

ON THE SUPERCONDUCTIVITY OF VANADIUM BASED ALLOYS

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Abstract

We have computed the electron density of states of solid solutions of vanadium based transition metal alloys $V_{90}X_{10}$ by using the tight-binding recursion method for degenerate d-bands in order to calculate the alloy superconducting transition temperature with the McMillan formula. As observed experimentally for X on the left hand side of V in the periodic table one obtains an increase of T_c while for X on the right hand side of V the critical temperature decreases.

The detailed comparison with experiments indicate that when the bandwidths of the two constituents are different, one cannot neglect the variation of the electron-phonon interactions.

Another important conclusion is that for alloys which are in the split-band limit like VAu, VPd and VPt, the agreement with

experimental data can be obtained only by assuming that these alloys have a short-range order favoring clusters of pure vanadium.

1. Introduction

There is currently an active interest in the effect of disorder on the superconducting properties of materials. Superconductivity in alloys and amorphous metals and alloys has been the subject of a great number of experimental and theoretical studies.

From these efforts, one expects to obtain not only a better understanding of the basic nature of superconductivity in highly disordered metallic systems but also some important technological applications of new class of materials. This interest is related among others to the search for superconductors which show minimum degradation of superconducting properties by neutron irradiation.

To analyze the variation of the critical superconducting temperature with disorder, experimentalists use the McMillan formula (McMillan 1968)

$$T_c \approx \frac{\theta_D}{1.45} \exp \left[- \frac{1.04(1 + \lambda)}{\lambda - \mu^* - 0.62\lambda\mu^*} \right] \quad (1)$$

θ_D is the Debye temperature and λ is the Fermi surface averaged enhancement of the electron mass which corresponds to a reduction of the electron velocity due to electron-phonon scattering by a factor $(1 + \lambda)$ McMillan formula (1) is an extension of the BCS formula

$$T_c = 1.13 \theta_D \exp \left[\frac{1}{\lambda} \right] \quad (2)$$

obtained by introducing an electron mass enhancement in the two-particle propagator of the "vertex function", which has the effect of replacing the exponent λ^{-1} by $(1 + \lambda)/\lambda$, by taking account of the effective Coulomb repulsion μ^* between the electrons and by considering the T-dependence of λ .

Moreover, McMillan (1968) showed that λ can be factorized into electronic and primarily phonon dependent factors by writing

$$\lambda = \frac{N(E_F) \langle I^2 \rangle}{M \langle \omega^2 \rangle} \quad (3)$$

where $N(E_F)$ is the bare density of states at Fermi level, $\langle I^2 \rangle$ the Fermi surface average of the square of the electron-phonon matrix elements and

$$\langle \omega^2 \rangle = \frac{\int d\omega \alpha^2(\omega) F(\omega)}{\int d\omega \alpha^2(\omega) F(\omega) \omega^{-1}} \quad (4)$$

and average over the frequency distribution function multiplied by a factor $\alpha(\omega)$ depending on the phonon induced electron-electron scattering.

For transition metals, the calculated values of $\langle I^2 \rangle$ and $M \langle \omega^2 \rangle$ show a maximum near the middle of the series.

It is not surprising that the electron-phonon interaction should be strong near the center of the transition metal series. Assuming the atomic orbitals to decay exponentially as $\phi(r) \exp(-q_0 r)$, one has

$$\langle I^2 \rangle \sim q_0^2 W_d^2 \quad (5)$$

where W_d is the d-bandwidth which peaks near the middle of the transition series.

Although the variation in $\langle I^2 \rangle$ overcomes the variation of $M \langle \omega^2 \rangle$, the parallel variation of $\langle I^2 \rangle$ and $M \langle \omega^2 \rangle$ with atomic number has led to the conclusion that one can consider the ratio constant and the effect of disorder on T_c has been mostly discussed by considering only the variation of $N(E_F)$ /Dynes and Varma 1976/. However, the comparison of the superconductivity of crystalline and amorphous phases of transition metals has shown deviations with respect to this simple rule.

Recent comparative studies of crystalline and amorphous phase of Nb_3Ge suggest that there is no strong correlation between $N(E_F)$ and T_c in strong coupled A15-superconductors /Tsui 1980/. In particular, the high T_c superconductivity of Nb_3Ge does not appear to stem from an unusually high $N(E_F)$, but rather from a relatively strong electron-phonon coupling enhanced by some localized electron states. Hanke et al. (1986), Cowan and Carbotte (1978).

These recent works show the interest of a systematic study of the variation of T_c with $N(E_F)$ and electron-phonon interaction in disordered systems.

In the present paper we want to analyze the experimental data of Däumler et al (1982) who have studied the superconductivity of vanadium solid solution $V_{90}X_{10}$ where X is a transition metal. These authors have applied the McMillan formula assuming that λ varies only with $N(E_F)$. The agreement is good for the alloys where specific heat measurements are available. For the others these authors have estimated $N(E_F)$ from the measured values of T_c .

We have made a systematic calculation of the density of states at Fermi-level of these solid solutions as well as other for which data are not yet available. We have used the technique of calculating the 5-fold degenerate d-band density of states from a continuous fraction expansion of the tight binding Green's function with the help of the recursion method of Haydock, Heine and Kelly (1980). We did not try to fit the experimental data. We have chosen the alloy and disorder parameters used by Van der Rest et al. (1975) to calculate alloy energies of formation.

From these results, we can conclude that, when the bandwidths of the two constituents are different, one cannot neglect the variation of the electron-phonon interaction as it was assumed by Daumer (1982).

2. Method of Calculation

We have calculated the density of states using the recursion method of Haydock, Heine and Kelly (1980).

For each alloy, we have calculated the local densities of states on a V and on a X atom for the seven most probable configurations of the first neighbors. The occupation of more distant atoms is chosen randomly. For a concentration of 90% of V, we have treated exactly 96% of the first neighbors possible configurations. The average density of states is obtained by averaging over these partial densities of states.

We have used the BCC structure and we have considered the first and second neighbors hopping integrals and calculated the first

seven steps of the continuous fraction. This corresponds to clusters of 1695 atoms. We have only considered the d-density of states. The s-density of states is supposed constant and equal to the inverse of the s-bandwidth.

The energy levels E_d , the electron numbers N_d as well as the d-bandwidths of the pure metals (W_d) are given in Table 1.

The hopping integrals between two V neighboring atoms are taken to be (in eV)

$$dd \sigma_1 = -1.05, \quad dd \pi_1 = 0.5, \quad dd \delta_1 = -0.065$$

The hopping integrals between second neighbors are taken to be (for a discussion of these values see Derenzo et al (1982))

$$dd \sigma_2 = -0.43, \quad dd \pi_2 = 0.16, \quad dd \delta_2 = -0.015.$$

The hopping integrals between the X atoms are obtained by multiplying the V-hopping integrals by the ratio W_d^X/W_d^V . The hopping integrals between a V-atom and a X-atom are obtained by taking the geometric average of V- and X- hopping integrals. When the s-density of states is added to the d-density of states, the filling of the d-band is fitted in order to obtain the pure vanadium $N(E_F)$ calculated by Glötzel et al. (1979).

The energy levels and charge transfers have been calculated self-consistently.

3. Numerical Results

The results of our calculations are summarized in Table 1.

The ϵ and W parameters are the ones used by Van der Rest et al. (1975). To calculate T_c we have used McMillan formula (1). The Debye temperature is the average of the pure θ_D . $T_c^{(1)}$ is the critical temperature assuming that λ depends only on $N(E_F)$. The proportionality constant is chosen to fit the experimental T_c of pure vanadium. $T_c^{(2)}$ is the calculated critical temperature assuming that the electron-phonon interaction varies as the averaged bandwidth following Eq. (5).

4. Conclusions

From the observation of Table 1, one can conclude that

- 1) when X is on the left hand side of the periodic table with respect to V , T_c is enhanced, when X is on the right hand side it decreases (Zr and Hf are between brackets because they do not form 10at% solid solutions);
- 2) when the d-bandwidths are different, one cannot neglect the variation of the electron-phonon interactions. It is interesting to note that such an effect appears already for alloys of relatively small (10at%) X -concentration.
- 3) The calculations (Broders and Van der Rest 1984) reveal that the three alloys which exhibit a large discrepancy with experimental data (AuV, PdV, PtV) are in the split d-band limit and have partial densities of states the shape of which varies strongly with local environment. Cohesive energy calculations indicate that the short-range order favours the formation of pure V -clusters in the alloy.

In that case, the density of states $N(E_F)$ of Pt and Au are reduced respectively to 1.1 and 1.7 and the respective T_c to 0.4 and 0.3 °K which is in agreement with experimental data.

Our calculation show that more correlated experimental data (specific heat and critical temperature measurements) are needed for more alloys and for different concentrations if one wants to have a better understanding of the effect of disorder on superconductivity of alloys.

TABLE 1

	E_d (eV)	W_d (eV)	$N(E_F)$ (States eV/at)	T_c (1)	T_c (2)	T_c^{obs} (°K)
V	0	7	1.80	5.3	5.3	5.3 ^{a)b)}
Cr	-0.5	6.5	1.51	2.6	2.5	2.81 ^{a)} - 2.16 ^{e)}
Mn	-1	6	1.45	2.1	1.9	2.11 ^{a)}
(Zr)	0.6	7	2.04	7.6	7.6	-
Nb	-0.1	9	1.75	4.2	5.9	4.08 ^{a)} - 5.6 ^{c)}
Mo	-0.8	9	1.45	2.3	3.1	2.85 ^{a)} - 3.1 ^{b)}
Pd	-3.6	6	1.25	0.8	0.7	0.37 ^{a)}
(HF)	0.6	8	2.00	7.2	7.5	-
Ta	-0.1	11	1.72	4.1	6.3	3.59 ^{a)} - 4.47 ^{c)}
W	-0.8	11	1.50	2.6	4	3.54 ^{a)} - 4.08 ^{d)}
Re	-1.5	10.5	1.17	0.6	1.1	0.76 ^{a)}
Pt	-3.6	7.5	1.22	0.7	0.7	0.37 ^{a)}
Au	-5	4.5	1.32	1.2	0.9	0.30 ^{a)}

- a) Daumer et al (1982)
- b) Andres et al (1969)
- c) Corsan and Cook (1970)
- d) Shivkov et al (1975)
- e) R. Kuentzler (1982)

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