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SUPERCONDUCTIVITY IN TIGHT-BINDING APPROXIMATION

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ABSTRACT

An interpretation of Barisic's relation for transition elements between the d-electron contribution to the cohesive energy and the local atomic parameter η is presented. We extend this relation to a lattice with more than one atom per unit cell in the tight-binding approximation of rigid ions. It is conjectured that Barisic's relation is correct to first order approximation for transition metal alloys, provided the phonon induced d-d coupling is the dominant mechanism for superconductivity.

In a recent paper, Poon and Johnson¹ pointed out correlations between superconducting transition temperature T_c and melting temperature T_m for transition metal (TM) alloys. Based on the relation $N\langle I^2 \rangle \cong q_o^2 E_d$ derived for transition elements by Barišić et al² between the coupling term $N\langle I^2 \rangle$ (or η as used by other authors) in McMillan's theory³ and the d-electron contribution to the cohesive energy E_d , they interpreted the correlations in terms of E_d of TM alloys. It was then suggested that the maximum obtainable T_c of a TM alloy is bounded by its available E_d . However, from a theoretical point of view, the previous conclusion posed two questions. First, one has to be sure that the d band dominates in the electron-phonon coupling.⁴ Second, one has to question the validity of Barišić's relation in the case of TM alloys. It is the purpose of this paper to provide an interpretation of Barišić's relation and to outline possible solutions to the above questions.

Concerning the first question, it has been well accepted that the d band dominates in the electron-phonon interaction for most TM alloys discussed in reference 1. These alloys include the A15 compounds^{5,6} and the TM solid solutions.⁷ For the least understood refractory metals (i.e. carbides and nitrides), we recently⁸ found that E_d only contributes partly to η in agreement with the theory of Gomersall and Gyorffy.⁹

Before we investigate the second question, it is necessary to make a remark concerning the interpretation of Barišić's relation. The calculations in reference 2 were based on the tight-binding approximation in an orthorhombic lattice with one atom per unit cell. However, a numerical comparison was made between the empirical values of η and the total cohesive energy E_c ($E_c > E_d$) instead of E_d which appeared in the theory. This point seems to have been overlooked by later authors.

Anderson¹⁰, Evans¹¹, and Allen¹² et al obtained by different means values of η which were far smaller than those given in reference 3. In particular, the values quoted by Allen are considered to be more accurate since they were obtained from self-consistent numerical solutions of the Eliashberg theory, and tunneling data. Thus, the apparently good agreement obtained in reference 2 is due to the fact that higher values of both parameters were taken. In order to establish the formulation in reference 2, one has to use proper values of E_d instead of E_c , and accurate η . Using Brewer's¹³ technique of decomposing E_c into E_d and the sp-electron contribution to E_c , one can roughly estimate E_d of the electronic valence state in a transition metal of given lattice structure. The values of the pairs $(q_0^2 E_d, \eta)$ and $(q_0^2 E_c, \eta^M)$ are given in Table I for comparison. The results of the first pair are in good agreement and thus the relation $N\langle I^2 \rangle \cong q_0^2 E_d$ is correct despite the simplified nature of the model. It is interesting to note that the values of E_d (or η) fluctuate rather than peak towards the mid series. The conventional interpretation for the trend of T_c in amorphous superconductors was based on the existence of a triangular peak in η at the mid series.^{14, 15} Thus, the result of the present study urges a new explanation which might shed new light on the theory of superconductivity in amorphous solids.

The second question is too complicated to treat in general. However, it can be made more intuitive by first returning to the elemental case without restricting to the simple cubic lattice. If the phonon-induced d-d coupling is assumed to be the main cause for T_c in the TM series, it can be shown⁸ within the tight-binding approximation by retaining only the nearest neighbor interaction between rigid ions that, $\eta \cong q_0^2 E_d + \sum_l$

other terms, where l denotes subband l . By excluding interband transitions, the 'other terms' consist of (i) terms with $\vec{\nabla}_k^2 \alpha^{l*} \alpha^l$ and $|\vec{\nabla}_k \alpha^{l*} \alpha^l|$ averaged over the Fermi surface, where $|\alpha^l|^2$ measures the coupling of orbitals of different symmetry within a subband l (e.g. the e_g and t_{2g} orbitals in b.c.c. metals); and (ii) terms with $(J_{AB} \vec{\nabla}_k^2 \alpha_A^{l*} \alpha_B^l) \cos \vec{k} \cdot \vec{R}_{AB}$ averaged over the Fermi surface measuring the second derivatives of the product coupling coefficients $\alpha_A^{l*} \alpha_B^l$ on different atomic sites A and B in a unit cell, where J_{AB} is the usual two-center integral. The above terms drop out in the nondegenerate band model. In fact, they are unimportant compared with the first term as can be seen in Table I containing the b.c.c., h.c.p., and f.c.c. structures. It is possible that either the second derivative terms $\vec{\nabla}_k^2$ are small when averaged over the Fermi surface, or they almost cancel with the interband transitions. Such possibilities are under investigation.

To supplement the above argument, it is perhaps useful to compare our calculations to those of reference 11. We made use of the Bloch formulation of electron-phonon interaction. Different Bloch sums were set up for orbitals of different symmetry and for each atomic site in a unit cell. Orbitals of different symmetry were mixed in the process of diagonalizing the Hubbard Hamiltonian. When we computed the electron-phonon interaction, adiabatic electron orbitals which follow the ion motion were assumed, and each subband was treated independently. Evans¹¹ et al also used the Bloch formulation but they treated the d electrons as conduction electrons in the muffin tin potential prescription. The five fold degeneracy of the d band was totally ignored and thus little knowledge concerning the band structure was known. However, they already obtained reasonable values of η compared to the more accurate results given in reference 12. This demonstrates the relative

TABLE I. Numerical results. q_o is the Slater coefficient of the d wave function as given in reference 2. E_d is obtained from the Engel-Brewer theory and spectroscopic data. Values of η are obtained by Anderson^(AN), Allen^(AL), Evans^(E) et al, and McMillan^(M).

	V	Zr	Nb	Mo	Ta	W	Re	Ir
$(q_o^2 E_d, \eta)$ eV/Å ² at	(2.7, 3.1 ^{AL})	(3.0, 2.2 ^E)	(4.3, 4.7 ^{AL})	(3.8, 4.2 ^{AL})	(4.9, 5.0 ^{AL})	(5.0, 4.5 ^{AL})	(4.9, 5.2 ^E)	(3.7, 4.5 ^{AN})
$(q_o^2 E_c, \eta^M)$ eV/Å ² at	(4.6, 4.6)	(5.2, /)	(6.3, 7.2)	(5.7, 6.8)	(6.1, 6.1)	(6.5, 6.3)	(6.1, /)	(5.2, /)

unimportance of the detail band structure in determining η .

We expect the relation $\eta \cong q_0^2 E_d$ to be correct to first order even for TM solid solutions in which the d band can be analyzed in the coherent potential approximations. In the highly anisotropic Al5 compounds, the intrachain coupling prevails over the interchain coupling in determining their electronic properties and the validity of the relation is obvious. For the refractory metals, one can decompose the electron-phonon coupling constant λ into λ_{TM} and λ_X where $X = C, N$. It is clear that the value of η_{TM} from λ_{TM} is given by the E_d of the metal component. However, it is not certain how E_d limits T_c in the refractory metals which are now believed to have a more complex origin⁸ than just the simple phase transformation from b.c.c. to f.c.c. structures of the metal component as conjectured by Haufe et al.¹⁶

The values of η for TM alloys considered in reference 1 with the exception of the refractory metals can in general be accounted for by the E_d of these alloys. Here, we again stress the importance of η (or equivalently E_d) in determining the maximum T_c in TM alloys. But a large η only characterizes strong bonding states, it does not guarantee a large λ . To obtain high T_c , one needs to stabilize a structure (i.e., with given η) with reasonably low mean phonon frequency $\langle \omega^2 \rangle$. The latter is governed by $N(E_F)$ (density of states at the Fermi surface) which is in turn determined by the number of valence electrons per atom. A theory for superconductivity in amorphous TM alloys based on the last fact will be presented.⁸

In summary, numerical results for Barišić's relation are given. We have extended the simple, one band, six-neighbors model formulation to the case of TM lattice. An expression of the form $\eta = q_0^2 E_d + \sum_{\ell} \text{other}$

terms is obtained, where ℓ denotes various subbands. We conjecture that the expression is valid to first order approximation for transition metal alloys.

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