off the center due to $s \rightarrow d$ scattering.

We propose that at the center of the TM series the requirements for the *d*-*d* bonds, the *sp*-*sp* bonds, and *sp*-*d* hybridization are no longer in conflict, but conspire together to favor the bcc structure. The stabilization of bcc at the center by this combined effect corroborates well with the aforementioned physical properties. Off the center, however, the maintenance of bcc indicates that the same structure can be favored by *sp*-*sp* bonds and *sp*-*d* hybridization, but now in the face of the conflicting requirements otherwise necessary for localized *d*-*d* bonds. The consequent delocalization of the *d*-*d* bonds leads to phonon softening by the long-range Coulomb repulsion of more itinerant *d* electrons. This anomalous phonon softening arises therefore from the above conflict, and is accompanied by high T_c as will be discussed in the following subsections.

We wish to point out that at the center of the series the high symmetry of the bcc, compared to usual low symmetries of covalent structures, need not be a drawback to d^5 covalency, considering that by Hund's rule all the five orbitals of the free atom are available for bonding. This is in contrast to the diamond structure in group IV*B*, where R_{nn} must approach $2R_c$ to release the paired atomic *s* orbitals, while maintaining R_a larger through bond-bond Pauli repulsion. Hund's rule thus paves the way for the compatibility of d^5 covalency and strongly resonating *sp*-*sp* bonds in a structure favorable to both.

In the first TM series, however, the *d* orbitals are too tightly bound to be so effective in bonding, except in the early TM, Sc, Ti, and V. While ΔE_d, the *d* bandwidth, is still large relative to ω_D, the Debye frequency, the strong intra-atomic *d* correlation polarizes the spin and prevents Cooper-pair formation. We note, incidentally, that in the configuration d^5, in Cr, the *d* electrons are more localized at the ionic sites, to draw the maximum benefit from Hund's rule. Thus the configuration d^5, which has the most to gain from Hund's rule when tightly bound, and from *d* bonding when less bound, imposes its requirements in all three series.

B. Superconductivity

The above viewpoint on electronic structure has the following consequences for superconductivity. Off the center of the series, where *d* electrons have been released and are available for scattering, one has all the right conditions for superconductivity described in I for nontransition polyvalent metals; i.e., the small inert-gas *d* core relative to lattice spacing leads to both strong *d* electron–phonon coupling and effective short-wavelength screening of inert-core ionic plasma frequency, both conspiring to enhance T_c. Therefore, the TM with its polyvalent *d* covalency broken by *sp* electrons should be compared to a polyvalent nontransition element with its covalency broken mechanically. Under pressure, covalent elements of groups IV*B*, V*B*, and VI*B* become superconductors with T_c comparable to the high T_c transition metals; see further in Sec. II E.

At the center of the series, the *d* electrons localized in covalent bonds do not participate in the scattering. By Hopfield's argument,[2] the loss of this participation would not significantly affect T_c directly. However, the covalent bonds formed resist the lattice vibrations. Conditions are then analogous to those in noble metals, as we shall now see.

T_c quenching in noble metals was discussed in I, following an idea originally expressed by Brout,[13] and hereafter called the Brout mechanism. To appreciate the analogy, therefore, we shall first discuss the electronic structure of noble metals, as a complement to Sec. II A. In noble-metal free atoms the *d* shell is filled and becomes an inert-gas core. Inert-gas solids are loosely bound by van der Waals forces, with Pauli repulsion resisting further compression. In the close-packed noble metals, however, the cohesion is due first to the resonating bonds formed by the *s* orbitals; second, since the atomic $d \rightarrow sp$ promotion energy is low, the *d*-core-core Pauli repulsion partially gives way in favor of bonding from *d-sp* hybridization.[18] In other words, the *d* wave functions acquire some *sp* amplitude in the solid and benefit from the low potential between ions. Further compression of the solid is resisted by the Pauli repulsion of all the electrons, *sp* and *d*, and the structure determined by the *sp*-electron gas, the *d-sp* bonding, and the inert-gas *d* cores. The analogy to our proposal on the center TM is apparent, the closed tightly bound *d* cores taking the place of the closed localized *d* bonds. The feature to be emphasized is that the *d* electrons are too localized to participate in the attractive phonon exchange scattering, since the *d* bands lie far below E_F on the scale of ω_D.

The essential physics of the superconductivity mechanism in these cases can be illustrated schematically in simple jellium models. For the noble metals we refer to Refs. 1 and 13. For off-center TM with broken *d* covalency we shall take two-band jellium (cf. Refs. 9 and 10). Ions with charge equal to the total *s* and *d* valency, $Z = Z_s + Z_d$, form a positive continuum in which is immersed the *sp*-electron gas and *d*-electron gas, both free-electron-like in the model. The effective electron-electron interaction is taken as $v(q)/\epsilon(q,\omega)$, where $v(q)$ is the direct Coulomb interaction and $\epsilon(q,\omega)$ the linear dielectric function of the medium,

$$\epsilon(q,\omega) = \epsilon_{\mathrm{el}}(q,\omega) - \omega_M^2/\omega^2 \,. \tag{1}$$

ϵ_{el} is here the linear electronic dielectric function, and $-\omega_M^2/\omega^2$ the bare ionic polarizability, ω_M being the ionic plasma frequency:

$$\epsilon_{\mathrm{el}} = 1 + \chi_s + \chi_{ds} + \chi_d \,, \tag{2}$$

where $\chi_{s(d)}$ is the *s*(*d*) polarizability and χ_{ds} the interband polarizability. At high *q* and relevant frequencies ω (i.e., ω not too large relative to phonon frequency ω_q), $v(q)/\epsilon(q,\omega)$ may be written

$$\frac{v(q)}{\epsilon(q,\omega)} = \frac{v(q)}{\epsilon_{\mathrm{el}}(q,0)}\left(1 - \frac{\omega_M^2}{\epsilon_{\mathrm{el}}(q,0)}\,\frac{1}{\omega_q^2 - \omega^2}\right), \tag{3}$$

where the direct screened Coulomb repulsion and the phonon-exchange term have been separated. $\epsilon_{\mathrm{el}}(q,0)$ has the form $1 + \kappa^2/q^2$. The phonon frequency ω_q is given by $\omega_q^2 = \omega_M^2/\epsilon_{\mathrm{el}}(q,0)$, with the possible addition of an inert core-core repulsion term ω_c^2[9,10] [in which case the ionic polarizability in Eq. (1) is $-\omega_M^2/(\omega^2 - \omega_c^2)$]. The model contains the essential feature that the *d* electrons are scattered by ionic displacements.

For covalent *d* bonding, however, where the *d-d* bonds resist the ionic displacements, we replace Eq. (3) by

$$\frac{v(q)}{\epsilon(q,\omega)} = \frac{v(q)}{1 + \chi_s + \chi_{ds}}\left(1 - \frac{\tilde{\omega}_M^2}{1 + \chi_s + \chi_{ds}}\,\frac{1}{\omega_q^2 - \omega^2}\right),$$

$$\omega_q^2 = \frac{\tilde{\omega}_M^2}{1 + \chi_s + \chi_{ds}} + \Omega_c^2 \,. \tag{4}$$

χ_s is again the static *sp* polarizability of the form κ_s^2/q^2 at small *q*. χ_{ds} is the *d* polarizability due to its mixing with both *sp*-band states and with higher itinerant *d*-band states. For $\omega \lesssim \omega_D \ll \Delta$, the energy gap between the localized *d* states and E_F, and q^{-1} greater than the range of *d*-bond localization, χ_{ds} is *q* independent, which reflects the inability of the localized *d* electrons to screen out charge deformations; the dependence on q^{-2} of the χ of a free-electron gas is presumably replaced by Δ^{-2} in analogy to semiconductors. At large *q*, χ_{ds} approaches the form of χ_s. $\tilde{\omega}_M$ denotes a bare ionic plus bond plasma frequency with an effective valence $\tilde{Z}$; $\tilde{Z}$ is a *q*-dependent form factor, reflecting the structure of the bond, and at zero *q* must equal Z_s for charge neutrality. The same form factor $\tilde{Z}(q)$ is seen by an *sp* electron scattering through *q*.

The most important feature of the model is the introduction of Ω_c to represent the resistance of *d-d* bonds to lattice vibrations by their Pauli repulsion. Ω_c will dominate over any ω_c due to the inner core. The usual simplifying assumptions common to jellium models have been made, to concentrate on the role of Ω_c. While the actual strength of the interaction has no bearing on reality, the aspect to be emphasized, in comparing Eqs. (3) and (4), is that the range of ω for which $v(q)/\epsilon(q,\omega)$ is attractive is reduced by the presence of Ω_c. This is reflected in the static limit (in terms of which the McMillan solution for T_c is expressed[19]), by $v(q)/\epsilon(q,0) > 0$ or $\lambda < \mu$ (μ is the average direct Coulomb repulsion[19]), in contrast to $v(q)/\epsilon(q,0)=0$ or $\lambda=\mu$. T_c is thus suppressed by a stiffening of lattice vibrations due to the inability of d electrons to scatter. We remark, however, on the one hand that the intra-sp-band electron-phonon coupling would still be enhanced by d hybridization, and on the other hand, recall[2] that T_c would not be specially sensitive directly to the loss of the d contribution to the scattering processes. Finally, the existence of tiny but observable T_c in the center TM, in contrast to the noble metals, would be related to the relative sizes of the $d \to s$ energy gaps, as reflected in the Ω_c and sp-electron–phonon coupling.

C. Engel-Brewer correlation

Our description of TM electronic structure in Sec. II A has much in common with the Engel-Brewer rules on cohesion and structure,[11] and may well provide the basis for these rules around the center TM, albeit with some differences. In Engel-Brewer theory, following Pauling, the cohesive energy is attributed to the bonds formed (whether resonating or localized) between the unpaired orbitals of the free atoms in their ground state, or if energetically advantageous, in an excited state; the assignments are made on the basis of the data on cohesive energy and atomic promotion energy. The Engel-Brewer correlation then associates the crystal structure of metals, both TM and non-TM, with the sp-electron configuration alone. We remark, however, that the association of a crystal structure with a definite electron configuration would, in general, hardly be expected to be reliable for metals, with the exception of the center of the TM series, where we have postulated a high degree of covalency. We shall first show how Brewer's calculations imply this covalency, and then refer to the crystal-structure correlation around the center TM.

Along the TM series from the left towards the center, the electron configurations $d^{Z-1}s$ and $d^{Z-2}sp$, Z being the total valency, which are most favorable for bonding, are close in free atomic energy, in the groups IIA, IIIA up to IVA. However, towards the center of the configurations most favorable for bonding, $d^{Z-1}s$ increasingly separates out as the lower-lying configuration, and we note that this is followed to some extent by d^5 in group VA. This tendency is favored by Hund's rule. On the right of the center, d-states are unpaired in favor of bonds as far as possible. Consequently, to the right of and near the center, the configuration $d^5(sp)^{Z-5}$ dominates the cohesion. However, further to the right, where it becomes increasingly difficult to "depair" the more tightly bound d electrons, a configuration making fewer bonds can give a cohesive energy relatively close to one obtained with more bonds but higher atomic promotion energy. Thus, the general tendency is towards a dominant d-configuration d^5 close to the center, while, on leaving the center on each side, there is growing configuration interaction. This is precisely what is expected if there is covalency and lattice stability at the center, and "broken covalency" (see Sec. II A) on each side. It should be emphasized that the energy intervals involved are small relative to the nontransition elements, since the effect here is more delicate. It is not surprising, therefore, that Brewer's result for the mean valency values Z, which are to correspond with the d-configuration d^5 in the series of TM and alloys, does not exactly agree with our expectation based on $g_d(E_F)$ and T_c.

The Engel-Brewer prescription for crystal structure, in which the bcc structure around the center is attributed to the requirements of the configuration $(sp)^x$, $x<1.5$, is in partial coincidence with our view; viz., we agree with the qualitative evaluation of the role of sp off the center TM, but we feel that they overlook the important concurrent role of d^5 on the center, as we have repeatedly emphasized. We believe that the true origin of the Engel-Brewer correlation around the center TM is to be found along the lines described in Sec. II A.

Previous proposals for the T_c systematics of TM and alloys based on Engel-Brewer have been put forward by Engelhardt *et al.*[12] and by Gualtieri.[20] These authors, in different ways, propose the d bonding itself as the mechanism responsible for electron-electron attraction. The advantage of our proposal is that it is based on dominance of the phonon-induced attraction, as the tunneling experiments[21] indicate.

D. Other transition-metal systems

So far we have considered the series of pure crystalline TM and their crystalline-alloy solutions. Now, we shall look at other systems.

Collver and Hammond[22] have found in amorphous TM alloy films that T_c becomes a triangular function of Z with peak near $Z\sim 7$. Whatever the origin of this behavior, and it is not explicable by mere smearing of $g(E_F)$, we may conjecture that the T_c curve has lost the anomaly in the $Z\sim 6$ region if the covalency has been broken up there.

The β-W compounds A_3B[23] (A is TM, B is TM or non-TM) exhibit the Matthias T_c plot against Z when the samples are well ordered, though they exist in a smaller range of Z about the center of the series. We propose on this basis, and the following considerations, that the ideas we have expressed encompass β-W. The drop in T_c is accompanied (but not necessarily directly caused[2]) by a drop in $g(E_F)$. In tight-binding models,[23] there are three wide d bands, strongly overlapping. Each band has high $g(E)$ at the low- and high-occupation ends, and their superposition leads to high $g(E)$ everywhere, except near $Z_d \sim 5$. It seems to us that this result could well be pointing to the situation described in Sec. II A; viz., the composition A_3B, when $Z_d = 5$, is most stable in the β-W structure which, we conjecture, is maintained by covalent d bonds and the *sp* (far from free) electron gas. Off the center of the series, while the *sp* electrons can still maintain the structure they do so only with difficulty, leading to instability while breaking the d covalency. We note that the β-W structure occurs in the $3d$ series, but rarely in the $5d$ series, where the d overlap is too strong for a sufficient degree of covalency. In Brewer's scheme, the β-W compounds aspire to the d^5 configuration just as in the pure TM and their alloys, which is consistent with our extension to β-W.

The highest T_c known are obtained in β-W structures off the center of the series; they are usually unstable, the tendency being for transitions to lower-symmetry phases with more covalency and lower T_c. We propose that the conflict between *sp* bonding leads to both the instability and the high T_c. We suggest that conceptually the high T_c can be traced to the release of d electrons from covalent bonding, see Sec. II B. The anomalous softening of a group of transverse phonons reflects the instability, but is not directly the major factor responsible for high T_c. This accords with recent work by Bergmann and Rainer and by Allen,[24] on specific phonon contributions in the Eliashberg equation. The drop in T_c on the center, we conjecture, occurs through the Brout mechanism, Sec. II B.

In the series of pure TM and alloys, T_c would presumably continue to rise about the center, if the single phase bcc structure could be maintained for a wider range of Z into a region of instability comparable to β-W; cf. Collings,[25] and see Sec. II E for a general discussion.

A simpler class than β-W of superconducting compounds is that of the so called hard metals, viz., carbides and nitrides of TM in the NaCl structure. For this class there exist phenomenological calculations of phonon spectra[26,27] based on electronic-structure calculations, which present the strongest indication of the mechanism we have proposed The model for electronic structure, initiated by Bilz,[28] postulates that the stability of the compounds is maintained by a covalent metal-nonmetal interaction formed by nonmetal p-states and metal d-states, with an electron transfer to the nonmetal. In crystals with total $Z = 8$ per unit cell, all the bonding p-d states are occupied; higher metallic d-bands begin to be occupied with higher Z. There is also an *sp* band with $Z \sim 0.1$ per unit cell in all these compounds, which is responsible for metallic conductivity. These features were incorporated phenomenologically into the calculations of phonon spectra by Weber *et al.*[26,27] using modified shell models, in which were included the long-range s- and d-electronic interactions. An anomalous softening of longitudinal phonons in a narrow range of frequency at high q, which occurs in group-VA carbides (Z per unit cell is 9), while absent in group-IVA carbides (Z per unit cell is 8), is accounted for by the long-range Coulomb repulsion of the itinerant electrons in the d band, which is partially occupied in the former and empty in the latter. In these compounds, high T_c occurs when Z per unit cell is about 9, and is rapidly suppressed when Z is about 8. We can understand the systematics just as in the previous cases. We note that the Bilz-Weber shell model was also fitted to the Nb-Mo alloy system,[27] which could well be indicating the electronic structure we have proposed for the bcc TM and alloy solutions.

E. Broken covalency and T_c

We have conjectured that the drop in $g(E_F)$ at the center of the TM series, common to pure TM, their solid solutions and TM compounds, has a common physical origin, viz., a strong tendency to covalent d bonding. In this way are related and unified the systematics of superconductivity and various other physical properties in these materials. It seems that the underlying principle governing T_c systematics is that of *broken covalency*, both in transition and nontransition metals (see further below). The conditions which favor superconductivity also favor, as an alternative choice, localized covalent bonding. The former occurs because the latter is overriden by a conflicting mechanism, which can be either inherent or imposed by external conditions, e.g., pressure, amorphous, thin film, etc. It is for this reason that high-T_c superconductors are associated with instability. Current research for higher T_c is orientated towards stabilizing inherently unstable materials.[29] It seems that basically the search is to stabilize a broken covalency. Broken covalency favors high T_c by either or both releasing the bonds which lock the lattice vibrations and enhancing the electron scattering processes. In the TM, it appears that the latter is not effective by Hopfield's argument.[2] Anomalous phonon softening at only special $\vec{q}$ and polarization (at or near Kohn anomalies) expresses the accompanying tendency towards instability, without apparently in itself being the prime factor responsible for the high values of T_c.[24]

We maintain that the link between high T_c and broken covalency is quite general, and can be seen also in the T_c systematics of nontransition elements as described in I (cf. also Cohen and Anderson[30]). Thus the general conditions stated in I to be favorable for superconductivity, in particular, small core R_c relative to mean lattice spacing R_a, are also precisely the conditions in which covalency exists, as discussed above in Sec. II A. Only, therefore, when the covalency is broken in some way does high T_c occur. We have already mentioned in this connection (in Sec. II B) the nonmetallic elements of groups IV*B*, V*B*, and VI*B*, and the effect of pressure. The high T_c in the metallic members of group IV*B*, viz., Pb and white Sn, is due to the inherent broken covalency which renders them metallic. The mechanism breaking covalency is the relativistic effect in heavy elements, which raises the atomic $s \rightarrow p$ promotion energy, and thereby prevents the formation of four equal and independent sp^3 bonds in a tetrahedral structure. At the same time, electron delocalization is facilitated by the lower atomic promotion energies to outer shells. Sn is an intermediate case, for which both covalent and metallic phases can be stabilized at normal pressure. The whole of group IV*B* is indeed intermediate between small- and large-core elements relative to mean lattice spacing.

III. FAR ENDS OF TRANSITION SERIES

A. Early and late TM

At the beginning of the transition series, the absence of superconductivity in Sc and Y is little understood.[17] An estimate of λ by Knapp and Jones[31] based on comparing the specific heat at $T > 2\Theta_D$ (Θ_D is the Debye temperature), where λ is zero, to low-T data, yields small λ values in Sc and Y. This may be indicating that these metals are of the pre-TM type like group II*A*, as discussed in I. In support of this, ω_{qL}^2/ω_M^2 (L denotes longitudinal) in Y is of the order 0.3 at high q, which is comparable to Sr and Ba, and the Kohn anomalies are very slight.[32] However, in Sc, ω_{qL}^2/ω_M^2 at high q is small, of the order 0.13.[33]

The drop in T_c below observation at the end of the TM series seems to be due to spin polarization.[17] In the magnetic materials of the first TM series and of the rare-earth series, spin polarization, by keeping electrons apart, acts counter to their attraction and suppresses superconductivity. Likewise, at the end of the second and third series, where d bands are more tightly bound, long-lived short-range spin order presumably reduces T_c.[17] Furthermore, the direct intra-atomic Coulomb repulsion between d electrons will be substantially greater than the screened Coulomb repulsion in the sp gas. These questions have been studied by Appel and Kohn.[34] At the extreme right of the TM series, in alloys beyond the Pt triad, there is an approach towards noble metals. With the increasing valency and tighter d binding, the d bands drop below E_F. The d bands are completely filled when the energy gap becomes larger than ω_D and d-electron–phonon scattering stops, then short-range spin order gives way to d-electron lattice stiffening in suppressing T_c. Thus, in going from Pd(Pt) to Ag(Au), there is a gradual change in the T_c suppression mechanism. On the other hand, hydrogenation (with H or D) fills the d band and quenches the spin fluctuations, while keeping the d cores well separated. The high T_c observed in these systems could therefore be accounted for in this way, in analogy to our proposal for noble-metal compounds and alloys in I, and might be the underlying mechanism in a recent calculation by Hertel.[35] The negative pressure coefficient dT_c/dP, observed by Buckel *et al.*,[36] would then also be consistent. An alternative proposal has been put forward, however,[36,37] that optical-phonon exchange (H or D vibrations) supplies an important contribution to high T_c. Anyway, the tendency to form covalent sp bonds, apparent in the covalent hydrides of the noble metals, is broken by the availability of d states, thereby leaving an sp-electron gas strongly interacting with ions. We should mention also that Duwez and his group[38] have studied a series of alloys of Pd and noble metals with high-valency nontransition elements, and found higher T_c than in the compounds quoted in I.

B. Rare-earth metals

The rare-earth series presents some interesting features with regard to superconductivity, which has been the subject of considerable debate, reviewed recently by Wittig.[39] Whereas in the magnetic materials with partially filled and well-localized $4f$ core (f bandwidth $\Delta E_f < \omega_D$), the spin polarization suppresses superconductivity, La has $T_c \sim 6$ K, which, under high pressure P, rises dramatically, $T_c \sim 12$ K at $P \sim 140$ kbar; Ce, in a high-pressure nonmagnetic phase, is a superconductor with $T_c \sim 1.8$ K at $P \sim 60$ kbar. In contrast, Lu and Yb with filled $4f$ core do not superconduct at normal pressure, and although at high pressure Lu has been seen to superconduct,[39] this first appears only above 100 kbar, and even at 140 kbar T_c rises to no more than about 0.5 K. Yb, at pressures up to 160 kbar, has not been found superconducting down to the lowest attainable temperature of 1.3 K. Of interest for comparison is the T_c-P behavior of other elements neighboring the rare earths in the Periodic Table. Y, which lies above La in group III*A*, becomes superconducting at $P \gtrsim 110$ kbar, with T_c rising to nearly 3 K at about 150 kbar. Ba, to the left of La and to be contrasted also with divalent Yb, is a good superconductor at high pressure, at $P \gtrsim 50$ kbar, $T_c \gtrsim 1$ K, and approaches 6 K above 150 kbar. Cs, in a high-pressure phase formed above 125 kbar, has $T_c \sim 1.6$ K. At the other end of the series, Hf and Ta, following Lu, can be noted to have somewhat depressed T_c *vis-à-vis* their 3*d* and 4*d* counterparts.

These facts have been variously interpreted.[39] With electron-tunneling data evidence,[21] the phonon-exchange mechanism has now quite definitely supplanted earlier speculations on a possible *f*-electron mechanism in La. Some now believe La to be a simple *sd* band superconductor, others give the 4*f* states an important role in electron-phonon coupling. Thus Coqblin *et al.*[40] propose that there is some occupation of a narrow 4*f* state ($\Delta E_f < \omega_D$) a few tenths of eV above E_F, which depresses T_c by spin polarization from an intrinsic high value of $\gtrsim 12$ K. This is recovered at high pressure when the *f* state is alleged to be shifted to higher energy and depopulated. The same mechanism is proposed for Ce with a lower-lying 4*f* state, and presumably for the trivalency of the lanthanide contracted elements. Wittig,[39] on the other hand, has suggested that La is a 4*f*-band metal with appreciable 4*f* occupation, which is responsible for the high T_c, and that in Ce under pressure the 4*f* level may also broaden by increased hybridization with the *sd* band, thereby losing its magnetism. This idea he has extended to the pre-rare-earths Ba and Cs, which he believes acquire *f*-band character at high pressure. In this way he differentiates between the supposedly *f*-band metals Cs, Ba, La, and Ce (at normal and or high pressure) on the one hand, and Y, Yb, and Lu on the other.

We feel however, on the contrary, that the data point to the quenching of T_c in elements with filled 4*f* shell by the Brout mechanism,[41] in analogy to the noble metals.[1,13] This explains the absence or depression of T_c at all pressures in Yb, to be contrasted with divalent Ba, and in Lu, to be contrasted with trivalent La *and* Y. *f*-band effects may then also exist in Cs, Ba, and La, enhancing these differences, and indeed Y with no *f* band is somewhat intermediate. Otherwise, however, the T_c-P behavior in the pre-TM is due to *d*-band effects.[1]

Evidence of increasing 4*f*-core-core repulsion as the 4*f* level fills and the lattice contracts with diminishing core size along the series, may be seen in the rise in the Debye frequency ω_D as obtained from specific-heat data,[42] or, where available, from neutron spectroscopy[43] or tunneling.[21] The ionic plasma frequency, on the other hand, remains relatively constant, since the lanthanide contraction counterbalances the increase in M in the trivalent metals. ω_D^2/ω_M^2, therefore, rises along the series from 0.1 in La,[21] to 0.3 in Lu,[42] which seems to suggest increasing 4*f*-core-core repulsion. The weakness of the Kohn anomaly in the heavy rare earth Ho[43] is consistent with this view.

At the low-frequency end, the bulk moduli are also seen to rise along the series.[42] However, as the conduction electrons become harder to compress due to lanthanide contraction, it is difficult to draw any conclusion. Indeed the (overly) simple free-electron compressibility, $\chi \propto r_s^5$, fits the trend; however, when corrected for pseudopotential, the high-r_s dependence is washed out, and a rising core-core repulsion does seem to suggest itself.

Apart from some metals where ω_D is difficult to estimate, there are two special cases, viz., Eu and Yb. These metals are not lanthanide contracted and therefore remain divalent, with electronic structure apparently similar to the pre-transition metals, Ba(Eu) and Sr(Yb).[42,44] It turns out that their lower-lying ω_D bear ratios to their respective ionic plasma frequencies, which place them "correctly" in the series. This does suggest 4*f*-core-core repulsion also in these metals, though the relatively high ω_D^2/ω_M^2 could be the effect of their pre-TM character.[1] Finally comparison of ω_D^2/ω_M^2 of[21] La with its neighbors[31] Y and[42] Ba, shows a sharp rise from 0.1 in La to 0.3 in both these pre-TM metals (cf. Lu above and I).

In the 5*d* transition series from Hf onwards, the filled 4*f* shell becomes more tightly bound and the ionic radius diminishes. This is reflected in a drop in ω_D^2/ω_M^2 in Hf to almost the value of La, followed by a much further drop in Ta. The drop in χ on the other hand, from Lu to Hf is due to *d* electrons, and is of the same order as in the 4*d* transition series. While therefore it seems unlikely that the depression of T_c in the early 5*d* TM relative to 3*d* and 4*d* TM can be linked to the *f* core, the *f* core may be making itself felt at high pressure. Indeed, in contrast to V and Nb where T_c rises at high pressures up to $P \sim 40$ kbar, in Ta T_c falls.[45]

The picture that emerges is that while the magnetic rare earths with $\Delta E_f < \omega_D$ suppress superconductivity mainly by spin polarization, Lu and Yb have their phonon exchange impeded by *f*-core-core repulsion, at normal and presently attainable high pressures. The absence of superconductivity in Yb at normal pressure may be due rather to its pre-TM character,[1] but, unlike pre-TM Ba, no appreciable T_c is induced under pressure, because the $4f$ core is being felt. (We should mention, however, that the possibility of "depairing" by some ions with deficient f cores[14] in Yb is perhaps not to be discounted.) Lu, on the other hand, takes its place as a group-III*A* TM with Y and La; being, moreover, precompressed by lanthanide contraction, Lu would therefore have been expected to superconduct even at normal pressure, but for f-core-core repulsion.

Corroboration for these ideas comes also from Lu compounds listed in Roberts's tables.[46] With the f cores well separated, Lu is brought into line with La and Y. Thus LuC_2 has $T_c = 3.33$ K, LaC_2 has 1.61 K, and YC_2 has 3.75 K; all bcc-tetragonal compounds. Similar results are reported for other compounds.

IV. CONCLUSION

In the spirit of our previous paper I, we have tried to achieve a conceptual understanding of the T_c systematics of transition metals. The problem is, however, inherently complex and transition metals far less well understood than simple metals. It seemed to us that the physical facts could be conceptually unified if one adopted an unconventional approach to the problem of electronic structure in transition-metal systems, an approach which the usual theories may be inadequately designed to reproduce. While our point of view has been presented schematically at this stage and is therefore somewhat exaggerated, we feel that the scheme outlined is highly persuasive. At the same time we have unified the discussion with that given for simple metals in I, by means of the concept of broken covalency. This includes the relationship between high T_c and lattice instability, as it appears in the scheme.

The discussion on rare earths and neighboring elements follows closely in parallel to that on noble metals and their neighbors, given in I. It would be interesting to see what future experiments will have to say on this suggestion.

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