SOVIET PHYSICS JETP VOLUME 34, NUMBER 3 MARCH, 1972

EFFECT OF PRESSURE ON THE MAGNETIC SUSCEPTIBILITY OF TITANIUM-VANADIUM AND VANADIUM-CHROMIUM ALLOYS

A. S. PANFILOV and I. V. SVECHKAREV

Low-temperature Physico-technical Institute, Ukrainian Academy of Sciences

Submitted March 29, 1971

Zh. Eksp. Teor. Fiz. 61, 1087–1091 (September, 1971)

The effect of hydrostatic pressure up to 4000 kg/cm^2 on the magnetic susceptibility of titanium-vanadium and vanadium-chromium alloys is investigated at room temperature. It is shown that deformation of the d-band is the main mechanism determining the behavior of the susceptibility under pressure.

INTRODUCTION

We have previously[1,2] considered the effect of hydrostatic pressure on the magnetic susceptibility of chromium and palladium alloys. We found that the behavior of the density of states curve N(q) under pressure is described satisfactorily in a certain interval of electron concentration q by the sum of two mechanisms—deformation of the relatively narrow d band and its shift relative to the band of almost free electrons, called for simplicity the s band. The Grüneisen electron parameter consequently has this form:

$$\gamma_e \equiv \frac{d\ln N}{d\ln V} = \frac{\partial \ln N}{\partial \ln V} + \frac{\partial \ln N}{\partial q}\frac{\partial q}{\partial \ln V}. \qquad (1)$$

We shall neglect the role of the density of states in the s band N_s in all effects except the relative band shift dE_{s-d}, which of course is responsible for the shift with concentration of the properties determined by the degree of population of the d band, by an amount

$$dq = 2N_s dE_{s-d}. \qquad (2)$$

Introducing the parameters γ and β to describe these two mechanisms,

$$d\ln N / d\ln V = \gamma + \beta \partial \ln N / \partial q, \qquad (3)$$

we obtain a similar expression for the spin susceptibility,

$$d\ln \chi / d\ln V = \gamma + \beta\, \partial \ln \chi / \partial q, \qquad (4)$$

which is also valid for the total susceptibility, including the orbital contribution, if, following Place and Rhodes,[3] we consider the latter to be inversely proportional to the width of the d band, i.e.,

$$\chi_{\text{orb}} \sim 1 / \Delta E_d. \qquad (5)$$

When there is a band shift, Eqs. (3) and (4) describe a step-like departure from monotonicity near the extremum of the density of states curve. It was just this step that made it possible to separate, in the alloys examined earlier, the shift effect from the deformation effect in specific portions of the N(q) curve. Of course, the interval of q values should be narrow enough that the parameters λ and β can be considered as constants. In this work we studied solid solutions of 3d-metals near the density of states peak, corresponding to q ~ 5 electron/atom.

OBJECTS, METHODS, AND RESULTS OF THE INVESTIGATION

The V-Ti (Ti up to 70 at.%) and V-Cr (Cr up to 40 at.%) alloys were prepared in an arc furnace and, after careful mixing, tempered in a copper mold. The purities of the starting materials were: V—99.7%, Ti (from iodide)—99.9%, Cr—99.95%. Two series of V-Ti alloys were prepared from materials of different sources. Most of them were annealed at 1000°C for two hours and cooled in the furnace. There was no difference in the effects of pressure on these alloys.

The measurements of magnetic susceptibility at room temperature and hydrostatic pressure to 4000 kg/cm^2 were made, as before,[1,2] by the method described in[4]. The experimental curves of susceptibility vs. pressure were linear within the limits of error (Fig. 1). The values of d ln χ/d ln V for alloys of 3d-metals are presented in Fig. 2 as a function of electron concentration; the black circles correspond to our data. The coefficients of compressibility of the alloys were obtained by interpolation from the values for the pure components.[5]

DISCUSSION OF RESULTS

In contrast to the earlier systems, the quantity d ln χ/d ln V for these alloys changes but slightly over a wide range of electron concentrations. This means that the band shift effect is small and can be masked by other effects. Consequently, the basic role is played by

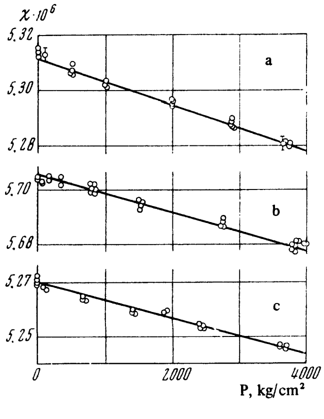

FIG. 1. Dependence of the susceptibility of some vanadium alloys on pressure at room temperature: a—V + 50 at.% Ti; b—pure V; c—V + 20 at.% Cr.

deformation of the d band, i.e., $d \ln \chi / d \ln V \approx \gamma_e \approx \gamma$. For vanadium and the alloys investigated here, $\gamma = 1.9 \pm 0.2$. This parameter increases to 2.6 in alloys with the maximum content of titanium, but non-monotonically (Fig. 2). This non-monotonic behavior may be due to the following factors:

1. Non-monotonicity of the deformation parameter itself over a wide interval of electron concentrations as a consequence of the complex structure of the electronic spectrum.

2. Manifestation of band shift. An estimate from (4) in the interval $4.6 < q < 5.2$ yields $\beta = -0.6 \pm 0.4$ atom^{-1}. Thus, if there is in fact a shift, its sign is opposite to the one found for alloys of the same period with $q \approx 6$ and alloys based on palladium.

3. Simplified calculation of the orbital contribution. For vanadium and its alloys this contribution is commensurate with the spin contribution,[6] and its behavior can scarcely be given by (5). Unfortunately, it is not yet possible to obtain a more correct evaluation of this contribution.

4. The character of the behavior of the compressibility coefficient of the alloys. Because of the lack of data for the vanadium-titanium system, we were forced to use a linear interpolation between the values for the pure components. The real situation may be far from linear, as the data for the Ti-Cr and Ti-Nb systems for the same values of q attest.[7] It is true that the use of a similar dependence of compressibility for the V-Ti alloys does not remove completely the non-monotonicity in the bheavior of $d \ln \chi / d \ln V$.

We take this opportunity to correct the results of[1], in which an erroneous handbook[8] value for the compressibility of chromium was used. The values of $d \ln \chi / d \ln V$ calculated with the correct value $\kappa = 0.62 \times 10^{-6}$ kg^{-1} cm^{2}[5] are shown by the open circles in Fig. 2 along with the empirical curve (4) with parameters $\gamma = 2.15\ (\pm 0.3)$, $\beta = 0.65\ (\pm 0.15)$ atom^{-1}. The corresponding band shift is $dE_{s\text{-}d}/d \ln V = 2.2 \pm 0.5$ eV, and the remaining conclusions and estimates in[1] are not changed. The value of γ found for vanadium agrees with the value of the Grüneisen parameter $\gamma_e = 1.65$[9] and is close to the theoretical estimate $-\partial \ln \Delta E_d / \partial \ln V \approx 1.4$.[10]

The conclusion about the relatively small magnitude and negative sign of the band shift (if it exists) is not paradoxical. It agrees qualitatively with the results of theoretical calculation of the band structure of vanadium[10] and is confirmed by the behavior of analogs in other transition periods. In particular, similar data are obtained from experiments on the effect of pressure on the superconducting transition temperature T_c of Zr-Nb-Mo alloys.[11] For convenience, we shall discuss these results using (1). The relation accepted in[12] between T_c and the density of states unperturbed by the electron-phonon interaction $N_0(q)$ is

$$\frac{d \ln T_c}{d \ln V} = \frac{\partial \ln \Theta}{\partial \ln V} + \gamma \frac{1}{N_0(q)\,(U_{\text{ph}} - U_c)} + \beta \frac{\partial \ln T_c}{\partial q}. \qquad (6)$$

Here Θ is the Debye temperature, which depends weakly on q,[11] U_{ph} is the electron-phonon interaction parameter, and U_C is the modified Coulomb repulsion parameter, which is independent of volume and q.[11] The experimental values of $d \ln T_c / d \ln V$ from Gey's work[11] are satisfactorily described by Eq. (6) (Fig. 3) with parameters $\gamma = 0.2\ (\pm 0.1)$ atom^{-1} and $\beta = -0.6\ (\pm 0.1)$ atom^{-1}, the values of the remaining quantities on the right-hand side of (6) being taken or calculated from the data given in[11]. For the alloys, linear interpolation between the compressibilities of the pure components was used.[13] The energy shift of states in the s and d bands can be estimated by using in (2) the value $N_s = 0.14$ (eV-atom)$^{-1}$ for silver[14]: $dE_{s\text{-}d}/d \ln V = -2$ eV. We see that the sign of the band shift in the Zr-Nb-Mo series agrees with the results for vanadium. The data on the behavior under pressure of the Fermi surfaces of molybdenum and tungsten[15] do not contradict this.

On the basis of this and the previous investigations[1,2], as well as[10,11,15-17], we may conclude that the sign of the relative shift of the states of the s and d bands changes along the periods.

Since the magnetic properties depend on states lying within rather narrow energy intervals, we cannot assert that the shifts we have found pertain to the bands as a whole. They describe the behavior only of individual peaks in the density of states of the d band. Nevertheless, this information can be useful for refining the structure of the lattice potential. It is regrettable that there are no theoretical calculations of the electronic structure of transition metals under pressure that are suitable for comparison with experiment.

The authors thank B. I. Verkin for his interest, V. N. Eremenko and R. G. Fedchenko for supplying the required alloys, and V. N. Manchenko for assistance with the measurements.

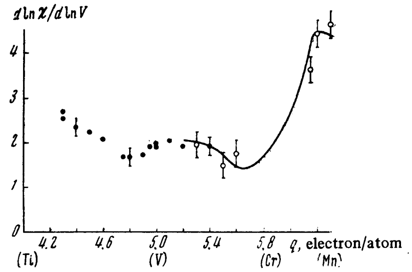

FIG. 2. Experimental values of d ln χ/d ln V as a function of electron concentration for alloys of 3d-metals (black circles, results of this research; open circles, corrected data of [1]; continuous curve, calculated from (4)).

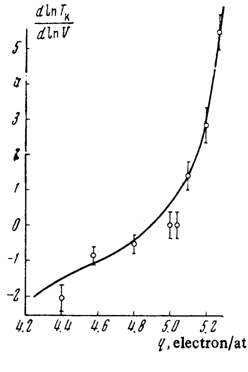

FIG. 3. Experimental [11] and calculated (curve) values of d ln T_c/d ln V as a function of electron concentration for alloys of 4d-metals.

[1] A. S. Panfilov and I. V. Svechkarev, Zh. Eksp. Teor. Fiz. **59**, 1156 (1970) [Sov. Phys.-JETP **32**, 630 (1971)].

[2] I. Ya. Dekhtyar, A. S. Panfilov, I. V. Svechkarev, and R. G. Fedchenko, Zh. Eksp. Teor. Fiz. **60**, 340 (1971) [Sov. Phys.-JETP **33**, 185 (1971)].

[3] C. M. Place and P. Rhodes, J. Appl. Phys. **39**, 1282 (1968).

[4] A. S. Panfilov and I. V. Svechkarev, Prib. Tekh. Eksp., No. 3, 179 (1967).

[5] E. S. Fisher, C. J. Renken, Phys. Rev. **135**, 482A (1964); D. I. Bolef, J. Appl. Phys. **32**, 100 (1961); D. I. Bolef and J. de Klerk, Phys. Rev. **129**, 1063 (1963).

[6] N. Mori, J. Phys. Soc. Japan **20**, 1383 (1965).

[7] E. S. Fisher and D. Dever, Acta Met. **18**, 265 (1970); I. M. Nedyukha and V. G. Chernyĭ, Fiz. Met. Metalloved. **22**, 114 (1966).

[8] Fiziko-khimicheskie svoĭstva élementov. Spravochnik (Physico-Chemical Properties of the Elements. A Handbook), Naukova Dumka Press, 1965, p. 338.

[9] J. G. Collins and G. K. White, Progr. Low Temp. Phys. **4**, North Holland Publ. Co., Amsterdam, 1964.

[10] J. R. Anderson, J. W. McCaffrey, and D. A. Papaconstantopoulos, Solid State Commun. **7**, 1439 (1969).

[11] W. Gey, Z. Phys. **229**, 85 (1969).

[12] M. A. Jensen and J. P. Maita, Phys. Rev. **149**, 409 (1966).

[13] A. Myers, Phil. Mag. **5**, 927 (1960); K. J. Carrol, J. Appl. Phys. **36**, 3689 (1965); F. H. Featherston and J. R. Neighbours, Phys. Rev. **130**, 1324 (1963).

[14] S. A. Nemnonov, Fiz. Met. Metalloved. **19**, 550 (1965).

[15] V. B. Pluzhnikov and I. V. Svechkarev, in Tr. FTINT Akad. Nauk. Ukr. SSR, No. 9, 1971, p. 71.

[16] H. L. Davis, J. S. Faulkner and H. W. Joy, Phys. Rev. **167**, 601 (1968).

[17] J. J. Vuillemin and H. J. Bryant, Phys. Rev. Lett. **23**, 914 (1969).

Translated by L. M. Matarrese
110