SOVIET PHYSICS JETP VOLUME 32, NUMBER 4 APRIL, 1971

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

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Submitted May 8, 1970

Zh. Eksp. Teor. Fiz. 59, 1156–1159 (October, 1970)

The effect of hydrostatic pressure of up to 4000 kg/cm^2 at room temperature on the magnetic susceptibility of chromium-vanadium and chromium-manganese alloys is investigated. The experimental results can be satisfactorily explained within the framework of a proposed simple model of changes in the electron spectrum induced by hydrostatic pressure, in which d-band deformation and a relative shift of the s- and d-bands are assumed. Values of parameters describing both mechanisms are obtained.

INTRODUCTION

ATOMIC states with different quantum numbers in the transition metals are resolved into bands, overlap, and are subjected to hybridization; the resulting spectrum, at least in d-metals, can, however, be successfully represented by a combination of a narrow band with a high density of states and a band of almost-free electrons, respectively designated d- and s-bands. It has been established[1] that the mutual disposition of these bands is a characteristic which is extremely sensitive to the detailed structure of the lattice potential. To distinguish the effects of shift and deformation of the bands under pressure is, consequently, important not only for practical use (e.g., for interpretation of experiments with change of interatomic distance), but also for a correct choice of the form of the lattice potential.

The extraction of such information is associated with systematic investigations of different parts of the curve of the density of states under pressure; to our knowledge there have as yet been no such investigations. We have tried to fill this gap by using the effect of pressure on the magnetic susceptibility of vanadium-chromium and chromium-manganese alloys.

THEORY

As indicated above, we shall treat the effect of pressure on the electron spectrum as a superposition of two effects.

The first, which we shall call deformational and which we shall describe by a parameter γ, is the decrease in the density of states $N(E_0)$ at the Fermi surface due to the increase ΔE_d of the d-band width with increase in the overlap of the wavefunctions.[2] The parameter γ is determined by the expression

$$\gamma \equiv \frac{\partial \ln N(E_0)}{\partial \ln V} \approx -\frac{\partial \ln \Delta E_d}{\partial \ln V}. \tag{1}$$

The second effect is a relative shift of the bands. This results in change of the density of states corresponding to change of the electron density by an amount

$$dq = 2N_s dE_{s-d}. \tag{2}$$

Here dE_{s-d} is the relative shift of the s- and d-states lying at the Fermi surface of the uncompressed metal (a negative sign corresponds to increase in the energy of the s-states), and N_s is the density of states in the s-band. Such a treatment is, of course, valid only for properties reflecting the total density of states at the Fermi surface (e.g., the electron specific heat or spin susceptibility). We shall characterize the shift by the parameter

$$\beta = \partial q / \partial \ln V. \tag{3}$$

Here it is assumed that

$$N \approx N_d, \quad N_s \approx \text{const}, \tag{4}$$

and we can rely upon the constancy, in a certain energy interval, of the parameters we have introduced. The sum of the enumerated contributions is the total derivative of the density of states with respect to the volume, i.e., the electron Gruneisen parameter γ_e:

$$\gamma_e \approx d \ln N / d \ln V = \gamma + \beta \, \partial \ln N / \partial q. \tag{5}$$

The density of states of the transition metals under pressure is conveniently studied using the magnetic susceptibility, if purely technical difficulties can be overcome. In fact, the overwhelming contributions to the susceptibility χ are the spin and orbital paramagnetism[3], which depend on the occupation of the d-band. For a given occupation, the spin paramagnetism is proportional to the density of states at the Fermi surface, while the orbital paramagnetism is inversely proportional to the width of the d-band,[4] so that, taking (1), (3) and (4) into account, we have

$$d \ln \chi / d \ln V = \gamma + \beta \, \partial \ln \chi / \partial q. \tag{6}$$

Clearly, it is possible to distinguish the effects of deformation and shift of the bands if the value of $\partial \ln \chi / \partial q$ varies steeply in the investigated region of $N(q)$. On the other hand, this region must be narrow enough for the parameters γ and β to be constant.

EXPERIMENTAL RESULTS AND DISCUSSION

As the object of our investigations we took alloys of chromium with vanadium (40, 60 and 70 at.% V) and with manganese (15, 20 and 30 at.% Mn), which, on the whole, satisfy the requirements listed above. The sam-

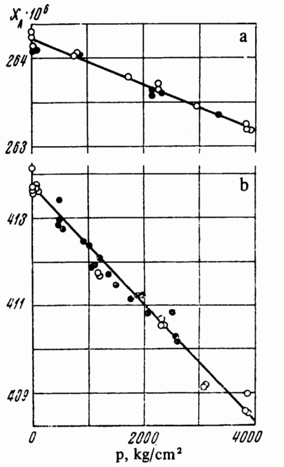

FIG. 1

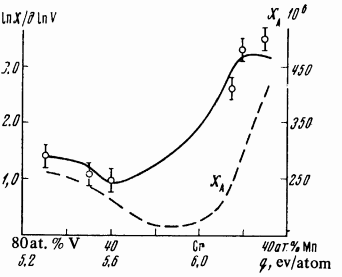

FIG. 2

FIG. 1. Atomic susceptibility of certain chromium alloys vs. pressure at room temperature: a—70 at.% V + Cr, b—30 At.% Mn + Cr. The two sets of points correspond to the different samples of the investigated alloy.

FIG. 2. Experimental and calculated (solid) values of $\partial \ln \chi/\partial \ln V$ and the atomic susceptibility χ_A (dashed) at room temperature from [8] for chromium alloys.

ples were prepared from the same ingots as were used in the work of Butylenko and Gridnev[5].

The dependence of the magnetic susceptibility on hydrostatic pressure up to 4000 kg/cm^2 at room temperature was measured by the method of freely suspending the sample in an inhomogeneous magnetic field, as described in[6]. The magnitude of the effect is a linear function of the pressure, within the error limits, and at maximum pressure is about 1% (Fig. 1).

The values found for $d \ln \chi/d \ln V$ as a function of the electron density per atom q are shown by the points in Fig. 2. Each point is the result of a measurement on not fewer than two samples. The compressibility was computed from[7] using the additivity law. The solid curve in Fig. 2 is the best approximation of Eq. (6) to experiment. To construct it, we used values of $\partial \ln \chi/\partial q$ obtained by graphical differentiation of the experimental dependence $\chi(q)$ at room temperature from the work of Taniguchi, Tebble, and Williams[8] (the absolute magnitudes of χ for our samples agree with the latter), and the following parameter values

$$\gamma = 1.55 \pm 0.15, \quad \beta = 0.48 \pm 0.1 \text{ atom}^{-1}.$$

Below we give a discussion of the main results of the work and a comparison of these with the existing experimental facts:

1. The behavior under pressure of the susceptibility of alloys of chromium with vanadium and manganese in a broad interval of electron densities is satisfactorily described by the model we have taken for changes in the spectrum, which contains two constant parameters, corresponding to deformation and shift of the bands.

2. Some disparity between the model and experiment for alloys with maximum manganese content is probably due to their antiferromagnetism. The transition of chromium alloys to an antiferromagnetic state leads to the appearance of a magnetic energy gap and a corresponding rearrangement of the spectrum[9]. However, close to the transition temperature T_N, the gap decreases sharply, and this, along with thermal excitation of the electrons, obliterates the boundary between the para- and antiferromagnetic states. Consequently, since T_N for chromium-manganese alloys is not far from room temperature, we can neglect antiferromagnetism. On increase of manganese concentration, the transition temperature, and with it the role of antiferromagnetism, rises rapidly[10]. The model loses its validity both in the low-temperature region and in alloys with large manganese content, the behavior of which requires a special treatment.

In passing, we note that at room temperature the fine structure in the spectrum is blurred out and does not mask the main processes in the bands.

3. The deformation parameter γ which we have introduced differs appreciably from the value $2/3$ corresponding to free electrons. According to (5), it corresponds with the Gruneisen parameter at the extremal points of the curve $N(q)$. In fact, the Gruneisen parameter $\gamma_e = 1.65 \pm 0.1$[11] of vanadium, which lies at a peak in the curve of the density of states (though outside the limits of the interval investigated) is in good agreement with γ and confirms the correctness of the value we have found.

4. Assuming that for copper[12], $N_s = 0.15$ (eV-atom)$^{-1}$, we obtain from β the following value for the shift of the bands:

$$\partial E_{s-d}/\partial \ln V = 1.6 \pm 0.5 \text{ eV}$$

With decrease of interatomic distance, the s-band is lowered relative to the d-band, as we should have expected on the basis of the most simple scheme of the electron spectrum of the transition metals[13].

Up to now there are no direct cases for comparison with our results for the properties of the shift, although its reality can be confirmed by the following fact. Assuming that the transition temperature in chromium is entirely determined by the occupation of the d-states, and knowing β and the dependence $T_N(q)$[10], we can compute the value of $(\partial T_N/\partial P)_{P \to 0}$; this is found to be equal to $(-5.3 \pm 2) \times 10^{-6}$ °K-atom^{-1}, which corresponds exactly to the measured value (-5.1×10^{-6}°K-atm^{-1}[14]).

We note that in parts of the spectrum with a high value of $\partial \ln N/\partial q$, the contribution to the Gruneisen parameter from the shift of the bands competes with the deformation.

Thus, the agreement of the model used with experiment, and the agreement of its parameters with known spectral data, confirm the validity of the model and justify the assumptions made, although an element of doubt remains, arising from the fact that the alloys investigated are associated with different subbands of the d-band, some of which show antiferromagnetism.

The authors are grateful to V. I. Verkin for his interest in the work and to A. K. Butylenko for providing the alloys.

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[1] W. M. Lomer, Proc. Phys. Soc. 80, 489 (1962).

[2] E. Fawcett and G. K. White, J. Appl. Phys. 39, 576 (1968).

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

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

[5] A. K. Butylenko and V. N. Gridnev, Fiz. Metal. Metaloved. 19, 205 (1965) [Phys. Metals Metallog. (USSR) 19, No. 2, 47 (1965)].

[6] A. S. Panfilov and I. V. Svechkarev, Prib. Tekh. Eksp. No. 3, 179 (1967) [Instrum, Exp. Tech. (USSR) No. 3, 655 (1967)].

[7] Fiziko-tekhnicheskie svoistva elementov (Physicotechnical Properties of the Elements), Naukova dumka, 1965.

[8] S. Taniguchi, R. S. Tebble and D. E. G. Williams, Proc. Roy. Soc. 265A, 502 (1962).

[9] F. Heiniger, E. Bucher and J. Muller, Phys. Lett. 19, 163 (1965).

[10] W. C. Koehler, R. M. Moon, A. L. Trego and A. R. Mackintosh, Phys. Rev. 151, 405 (1966).

[11] J. G. Collins and G. K. White, Progr. Low Temp. Phys. 4, 450 (1964).

[12] S. A. Nemnonov, Fiz. Metal. Metaloved. 19, 550 (1965) [Phys. Metals Metallog. (USSR) 19, No. 4, 66 (1965)].

[13] J. M. Ziman, Proc. Phys. Soc. 91, 701 (1967).

[14] D. B. McWhan and T. M. Rice, Phys. Rev. Lett. 19, 846 (1967).

Translated by P. J. Shepherd
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