Effect of pressure on the magnetic susceptibility of ternary alloys of palladium with rhodium and silver

V. N. Manchenko, A. S. Panfilov, and I. V. Svechkarev

Physico-technical Institute of Low Temperatures, Ukranian Academy of Sciences
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The magnetic susceptibility of ternary alloys of palladium with rhodium and silver was measured at room temperature and under hydrostatic pressures up to 4000 atm. The effect of pressure on the structure of the spectrum and the effect of the electron scattering in the alloys are considered within the frameworks of simple models. An analysis of the experimental results for the ternary alloys and for the previously investigated binary alloys yields the parameters that describe the scattering, as well as the dependence of the density of the electronic states at the Fermi level and of the exchange enhancement of spin paramagnetism on the atomic volume.

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The appreciable peak in the density of the electronic states below the Fermi level and the proximity of palladium to ferromagnetic instability make palladium alloys interesting objects for the study of the properties of the electronic structure, exchange interactions, and the connection between them.

The mechanisms whereby changes of the atomic volume affect the electronic spectrum of palladium were established by investigating the susceptibility of its binary alloys with rhodium and with silver under pressure.[1] These mechanisms were described by using the rigid-band approximation, so that the degree of reliability of the quantitative conclusions of[1] is not clear. In the present paper we report an analogous investigation of ternary alloys of palladium, in which the same region of electron concentrations can be realized with a larger total impurity content. A simultaneous analysis of the results obtained for ternary and binary systems makes it possible to determine the effect of the impurity on the structure of the density-of-states curve and to obtain more accurate values for the parameters that describe the behavior of the electron spectrum and the exchange enhancement of the paramagnetism with changing atomic volume.

The magnetic susceptibility of the ternary alloys $Rh_xPd_{100-x-y}Ag_y$ ($y=5$, $3\leqslant x\leqslant 10$), and also of certain binary alloys ($y=0$, $x=20$ and $y=1$, $x=0$), was investigated under conditions of hydrostatic pressures up to 4000 atm at room temperature. We used the method of freely suspending the sample in an inhomogeneous magnetic field.[2] The relative error in the measurement of the susceptibility did not exceed 0.1%. The pressure-transmitting medium was propyl alcohol. The purity of the initial components and the procedure of preparing the alloys and the samples were the same as in[1]. In all the samples we observed a linear decrease of the susceptibility with increasing pressure (Fig. 1). The values of $d\ln\chi/d\ln V$ at the corresponding electron concentrations in the alloy q (the total number of valence electrons per atom) are shown in Fig. 2 together with the data obtained here and in[1] for the binary alloys. The compressibility coefficients of the alloys are calculated by an additivity law from their values for the pure components.[3] The excess impurity content (~ 10 at. %) in the ternary systems in comparison with the binary systems changes the behavior of $d\ln\chi/d\ln V$ as a function of q (Fig. 2) and $\chi(q)$ (see Fig. 3), i.e., the spectrum itself is subjected by the impurity atoms to noticable distortions that must be taken into account in the analysis of the susceptibility.

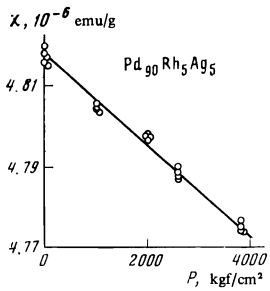

FIG. 1. Typical experimental plots of $\chi(P)$.

It is known that the decisive contribution to the magnetic susceptibility of palladium alloys is the spin paramagnetism χ_s, enhanced by exchange interaction[4]:

$$\chi^{-1}=\chi_s^{-1}-\alpha. \tag{1}$$

Here α is the effective exchange interaction between the electron spin, χ is the observed susceptibility, and

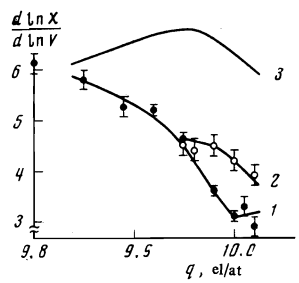

FIG. 2. Experimental values of $d\ln\chi/d\ln V$ as functions of the electron concentration in binary (●) and ternary (○) alloys, and the corresponding curves 1 and 2 calculated from Eq. (3), Curve 3 is the result of the use of the model (3) for binary alloys without allowance for the bandshift ($\beta=0$).

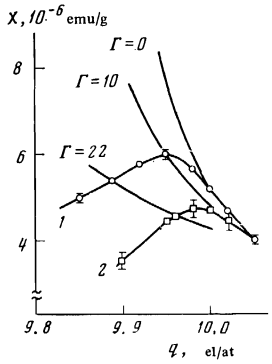

FIG. 3. Experimental plots of the susceptibility against the electron concentration in binary (1) and ternary (2) alloys of palladium with rhodium and silver, and the calculated plots of $\chi(q)\Gamma = \text{const}$ at scattering-parameter values $\Gamma = 0$, 10, and 22 (arbitrary units) corresponding to pure palladium and its alloys with 5 and 11 at. % rhodium.

$\chi_s \sim N(\varepsilon_F)$, where $N(\varepsilon_F)$ is the density of states at the Fermi level. The behavior of the electron spectrum of a transition metal under pressure will be described by a simplified model, in which the total change of the density of states is due to the deformation and to the relative displacement of the $s(p)$ and d bands[5]:

$$\frac{d\ln N}{d\ln V} = \gamma + \beta \frac{\partial \ln N}{\partial q}. \tag{2}$$

The first mechanism is described by the parameter $\gamma = \partial \ln N/\partial \ln V$ and the second by the parameter $\beta = dq/d\ln V$, which characterizes the overflow of the electrons from one band to the other as a result of the displacement.[5] Within the framework of such a model we have

$$\frac{d\ln\chi}{d\ln V} = (1+\alpha\chi)\gamma + \alpha\chi \frac{\partial \ln \alpha}{\partial \ln V} + \beta \frac{\partial \ln \chi}{\partial q}. \tag{3}$$

In a small interval of electron concentrations, the parameters of the model can be regarded as constants, i.e., γ, β, $\partial \ln\alpha/\partial \ln V \approx \text{const}$.

The fact that α is constant for the considered alloys is from known earlier studies.[4]

To describe the experimental data (Fig. 2) with the aid of expression (3) it is necessary to know the real values of $\partial \ln\chi/\partial q$, i.e., to take into account and exclude the influence of the impurities on the structure of the spectrum and on the susceptibility. In first-order approximation, this influence reduces to the effect of electron scattering by impurity atoms, as a result of which the initial plot of the density of states broadens and becomes smoother. In analogy with[6], we shall characterize the alloy by means of the scattering parameter Γ:

$$\Gamma = \delta_{Rh} x + \delta_{Ag} y. \tag{4}$$

We choose the ratio δ_{Rh}/δ_{Ag} of the impurity scattering abilities equal to the ratio of the impurity resistances of the rhodium and silver in palladium: $\Delta\rho_{Rh}/\Delta\rho_{Ag} \approx 2$.[7] The susceptibility of isoelectronic alloys containing an aribtrary combination of impurities of rhodium and silver can be represented therefore as a function of the scattering parameter $\chi(\Gamma)_{q=\text{const}}$ (Fig. 4). Having a sufficiently large set of such functions, it is easy to determine a function of the type $\chi(q)_{\Gamma=\text{const}}$, which corresponds to the state-density curve of an alloy with a specified scattering parameter, and yields for this alloy the sought value of the derivative $\partial \ln\chi/\partial q$ at the corresponding electronic concentrations. Typical plots of $\chi(q)_{\Gamma=\text{const}}$ for the values of Γ corresponding to pure palladium and its alloys with 5 and 11 at.% of rhodium are shown in Fig. 3 and demonstrate the strong smoothing action of the scattering and the susceptibility—the reason for the deviation of the actually observed concentration curves 1 and 2 from the rigid-band model. The available information on the susceptibility of the palladium alloys ([1,6,8] and the present paper) make it possible to obtain the required derivatives for almost all the alloys investigated under pressure. The procedure is to differentiate graphically the function $\chi^{-1}(q)_{\Gamma=\text{const}}$, which is close to linear and ensures that the derivative is determined with accuracy not worse than ±10%. (We note that the result is not critical to the choice of the ratio δ_{Rh}/δ_{Ag} in (4)). Substitution of the values of $\partial \ln\chi/\partial q$ obtained for the actual alloys in expression (3) and variation of its parameters leads to good agreement between the model and experiment for both binary and tenary alloys at $\gamma + \partial \ln\alpha/\partial \ln V = 0.50 \pm 0.10$, $\beta = 0.50 \pm 0.05$ e/at—curves 1 and 2 of Fig. 2. The behavior of the susceptibility under pressure makes it possible to establish reliably only the sum of the parameters γ and $\partial \ln\alpha/\partial \ln V$, and additional information is desirable to be able to separate the two. Using in (2) the obtained value of β, the electron Grüneisen parameter of palladium $\gamma_e = 2.1$ ($\approx d\ln N/d\ln V$),[9] and the value $\partial \ln N/\partial q \approx -2$ $(e/\text{at})^{-1}$ obtained from theoretical calculations of the spectrum,[10,11] we get

$$\gamma = 3.0 \pm 0.5, \quad \partial \ln\alpha/\partial \ln V = -2.5 \mp 0.5.$$

From a comparison of the results of the analysis with[1] it follows that allowance for the scattering influences noticably only the value of β: the overflow effect is 1.5 times larger than that obtained in the rigid-band approximation.

It is curious that in palladium alloys the variation of α under pressure is similar to that of the width Δ_d of the d band:

$$\frac{\partial \ln\alpha}{\partial \ln V} \approx -\gamma \approx \frac{\partial \ln \Delta_d}{\partial \ln V}. \tag{5}$$

This result follows also from the simplified model of strong electron correlations in the d band with a constant number of particles (it can be easily obtained directly

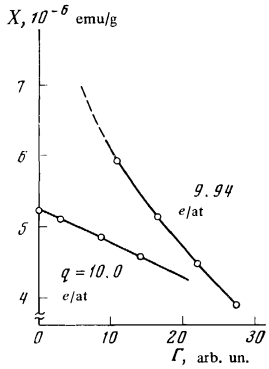

FIG. 4. Typical plots of $\chi(\Gamma)_{q=\text{const}}$: the electron concentrations correspond to Pd ($q = 10$) and to the alloy $Rh_{0.06}Pd_{0.94}$ ($q = 9.94$).

from dimensionality considerations).[12] It is possible that in palladium alloys the ratio (5) is approximately satisfied because of the weak dependence of α on the electron concentration,[4] although the overflow of electrons in this system is appreciable. To illustrate its role, Fig. 2 shows curve 3, which represents the pressure effect expected from the model (3) in the absence of overflow ($\beta = 0$). We note that the intersection of curves 1 and 3 corresponds to an extremem of the functions $\chi(q)_{\Gamma=\text{const}}$. Its position ($q \approx 9.8$ e/at) agrees well with the theoretical estimate of the position of the peak of the density of states in palladium.[10,11]

Since the susceptibility of the palladium alloys is very sensitive to the quantity α, this fact confirms indirectly the constancy of α in the course of alloying and makes it possible to reconstruct from the functions $\chi(q)_{\Gamma=\text{const}}$ the form of the density-of-states curves in alloys. The rapid scattering-induced smoothing of the peak of the density of states does not make it possible, in particular, to realize band ferromagnetism ($\alpha\chi \approx 1$) in disordered alloys of palladium with rhodium.

From a comparison of the data of Fig. 4 with the temperature dependences of χ of the corresponding objects[6,8] it is possible to determine the absolute value of the scattering parameter Γ in terms of the effective temperature $\delta_{Rh} \approx 20$ °K/at.%. It agrees with the known values of the Dingle factor,[13] but is only a rough estimate, inasmuch as the role of the temperature in the susceptibility is not confined to electron excitation (the scattering by thermal vibrations of the lattice increases, the spectrum is changed under the influence of the Debye–Waller factor and of changes in the volume, etc.).

Thus, the model of restructuring of the spectrum of transition metals with allowance for the electron scattering describes adequately the behavior of the magnetic susceptibility under pressure in alloys based on palladium with different combinations of impurities. The model analysis yielded the following:

a) more accurate parameters that describe the deformation of the spectrum under pressure; the broadening of the d band and the overflow of the electrons;

b) the behavior of the exchange enhancement of the magnetism under pressure;

c) separation of the effect of "non-rigidity" of the bands in the density of states of alloys, due to electron scattering;

d) the position of the true maximum of the state-density curves of palladium;

e) demonstration of the feasibility of reconstructing sections of the state-density curve of an alloy with the aid of the susceptibility.

The simple models are convenient because they can be used to describe other systems under analogous situations. Further refinement and systematization of the model parameters will make it possible to predict the behavior of the electronic properties of a large class of alloys and compounds of transition metals.[5] Worthy of special attention, in our opinion, is a verification, with other systems, of the connection observed in palladium between the exchange interaction and the width of the d band.

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