Superconducting transition temperatures in pseudobinary $A15$ compounds

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(Received 25 June 1979)

Results of previous experimental studies on superconducting transition temperatures in $A15$ pseudobinary compounds are compared with rigid-band extensions of recent band-structure calculations. The comparisons indicate that the electron-phonon interaction parameter η is reasonably well approximated by the rigid-band model if the third constituent is a $3d$ ($4d$) transition metal substitution for vanadium (niobium). On the basis of this model we predict that $(V_{1-x}Ti_x)_3Ge$ compounds should have superconducting temperatures exceeding 15 K.

Recently Gubser et al.[1] have shown that superconducting transition temperatures T_c in the pseudobinary $A15$ compounds $(V_{1-x}M_x)_3Ga$, where $M = Ti$, Cr, Mn, Fe, Co, and Ni, are in qualitative agreement with expectations based on a rigid-band extension of the V_3Ga electronic density-of-states calculation of Klein et al.[2] We have now used the same rigid-band approximation to calculate the electron-phonon interaction parameter $\eta \equiv N(E_F) \langle I^2 \rangle$, as a function of the average number of valence electrons per atom z for $(V_{1-x}M_x)_3Ga$, $(V_{1-x}M_x)_3Si$, $(V_{1-x}M_x)_3Ge$, and $(Cr_{1-x}M_x)_3Si$ pseudobinary systems. Here $N(E_F)$ is the electronic density of states at the Fermi energy E_F, and $\langle I^2 \rangle$ is an average electron-phonon matrix element which is calculated by the theory of Gaspari and Gyorffy.[3] Only the transition-metal contribution to $\langle I^2 \rangle$ is used in these calculations since the contribution of the nontransition metal has been shown to be negligible.[4] Our results indicate that $\langle I^2 \rangle$ is a relatively slowly varying function of z; hence, the variation of η is mainly due to the change of $N(E_F)$. This result explains the earlier[1] noted qualitative agreement between $N(E_F)$ and T_c.

In Fig. 1 we compare our calculated $\eta_{cal}(z)$ with experimental $\eta_{exp}(z)$ values for vanadium-based $A15$ compounds. The latter are found by inverting the experimental T_c results using the following equation due to Allen and Dynes[5] to obtain λ, the electron-phonon coupling parameter

$$T_c = \frac{\omega_{\log}}{1.2} \exp \left[\frac{-1.04(1+\lambda)}{\lambda - \mu^*(1+0.62\lambda)} \right], \qquad (1)$$

where $\omega_{\log}$ is a phonon frequency moment obtained from the measured phonon density of states given by Schweiss et al.[6] for stoichiometric compounds, and μ^* is the Coulomb pseudopotential taken to be 0.13 throughout. $\eta_{exp}(z)$ was then obtained from the expression

$$\lambda = \frac{\eta_{exp}}{M \langle \omega^2 \rangle}, \qquad (2)$$

where M is the atomic mass of vanadium and $\langle \omega^2 \rangle$ is

another phonon moment. Due to the uncertainties in estimating μ^*, the various phonon moments, and even the exact form of the T_c equation itself for $A15$ compounds, it is difficult to establish the absolute value of η_{exp} to an accuracy greater than 20%; hence, only the z variation of η_{exp} is considered significant—not its absolute magnitude. The product $M \langle \omega^2 \rangle$ was treated as a constant for a particular pseudobinary system equal to that of the stoichiometric compound.

In Fig. 1(a) we show the comparison of $\eta_{exp}(z)$ (dashed line), obtained from the data of Ref. 1, with $\eta_{cal}(z)$ for V_3Ga-based pseudobinaries in which the V sites are alloyed with other $3d$ transition metals. The
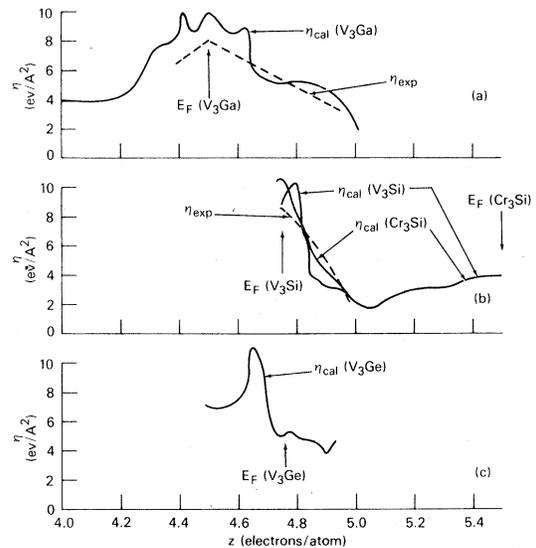

FIG. 1. Rigid-band comparison for V-based $A15$ systems. Solid lines are calculations for the electron-phonon interaction η based on rigid-band extensions of band-structure results for the indicated stoichiometric compounds. Dashed lines are a fit to the experimental data obtained for the $(V_{1-x}M_x)_3Ga$ systems (Ref. 1) in (a) and for the $(V_{1-x}Cr_x)_3Si$ system (Ref. 7) in (b).

trend of $\eta_{exp}(z)$ is in accord with $\eta_{cal}(z)$ although the detailed structure is not reproduced. Figure 1(b) shows a comparison of $\eta_{exp}(z)$ (dashed line), obtained from the pseudobinary $(V_{1-x}Cr_x)_3Si$ system reported by Junod,[7] with $\eta_{cal}(z)$ for both V_3Si and Cr_3Si. Again the overall trend is similar. The more rapid fall of T_c with z in $(V_{1-x}Cr_x)_3Si$ alloys as compared to $(V_{1-x}Cr_x)_3Ga$ alloys is compatible with the present calculations.

A theoretical basis for the validity of rigid-band extensions of binary-band-structure results is provided by comparison of the V_3Si and Cr_3Si calculations shown in Fig. 1(b). η_{cal} is essentially identical for V_3Si and Cr_3Si over the z range shown except for the detailed structure between $4.75 < z < 5.0$. To emphasize further the similarity between V_3Si and Cr_3Si, we show in Fig. 2 the densities of states of V_3Si and Cr_3Si over a much wider energy range. The reader should note the striking resemblence of these figures. The only real difference is the positions of the respective Fermi energies. Additional support for the rigid-band picture comes from band-structure calculations of pure vanadium[8] which indicate an increase in $N(E_F)$ for V-Ti alloys that is in qualitative agreement with the experimentally observed enhancement of T_c.[9] However, we emphasize that the rigid-band assumption is not valid for estimating $\eta(z)$ variations due to substitutions on the non-transition-metal site. This can be seen in Fig. 1 by comparing the results for V_3Ga, V_3Si, and V_3Ge.

Data for Nb-based transition-metal pseudobinary systems are not as readily available to test the rigid-band hypothesis; however, Fig. 3 gives the comparison for one such system, the Nb_3Al-Mo_3Al system. The figure shows the density-of-states calculation[2] $N(z)$ (solid line) and the experimental $\lambda(z)$ values (dashed line) deduced from the data of Alekreevskii et al.[10] using Eq. (1). As noted in the V-based $A15$ systems, the trend of $\lambda(z)$ is in accord with $N(z)$ as expected from Eq. (2), provided the
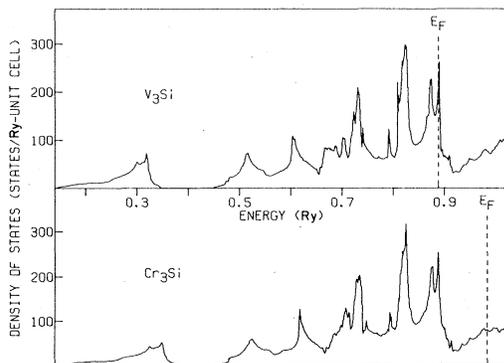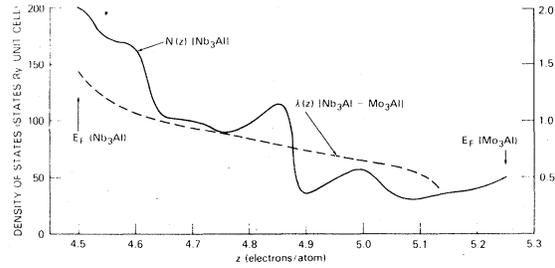

FIG. 3. Rigid-band comparison for a Nb-based $A15$ system. The solid line is the result of band-structure calculations of the electronic density of states for Nb_3Al while the dashed line represents a fit to the experimentally deduced λ values obtained from the $Nb_3Al - Mo_3Al$ pseudobinary system (Ref. 10).

variation of $\langle I^2 \rangle / M \langle \omega^2 \rangle$ is small and the rigid-band picture is valid. As with the vanadium-based pseudobinary systems, the detailed structure in $N(z)$ is not reproduced.

From the above results, namely, (i) the similarity in $\eta_{cal}(z)$ for V_3Si and Cr_3Si, (ii) the similarity between $\eta_{exp}(z)$ and $\eta_{cal}(z)$ for V_3Ga-and V_3Si-based pseudobinary systems, and (iii) the similarity between $N(z)$ and $\lambda(z)$ for the Nb_3Al-Mo_3Al pseudobinary system, it appears that a rigid-band extension of stoichiometric band-structure calculations can be used to predict the T_c dependence of pseudobinary $A15$ compounds when the transition-metal sites are alloyed with other $3d$ (V-based) or $4d$ (Nb-based) transition metals. On the other hand, our calculations show that the rigid-band approximation is not valid for pseudobinary compounds when the non-transition-metal sites are alloyed with other elements. Since phonon-frequency changes due to third-element additions are ignored in the present approach, it is anticipated that the rigid-band picture for predicting T_c will be limited to pseudobinary compounds where the mass differences of the transition metals are not greatly different, i.e., $3d$ substitutions for V and $4d$ substitutions for Nb. Likewise the effects of atomic order on T_c are not included in the rigid-band model. Chemical disorder accompanying the third-element addition will shorten the electron-scattering time and average the fine structure apparent in the calculations. This averaging effect probably accounts for the relatively smooth experimental $\eta(z)$ and $\lambda(z)$ curves noted in Figs. 1 and 3.

We wish to conclude this comment by offering a prediction for superconducting temperatures in V_3Ge-based pseudobinary compounds. We note from Fig. 1(c) that in V_3Ge E_F falls at $z = 4.75$ for which η_{cal} is small (~ 5 eV/$Å^2$) and T_c is correspondingly low (~ 6.1 K). By shifting the z value down to

FIG. 2. Comparison of the densities of states for V_3Si and Cr_3Si.

$z = 4.65$ [where there is a peak in $N(E)$ and η], η_{cal} is more than doubled, and T_c of this compound should increase to a value near that of V_3Ga or V_3Si (15 and 17 K, respectively). The shift of z could be accomplished in the pseudobinary compound system $(V_{1-x}Ti_x)_3Ge$. Since Ti is a $3d$ transition-metal sub-stitution for V, predictions based on rigid-band approximations would be valid. To reach the peak in η_{cal}, x should be approximately 0.13, i.e., we predict that $(V_{0.87}Ti_{0.13})_3Ge$ will have a T_c in excess of 15 K.

We thank L. S. Birks for a critical reading of the manuscript.

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