

INFLUENCE OF PRESSURE ON THE MAGNETIC SUSCEPTIBILITY OF ALLOYS OF PALLADIUM WITH RHODIUM AND SILVER

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The effect of hydrostatic pressures up to 4,000 kg/cm<sup>2</sup> on the magnetic susceptibility at room temperature is investigated in alloys of palladium with rhodium and with silver, by the method of free suspension of the sample with an inhomogeneous magnetic field. The experimental results are discussed within the framework of a simple empirical description of the variation of the electron spectrum of transition metals under pressure, containing deformation of the d-band and a relative shift of the s- and d-states on the Fermi level.

INTRODUCTION

FROM the few published rigorous calculations of the electronic spectra of transition metals under pressure<sup>[1]</sup> it is difficult to separate the main mechanisms governing the change of the spectrum and the curve of the density of states. Yet it is possible to construct a simple empirical model suitable for the description of the dependence of the density of states on the pressure. With the aid of such a model it is possible to describe satisfactorily the behavior of the magnetic susceptibility of chromium alloys under conditions of hydrostatic compression at room temperature<sup>[2]</sup>, and the parameters of the model are in good agreement with experimental information on other electronic properties of these alloys. In the model, according to the customarily accepted representations, the density of states N is regarded as a sum of the contributions of two bands—a narrow d-band and a band of almost free electrons, called the s-band, while the influence of the pressure is regarded as the sum of the contributions of two mechanisms—the deformation of the d-band and its shift relative to the s-band. Taking into account the inequality  $N_d \gg N_s$ , we neglect the role of the s-band in all the effects with the exception of the band shift, and assume that  $N_s \approx \text{const}$ . Thus, the electronic Gruneisen parameter  $\gamma_e$  takes the form

$$\gamma_e \equiv d \ln N / d \ln V = \gamma + \beta \partial \ln N / \partial q. \tag{1}$$

Here V is the volume and the number of electrons per atom, and the parameters  $\gamma$  and  $\beta$  have the following meaning. The first mechanism—the deformation of the d-band—is described by the parameter  $\gamma = \partial \ln N / \partial \ln V$ . The second mechanism—the relative shift of the states of the s- and d-bands on the Fermi boundary,  $\Delta E_{s-d}$ , leads to a shift of the curve of the density of states N(q) by an amount  $\Delta q = 2N_s \Delta E_{s-d}$  and is described by the parameter  $\beta = \partial q / \partial \ln V$ . It is assumed that the parameters  $\gamma$  and  $\beta$  can be regarded as constants in a limited interval of the state-density curve.

The present paper is a continuation of investigations of the deformability of the spectra of transition metals by pressure and a verification of the feasibility of the described model. The most interesting result—the

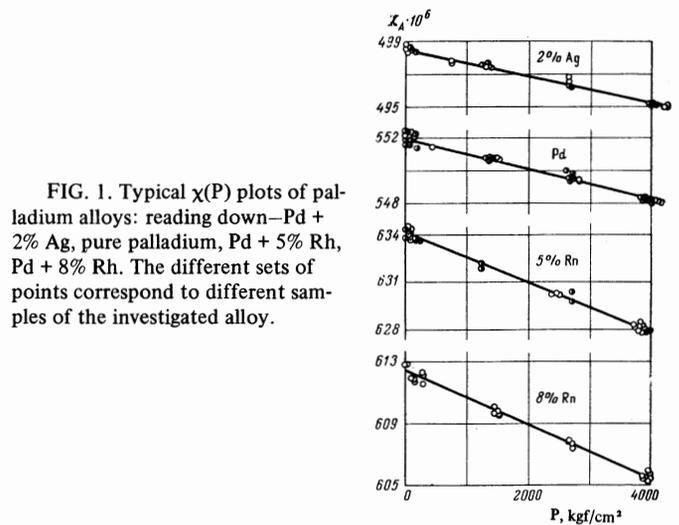


FIG. 1. Typical  $\chi(P)$  plots of palladium alloys: reading down—Pd + 2% Ag, pure palladium, Pd + 5% Rh, Pd + 8% Rh. The different sets of points correspond to different samples of the investigated alloy.

separation of the effect of the band shift—can be obtained only by a special choice of the investigated portion of the spectrum—the vicinities of the maximum of the state-density curve. In this connection, we consider the influence of pressure on the magnetic susceptibility of binary alloys of palladium with silver and rhodium, having a maximum of the state density at a rhodium content of approximately 5 at.%.

SAMPLES, EXPERIMENTAL TECHNIQUE, RESULTS

Binary alloys of palladium (99.9%), containing up to 15 at.% rhodium (99.7%) and 2 at.% silver (99.9%) were prepared in an arc furnace followed by two-hour annealing at 1000°C in vacuum.

The magnetic susceptibility  $\chi$  under pressure was measured, as in the preceding investigation<sup>[2]</sup>, using propyl alcohol to transfer the pressure to the sample. Typical experimental plots of  $\chi(P)$  are shown in Fig. 1 and are similar to those given in<sup>[2]</sup>. The values of the susceptibility at  $P = 0$  coincide with the data by others (for example,<sup>[3]</sup>).

The values of  $d \ln \chi / d \ln V$  are represented by the points in Fig. 2 as functions of the electron density (the compressibility coefficient of the alloys—linear inter-

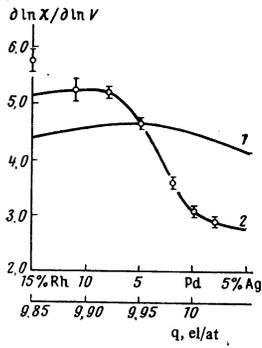


FIG. 2. Experimental values of the derivatives  $d \ln \chi / d \ln V$  and plots of Eq. (5) for different values of the parameter  $\beta$ : 1— $\beta = 0$ , 2— $\beta = 0.30 \text{ atom}^{-1}$

polation of the values for the pure components from<sup>[4]</sup>.

In non-annealed alloys containing more than 5 at.% rhodium, the absolute values of the susceptibility are somewhat higher than in annealed ones, but the value of  $d \ln \chi / d \ln V$  remains practically the same.

### DISCUSSION OF RESULTS

A feature of the system of alloys of palladium is the increase of their spin susceptibility  $\chi_s$  by the exchange interaction<sup>[5]</sup>. While facilitating the experiment, this circumstance makes the interpretation more complicated, in view of the appearance of additional parameters. Taking into account the exchange interaction<sup>[5]</sup> we have

$$\chi = \chi_s / (1 - \alpha \chi_s). \quad (2)$$

Recognizing that

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

we can obtain from (2) and (3)

$$\frac{d \ln \chi}{d \ln V} = [\gamma + \alpha \chi (\gamma + \partial \ln \alpha / \partial \ln V)] + \beta \partial \ln \chi / \partial q. \quad (4)$$

Expression (4) contains four parameters ( $\alpha$ ,  $\beta$ ,  $\gamma$ ,  $\partial \ln \alpha / \partial \ln V$ ), which we assume to be constant for the entire series of the investigated alloys. Using (4) at the point of the maximum  $\chi(q)$  (at 5 at.% rhodium), we can easily replace two of them, pertaining to the exchange interaction, by the experimental values  $\chi_{\max}$  ( $635 \times 10^{-6} \text{ mole}^{-1}$ ) and  $d \ln \chi_{\max} / d \ln V$  (4.66):

$$\frac{d \ln \chi}{d \ln V} = \gamma + \frac{\chi}{\chi_{\max}} \left( \frac{d \ln \chi_{\max}}{d \ln V} - \gamma \right) + \beta \frac{\partial \ln \chi}{\partial q}. \quad (5)$$

The determination of the remaining parameters reduces to their choice in (5) until a best description of the data of Fig. 2 is obtained. It turned out that the curve specified by expression (5) is stable against changes in the deformation parameter  $\gamma$ , and to refine it with the aid of (1) we used the experimental values of the Gruneisen parameter  $\gamma_e = 2.1$ <sup>[6]</sup>, and the value  $\partial \ln N / \partial q = -4$  for palladium, which was determined from the low-temperature susceptibility<sup>[3]</sup>:

The final values of the parameters are:

$$\begin{aligned} \gamma &= 3.3 \pm 0.3, \\ \beta &= 0.30 \pm 0.02 \text{ atom}^{-1}. \end{aligned}$$

Figure 2 shows curves described by Eq. (5), illustrating the last stage of the selection of  $\beta$  and the degree of attained agreement with experiment.

Let us consider the main conclusions of the investigation.

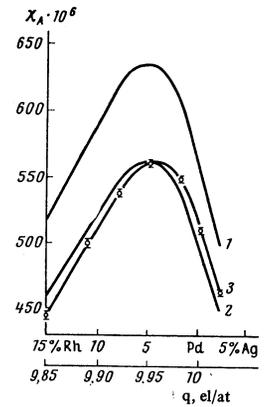


FIG. 3. Plots of  $\chi(q)$  at zero pressure (1) and at a pressure corresponding to  $\Delta V/V = -0.025$  ( $5 \times 10^4 \text{ atm}$ ): 2—calculation from Eq. (5) without allowance for the band shift, 3—extrapolation of experimental data.

1. It turns out that the model proposed in<sup>[2]</sup> for the variation of the spectrum under pressure describes successfully the experiment with the aid of parameters that are constant in a considerable interval of the electron concentrations (at least in the region of the maximum of the density of states curve).

2. An important result is also the distinct separation of the effect of the band shift. The corresponding shift of the state-density curve is clearly demonstrated in Fig. 3 by the difference between the positions of the  $\chi(q)$  curves for  $\Delta V/V = -0.025$  ( $P \sim 5 \times 10^4 \text{ atm}$ ), namely, curve 2 was calculated from Eq. (5) without allowance for the band shifts, and curve 3 is extrapolation of the experimental data (curve 1— $\chi(q)$  at  $P = 0$ ). The energy shift of the states of the s and d bands on the Fermi level amounts to (putting  $N_s = 0.14 \text{ eV/atom}$ , as in silver<sup>[7]</sup>)

$$\partial E_{s-d} / \partial \ln V = 1.05 \pm 0.15 \text{ eV},$$

i.e., it is close to the analogous characteristic in chromium alloys<sup>[2]</sup> ( $1.6 \pm 0.5$ ) and has the same sign: under pressure, the s-states drop relative to the d-states.

The manifestation of the band-shift effect should become sharper with decreasing temperature, owing to the increase of  $\partial \ln \chi / \partial q$ . Substitution in (4) of the corresponding low-temperature value of the derivative<sup>[3]</sup> shows that at liquid-helium temperature the effect of the band shift for palladium is predominant, as a result of which the derivative  $d \ln \chi / d \ln V$  reverses sign ( $-3.7$ ). The agreement between the calculated value and the one measured by magnetostriction<sup>[8]</sup> ( $d \ln \chi / d \ln V = -3.5$ ) confirms both the existence of the band shift and the value found for it<sup>1)</sup>.

3. The correctness of the obtained parameter  $\gamma$  is confirmed by the following facts: using Eq. (4) at the point of maximum susceptibility and putting  $\alpha = 0.78 \times 10^4 \text{ mole}$  from<sup>[10]</sup>, we obtain the value  $\partial \ln \alpha / \partial \ln V = -3.0 \pm 0.5$ , which depends on the choice of the parameter  $\gamma$ . It agrees with the results obtained in<sup>[8]</sup>, if one uses the experimental value of the Gruneisen parameter ( $2.1$ <sup>[6]</sup> in lieu of 1.5), namely,  $\partial \ln \alpha / \partial \ln V = -2.7$ .

<sup>1)</sup> After completing the work on this article, the authors became acquainted with the results of investigations of the de Haas-van Alphen effect in palladium under conditions of hydrostatic pressure<sup>[9]</sup>. The character of the change of the extremal section of the Fermi surface, corresponding to s electrons, is in qualitative agreement with the band-shift effect observed by us.

The parameter  $\gamma$  is close to the Gruneisen parameter obtained for the alloy Pd + 50 at.% Rh, for which  $\gamma = \gamma_e = 3.6 \pm 0.3$ <sup>[6]</sup>. It is doubtful, however, whether the parameters obtained by us remain valid in such a wide range of concentrations. In general, on the gently-sloping sections of the  $N(q)$  curve, it is hardly possible to separate distinctly the effects of the shift and of the deformation, all the more since the shift of the states on the Fermi level, as observed by us, contains an admixture of the deformation effect; this admixture depends on its position in the band.

Thus, the first systematic investigation of the magnetic susceptibility of alloys of transition metals under pressure makes it possible to propose a simple and lucid model of the variations of the spectrum, to determine its parameters, and to obtain, in the case of palladium alloys, information concerning the change of the exchange interaction under pressure.

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