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[49]After this paper had been submitted, in reading the paper by R. Colella and B. W. Batterman [Phys. Rev. B 1, 3913 (1970)] we became aware of the work of G. A. Alers [Phys. Rev. 119, 1532 (1960)] in which the discrepancy between the Debye temperatures deduced from the elastic constants and the specific heat in V, led him to suggest that "the low-temperature specific heat includes a contribution which varies as T^3 in addition to the lattice T^3 term." The work of Colella and Batterman supports Alers' s hypothesis and, hence, V also appears to be a material in which acoustic plasmons are present. From the specific-heat Debye temperature and that deduced from elastic constants we can obtain a value for $f/\theta_1^3 \sim 8.5\times10^{-9}$ (K)^3. Since there appears to be no unambiguous data from which a value of $\Delta\gamma_e$ or a "break" temperature can be obtained, we have not evaluated the parameters for V. The need for specific-heat measurements on V over an extended range of temperatures, on the same sample, is also manifest in the work of J. A. Morrison and L. S. Salter [Phys. Letters 9, 110 (1964)], in which the uncertainties in comparing various data were pointed out.

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Correlation of the Superconducting Transition Temperature with an Empirical Pseudopotential Determined from Atomic Spectra

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We have observed a correlation between the superconducting transition temperature and the energy of the first excited electronic configuration of the atom as determined from the optical spectra. This has led to the formulation of an empirical pseudopotential using atomic spectral data. Using this pseudopotential we have shown it to be the dominant factor in accounting for the cohesive energy, melting temperature, Debye temperature, thermal expansion coefficient, and superconducting transition temperature.

Two rather distinct approaches to the study of superconductivity have evolved over the years. One approach has emphasized empirical correlations between superconductivity and a variety of other properties such as melting point, hardness, and position in the Periodic Table.[1] The other approach has attempted to explain superconductivity from first principles using simplified but still mathematically increasingly complex models.[2] These two viewpoints have on occasion complemented each other. For example, the observation that the tendency toward superconductivity is inversely related to the normal state conductivity provided one of the earliest clues that superconductivity arises from an electron-phonon interaction since a strong electron-phonon interaction is generally responsible for a low normal state conductivity.

On the other hand, the two approaches diverge

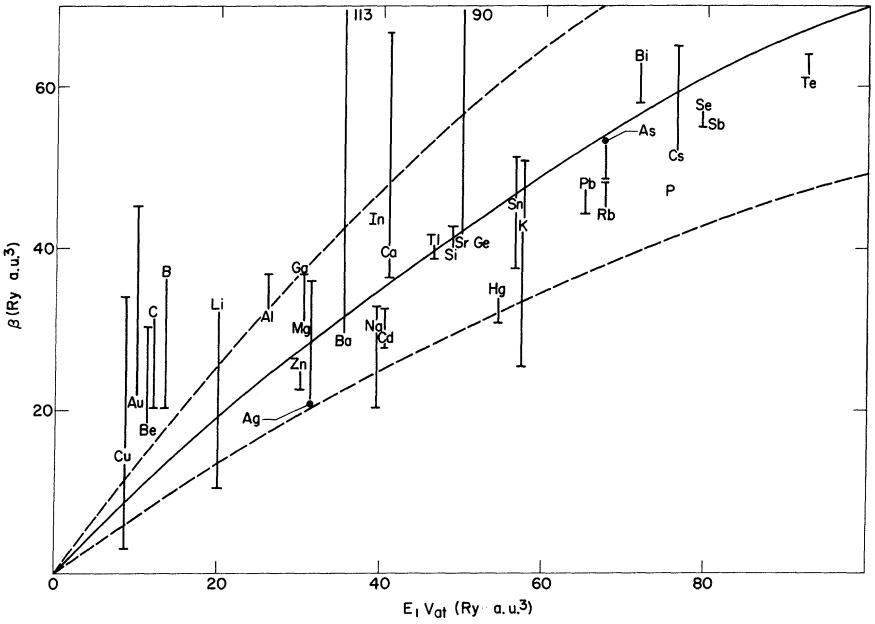

FIG. 1. Point-ion repulsion (β) versus $E_1 V_{at}$. The element symbol is plotted at the best value; the error bars represent the uncertainty of a single calculation or the range of values reported in the literature.

in at least one important respect. The first principles approach, by its very nature, dealing as it must with a highly simplified model, has not been very successful at treating the most interesting class of superconductors, namely, the transition metals. In particular, it has not very satisfactorily explained certain observed trends, e.g., the oscillatory dependence of T_c on Z across the transition series or the fact that in the group IIIb elements Sc, Y, and La, only La is a superconductor. Conversely, the empirical correlations have, for the most part, offered relationships between equally complex phenomena and, therefore, have not provided much insight into the fundamental physics of the problem.

In the final analysis, these correlations can be reduced to the statement that some elements have high superconducting transition temperatures (and low melting point, and low normal state conductivity, and low hardness) while others do not. Such a statement is an extremely useful rule of thumb, but hardly the basis for a theoretical model.

We have observed another correlation, the interpretation of which establishes the basic physical connection between the phenomena involved. We have found that the superconducting transition temperatures of the elements can be correlated with the energy of the first excited configuration of the free gaseous atom (E_1). In addition, it has been found that a correlation exists between E_1 and a number of other physical properties including melting point, cohesive energy, thermal expansion coefficient, and Debye temperature.[3] This correlation provides a better understanding of the theory of superconductivity since E_1 can be directly related to the electron-ion potential in the metal. In addition, we have been able to formulate a simple prescription for at least roughly determining this potential.

The correletion between the energy of the first excited configuration of the atom and the superconducting transition temperature is very striking. It was observed that for nontransition metals the transition temperature (T_c) is proportional to E_1; however, in the case of the transition metals, T_c

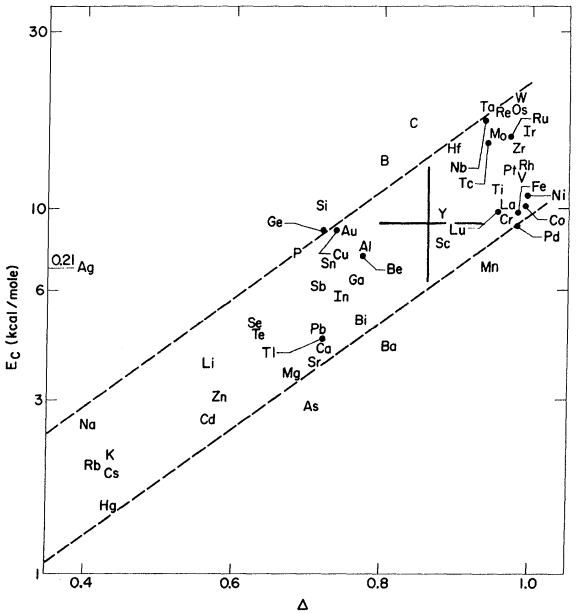

FIG. 2. Cohesive energies of the metallic elements versus Δ.

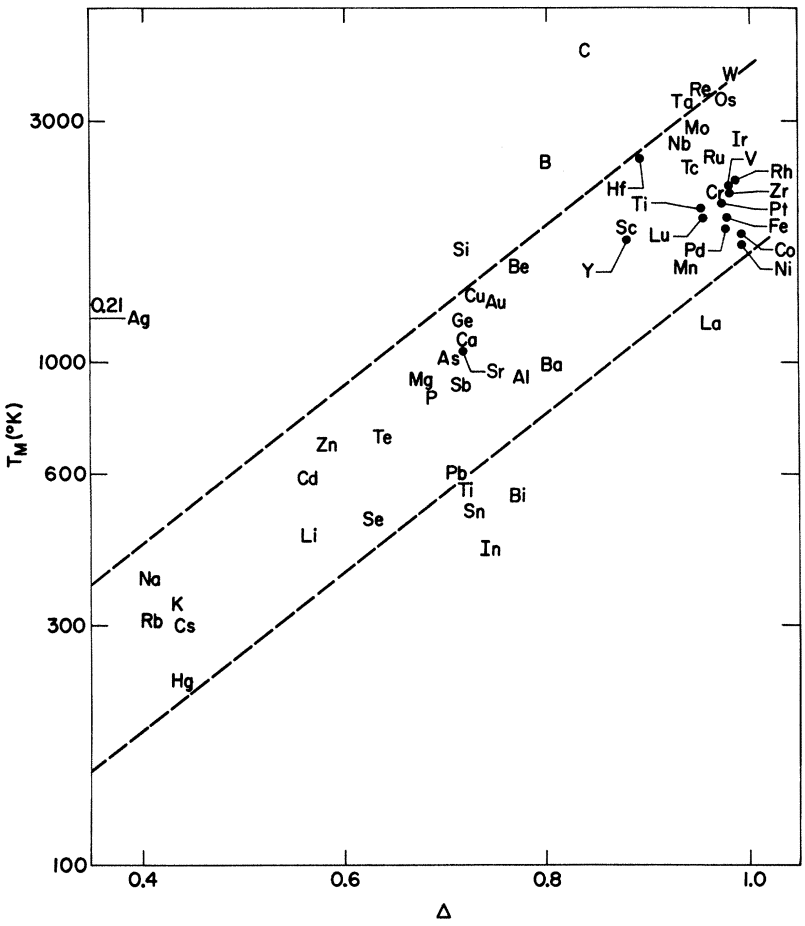

FIG. 3. Melting points of the metals versus Δ.

is inversely proportional to E_1. In general, E_1 for the transition metals is considerably less than for the nontransition metals because the d levels are only slightly lower in energy than the s and p levels in this region of the Periodic Table. As a result, T_c has a U-shaped dependence on E_1.

The physical significance of this correlation must go deeper than the free-electron properties or phonon spectrum which clearly cannot be involved in the optical-absorption spectra of free gaseous atoms. We believe the answer lies in the electron-ion potential in the metal. For nontransition elements one usually chooses a pseudopotential to represent the effective potential in the metal. If we approximate the pseudopotential by a Coulomb attraction plus a core repulsion obtained from a point-ion model we find[4]

$$V(r) = (1/\epsilon)[-Ze^2/r + \beta\delta(r)], \tag{1}$$

where ϵ is the dielectric constant (including screening) and β is the strength of the repulsion due to the ion cores at $r = 0$. The Fourier transform gives

$$V_q = \frac{1}{\epsilon(q)}\left(-\frac{4\pi Ze^2}{q^2} + \beta\right). \tag{2}$$

Since we will be interested in small momentum transfers, e.g., for superconductivity $q \leq 2k_F$, the point-ion pseudopotential is a reasonable approximation. The oscillations in the potential which occur at large q for more exact pseudopotentials are of no concern here.

The first term of this potential is just the Coulomb interaction. The second term is the repulsion felt by the electron as it tries to enter the ionic core. To see how this is related to the energy of the excited state consider the following simplified model of a metal. Ionic cores are located at the ion sites. Electrons in the intervening region between the ions are in plane-wave states while electrons in the core are in atomic states. If an electron tries to go from the intervening region into the core it must go into an atomic state in the core. The first state available is the next configuration above the ground state. The ease of entering the core is then inversely proportional to the energy separation of this state from the ground state. The strength of the repulsion is just measured by β, so that qualitatively we can see that

$$\beta = f(E_1).$$

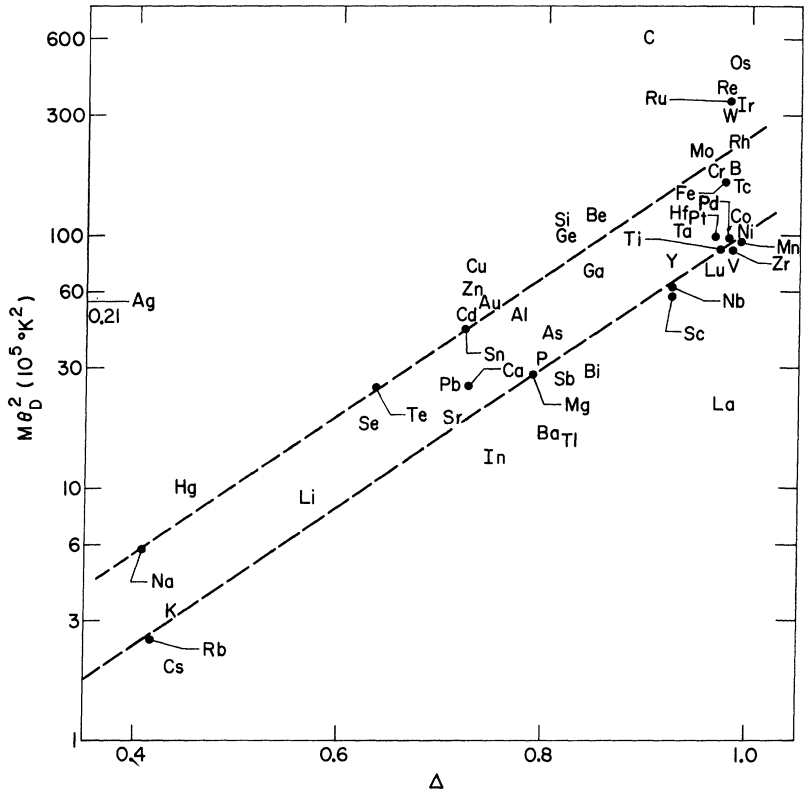

FIG. 4. Force constant for a Debye lattice of harmonic oscillators versus Δ.

Pseudopotential calculations exists for 29 nontransition metals[5] for which we can compare β and E_1 directly.[6] Fig. 1 shows a plot of β as a function of $E_1 V_{at}$ (β is in rydberg-atomic units of volume so $E_1 \times$ atomic volume gives the energy of the excited state directly comparable with β). It can be seen that there is a strong correlation between $\beta \simeq E_1 V_{at}$. In fact, crudely we find the interesting result that $\beta \simeq E_1 V_{at}$. One empirical fit to the data is[7]

$$\beta = E_1 V_{at} (1 - 0.003 E_1 V_{at}) . \tag{3}$$

The results for 24 nontransition elements give good agreement with this result to about ± 25% (the dashed lines in Fig. 1). The only strong deviations are seen for Au and the first row of the Periodic Table Li, Be, B, and C. Figure 1 contains only nontransition metals because it is only for these that pseudopotential calculations have been done. We will make the *assumption* that the prescription given in Eq. (3) is generally valid and use it to extend the discussion to transition metals.

We can now examine the correlations found between the pseudopotential and the properties mentioned earlier, T_c, the melting temperature, cohesive energy, etc. It is certainly reasonable that the potential should have an important influence on these properties since it is the quantity that determines the strength of the interaction between the electrons and ions. Let us first consider the cohesive energy. The factor which expresses the deviation of the pseudopotential from the screened Coulomb potential is just

$$1 - (\beta/4\pi Ze^2) q^2 . \tag{4}$$

To get an estimate of the relative strength of the potential let us look at the largest momentum transfer in the lattice $q_m = 2\pi / V_{at}^{1/3}$ and take as a measure of this strength the deviation from the screened Coulomb potential at this momentum transfer

$$\Delta = 1 - (\beta/4\pi Ze^2)[(2\pi^2)/V_{at}^{2/3}] , \tag{5}$$

where β is determined from Eq. (3). We might expect this to be correlated with the cohesive energy. Figure 2 shows the cohesive energy[8] (E_c) plotted as a function of Δ. The dashed lines give a range of E_c to within a factor of 1.5. Equation (5) gives the dependence of the cohesive energy on the potential to well within this factor for almost all of the 57 metals[9] plotted on Fig. 2. One would expect the melting temperature[8] (T_m) to behave in a manner similar to the cohesive energy and as can be seen from Fig. 3, it does. Note that the transition metals, which have small E_1, have large cohesive energies and high melting points while the nontransition metals have smaller cohesive energies and melting points due to their larger E_1 and thereby smaller net potentials. In fact, in Figure 2 we have placed a cross in the upper right-hand part of the

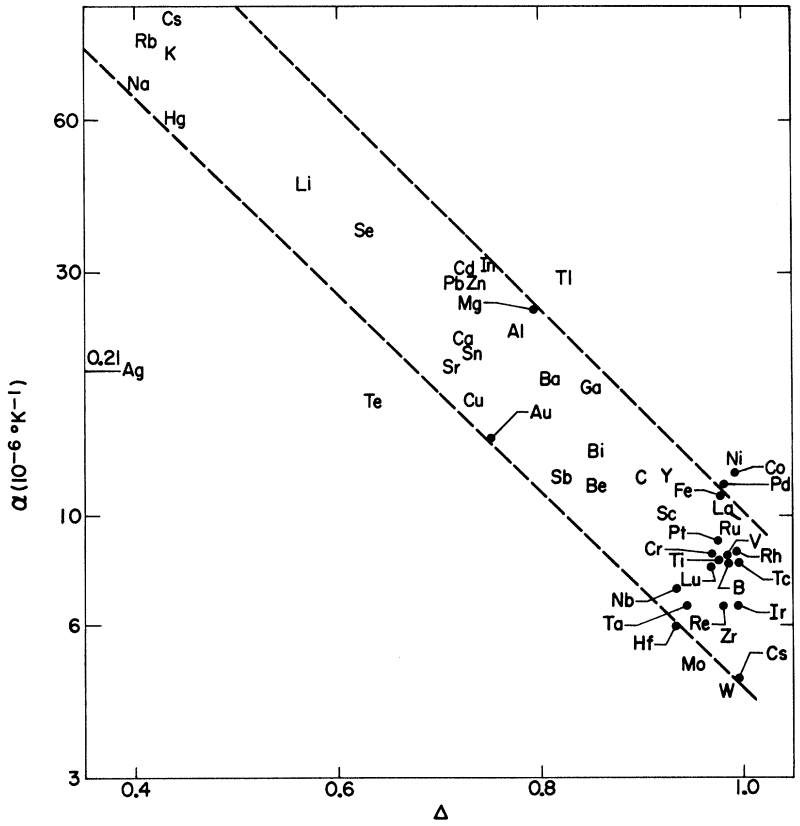

FIG. 5. Thermal expansion coefficient versus Δ.

figure which separates the elements. Almost all the transition elements are in the first quadrant while the third quadrant holds almost all the nontransition elements.

The next quantity we consider is the Debye temperature.[8] This parameter is a measure of the phonon frequencies and since we know for a harmonic oscillator $\omega = (k/M)^{1/2}$ where k is the force constant (proportional to the potential) and M is the atomic mass, we can take $M\theta_D^2$ as a measure of the potential. In this case of a well-ordered lattice the maximum q is just the Debye wave vector q_D (this is identical to $2\pi/V_{at}^{1/3}$ for a Bravais lattice). Figure 4 shows $M\theta_D^2$ plotted as a function of Δ and the correlations are again apparent.

A fourth quantity we consider is the thermal expansion coeffecient[8] since the ease of expansion against the binding potential is certainly a function of the potential. This plot is shown in Fig. 5 and exhibits a correlation similar to that seen for the other parameters.

Last, let us consider the most interesting quantity T_c. We stated before that T_c had a U-shaped behavior with respect to the potential. This is due to two factors: First, the potential enters the electron-phonon interaction quadratically (since it is really the electron-phonon-electron interaction that is of interest) and second, the larger momentum transfers possible for the electrons ($2k_f$, twice the Fermi momentum) let Δ become negative. Consider what happens when a small β is added to the screened Coulomb potential Fig. 6 (curve B). The area under the potential is reduced so that T_c decreases. As β gets larger (curve C) V crosses zero at $q/2k_F = 1$. After this point (curve D) the area in the region $q/2k_F = 1$ increases and since this region is the most significant for the electron-phonon interaction (especially for umklapp processes) T_c now begins to increase.

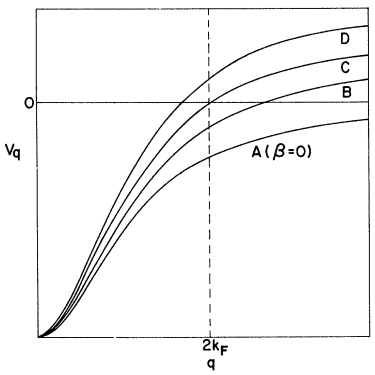

FIG. 6. Fourier transform of the screened point-ion pseudopotential. Curve A is for $\beta = 0$ and curves B, C, and D are for increasing values of β.

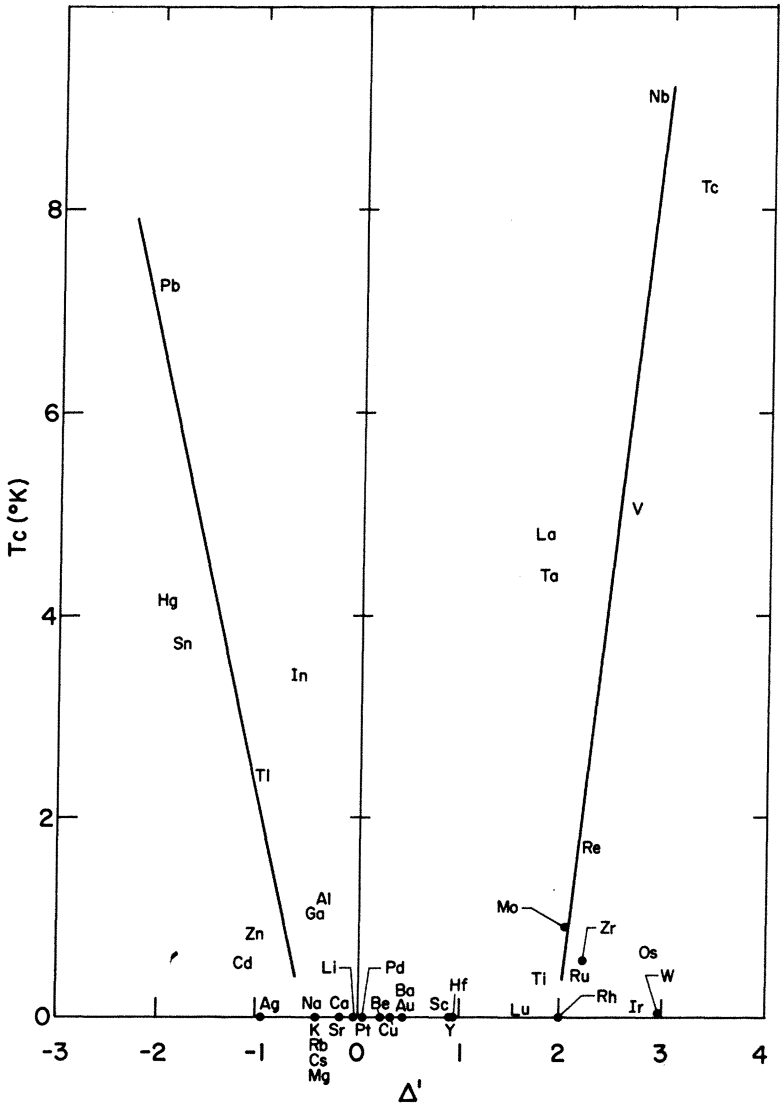

FIG. 7. The superconducting transition temperature versus Δ'.

Δ is now given by Eq. (4) with $q = 2k_F$ and gives the maximum interaction for each Brillouin zone that the Fermi surface overlaps. To get a measure of the total contribution we multiply by $Z^{2/3}$ which is proportional to the area of the Fermi surface relative to the area of a Brillouin zone and thereby a crude measure of the total number of Brillouin zones involved. Therefore, we write

$$\Delta' = Z^{2/3}[1 - (\beta/\pi Ze^2)k_F^2]. \quad (6)$$

Figure 7 shows T_c plotted as a function of Δ'. The left-hand side (negative Δ') contains the nontransition metals while the right-hand side shows the transition metals. The characteristic U-shaped dependence is clear. Note that all the nonsuperconducting elements lie in between the superconductors. Also, one can see the reason that La is a superconductor while Sc and Y are not rests in the lower energy of the first excited state of La and thereby greater Δ'.

These results seem to support the rather surprising conculsion that diverse metallic properties such as we have discussed can be regarded in a certain sense as *atomic* properties, at least insofar as they are strongly correlated to the atomic energy level structure. It should be pointed out that many effects have been neglected so the fact that a good correlation is observed indicates that for the properties considered here, the potential provides the dominant factor, the neglected effects being smaller. To the extent that the potential is dependent on the core states, these properties are indeed atomic in character. At the same time, the pseudopotential formalism provides a means for incorporating this essentially atomic contribution into the usual metallic approaches.

One virtue of these results is that they give confidence in the prescription of β from spectroscopic data as an effective pseudopotential for the transition metals. This is extremely valuable since pseudopotential calculations for these materials have not been done. The technique is, in principle, extendable to compounds and perhaps even alloys. The simplest approximation would be to take as a pseudopotential the sum of the "atomic" potentials of every atom in the unit cell along with the appropriate structure factors. An extension of this type would allow a great simplification in the calculation of many properties for these materials.

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[5]The "best" values of Fig. 1 are taken from A. O. E. Animalu and V. Heine, Phil. Mag. 12, 1249 (1965) (tabulated values given in Ref. 4); A. O. E. Animalu, Proc. Roy. Soc. (London) 294, 376 (1966); J. A. Moriarty, Phys. Rev. B 1, 1363 (1970), where β is evaluated at $q = 2k_F$. The range of values given come both from other sources (see Ref. 4 and Allen and Cohen, Ref. 2) and the evaluation of β at the point where the pseudopotential equals zero. The ranges given then denote a range of "reliability" for the point-ion pseudopotential approximation for the metal.

[6]C. E. Moore, *Atomic Energy Levels*, NBS circular No. 467 (U. S. GPO, Washington, D. C., 1949, 1952, 1958), Vols. I–III.

[7]One could, of course, fit the data of Fig. 1 in a number of ways (e. g., a straight line with a positive intercept at $E_1 V_{at} = 0$). Alternative choices cause no qualitative changes in the results presented here, the only effect being a shift in the values of Δ [Eqs. (5) and (6)]. Lacking a real theoretical model for Eq. (3) or its equivalent, it does not pay to get any fancier. Equation (3) has the simple result that for the transition metals $\beta \simeq E_1 V_{at}$.

[8]K. A. Gschneidner, Jr., in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16.

[9]The one great deviation is for Ag, and results from the fact that E_1 in this case is quite large, of the order found for typical nontransition metals. The values of E_1 found for the related elements Cu and Au are much smaller. Why this difference occurs is not understood.

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Healing Length of the Superconducting Order Parameter*

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Using the Bardeen-Kümmel-Jacobs-Tewordt approach to the BCS theory of a nonuniform superconductor, we study the problem of a semi-infinite superconductor with a rigid potential barrier at the interface. Very close to T_c, the spatial variation of the order parameter is given by the Ginzburg-Landau formula $\Delta(z, T)/\Delta_\infty(T) = \tanh[z/\sqrt{2}\,\xi_{GL}(T)]$. At decreasing temperatures, however, the order parameter heals much more rapidly than $\xi(T) = v_F/\pi\Delta_\infty(T)$, where $\xi_{GL}(T) = \lim 0.74\,\xi(T)$ as $T \to T_c$; and, at low and intermediate temperatures, does so over atomic distances.

I. INTRODUCTION

Very close to T_c, if the superconducting order parameter is required to vanish on a plane, it heals as the hyperbolic tangent, $\Delta(z, T) = \Delta_\infty(T) \times \tanh[z/\sqrt{2}\xi_{GL}(T)]$, in an approximate length $\sqrt{2}\xi_{GL}(T)$.[1] Here $\xi_{GL}(T)$ is the coherence length of Ginzburg-Landau.[2] The technique of Bardeen, Kümmel, Jacobs, and Tewordt (BKJT) for calculating vortex structure lends itself well to a variational calculation of the healing length below the immediate vicinity of T_c.[3] Only modification of the