

Magnetic and Crystallographic Characteristics of Solid Solutions of Gd in Pd and Pd-Ag Alloys*

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The range of solid solubility of gadolinium in palladium was determined by X ray analysis. The lattice parameters showed a linear increase from pure palladium to $\text{Pd}_{0.88}\text{Gd}_{0.12}$. At higher gadolinium concentrations ($0.12 < X_{\text{Gd}} < 0.25$) the existence of a two phase region was observed, the compositions of the phases being represented by the formulas $\text{Pd}_{0.88}\text{Gd}_{0.12}$ and Pd_3Gd . Magnetic measurements indicated ferromagnetic ordering at 6°K for $\text{Pd}_{0.9}\text{Gd}_{0.1}$ and at 4°K for $\text{Pd}_{0.98}\text{Gd}_{0.02}$. From the saturation magnetization at liquid helium temperatures the moment associated with a solute gadolinium atom was determined to be $6.5 \mu_B$. Measurements of the susceptibility on $(\text{Pd}_{1-x}\text{Ag}_x)_{0.93}\text{Gd}_{0.07}$ alloys showed that gadolinium atoms in solid solution donate their valence electrons to the $4d$ and $5s$ band of palladium.

I. Introduction

Solid solutions of hydrogen, boron, tin, indium, cadmium, and silver in palladium have been intensively investigated by measurements of the heat capacity (1-3), susceptibility (4, 5), and determinations of activity coefficients (6-9). In these studies the conclusion was reached that the solute atoms donate their valence electrons to the $4d$ and $5s$ band of palladium. These investigations provided information about the band structure of palladium, which is shown schematically in the inset of Fig. 4. The high density of states at the Fermi level $N(E_F)$ produces a large value of the heat capacity, and the 0.56 holes in the $4d$ band are responsible for the substantial paramagnetism of palladium. The band structure further indicates that palladium should be a very suitable metal for studying the electronic nature of solute atoms. The rapid decrease in the density of states with rising Fermi energy which occurs when electrons from solute atoms are added to the palladium bands influences the heat capacity and susceptibility to a large extent. Measurements of these quantities make possible an evaluation of certain important electronic characteristics of the system, e.g., the

number of holes in the d band and the number of electrons donated per solute atom.

The present paper represents a study of solid solutions of gadolinium in palladium. The range of solid solubility was determined by X ray analysis. Saturation magnetization values at liquid helium temperatures and thermomagnetic data of some Pd-Gd alloys are reported. In view of previous results (1-9) we would expect that gadolinium also would serve as a donor of electrons. This assumption is based on the idea that the electronic states of gadolinium solute atoms are higher than the Fermi energy so that the electrons will not occupy localized states but instead will enter the conduction band of palladium (10). To substantiate this assumption by heat capacity measurements is not feasible, as recently published results indicate (11). Heat effects associated with the magnetic ordering at low temperatures prevent a determination of the electronic specific heat. Magnetic susceptibility measurements on Pd-Gd alloys are also not a completely satisfactory method of demonstrating the assumed behavior since the range of homogeneous solid solution is limited to 12 atomic percent gadolinium and hence the increase in electron concentration is not sufficient to fill up all $4d$ holes.

The method employed in this study for

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evaluating the number of electrons donated by the gadolinium involved magnetic susceptibility measurements on alloys of the ternary system Pd-Gd-Ag. X ray diffraction measurements showed that palladium can be replaced by silver in the palladium-gadolinium solid solution. Silver has the same band structure as palladium and in solid solutions the valence electron of silver is donated to the palladium band (1, 3) (see Fig. 4). The variation of the magnetic susceptibility with silver content measured on solid solutions with a constant gadolinium concentration can therefore be used to determine the number of electrons donated by the rare earth element.

II. Experimental Details

The samples used in the present study were prepared by induction melting in a water-cooled copper boat under a purified argon atmosphere. The starting materials were of 99.9% purity or better. Annealing was carried out under vacuum for 10 days at 900°C.

Lattice parameters were determined with a GEXRD-5 diffractometer using Zr-filtered molybdenum radiation. Magnetic results were obtained by the Faraday method using equipment that has been described elsewhere (12). Paramagnetic susceptibilities of $(\text{Pd}_{1-x}\text{Ag}_x)_{0.93}\text{Gd}_{0.07}$ solid solutions were determined with the same equipment at room temperature, using pressed powder samples with weights of about 1 g.

III. Results and Discussion

The results of the X ray investigation are given in Fig. 1. The lattice parameters increase linearly from $a = 3.89$ for pure palladium to $a = 3.987$ for $\text{Pd}_{0.88}\text{Gd}_{0.12}$, indicating that gadolinium forms continuous solid solutions with palladium over this composition range. The volume per gram atom of the alloy of composition $\text{Pd}_{0.88}\text{Gd}_{0.12}$ is found from the measured lattice parameter to be $9.54 \text{ cm}^3/\text{g-atom}$. An ideal solution would have the value $10.61 \text{ cm}^3/\text{g-atom}$. This negative deviation from ideal behavior is consistent with the observed stability of the alloys. At higher gadolinium concentrations ($0.12 < X_{\text{Gd}} < 0.25$) a second phase was observed which occurred together with $\text{Pd}_{0.88}\text{Gd}_{0.12}$. The additional phase was identified as Pd_3Gd ($a = 4.09 \text{ \AA}$).

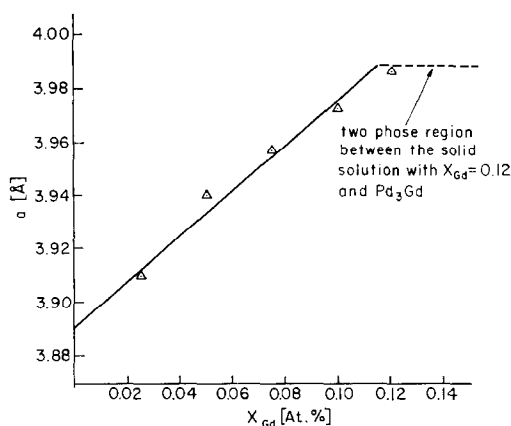


FIG. 1. Lattice parameters of Pd-Gd alloys versus Gd concentration.

The saturation magnetization μ_s at 4.2°K, which is plotted in Fig. 2 as a function of the gadolinium concentration, was determined by extrapolating the measured magnetization to $1/H = 0$. The difference between this curve and the paramagnetic contribution of palladium is due to the ferromagnetic ordering of the gadolinium spins. The moment per gadolinium atom, derived from this plot is $6.5 \mu_B$, which is about $0.5 \mu_B$ smaller than the expected value of $7 \mu_B$ for gadolinium. This deficiency could arise from failure to reach saturation at 4.2°K. In this case, however, alloys with a lower gadolinium concentration and hence also a lower Curie temperature (see Fig. 3) should exhibit greater deficiencies. The slope of the line in Fig. 2, however, is constant within the limits of experimental accuracy, indicating a constant atomic moment for Gd. This leads us to believe that the polarization of the palladium 4d band with a net

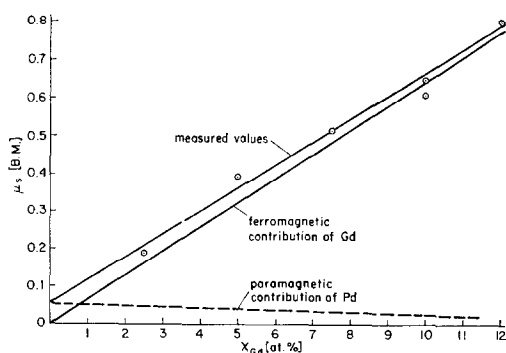


FIG. 2. Saturation magnetization of Pd-Gd alloys versus Gd concentration in Bohr magnetons per gram atom.

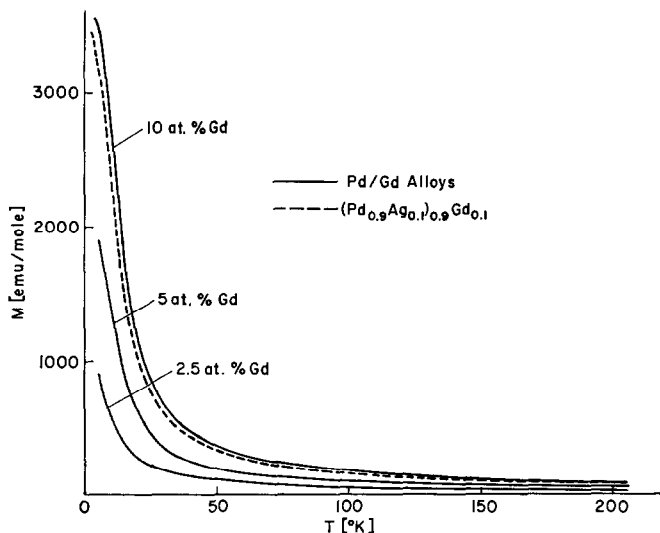


FIG. 3. Magnetization versus temperature curves at 19,000 Oe for some Pd-Gd alloys and for $(\text{Pd}_{0.9}\text{Ag}_{0.1})_{0.9}\text{Gd}_{0.1}$.

alignment of spins opposite to the gadolinium moment is responsible for the diminished Gd moment. This conclusion is in agreement with measurements of the g -shift by EPR on gadolinium-doped palladium-silver alloys (13). The g -shift, due to interactions between gadolinium ions and the $4d$ electrons, disappears at a silver concentration of about 55 atomic percent, when the $4d$ band is filled up.

Magnetization versus temperature curves for some Pd-Gd alloys and $(\text{Pd}_{0.9}\text{Ag}_{0.1})\text{Gd}_{0.1}$, measured with an applied field of 19 kOe are given in Fig. 3. Even alloys with a small gadolinium concentration exhibit magnetic ordering at low temperatures, indicating a long-range

interaction between the gadolinium atoms. The Curie temperatures, determined from measurements at relatively low field (2000 Oe) by a plot of M^2 versus temperature, are between 6°K for $\text{Pd}_{0.9}\text{Gd}_{0.1}$ and 4°K for $\text{Pd}_{0.975}\text{Gd}_{0.025}$. The substitution of silver for palladium has only a negligible influence on the magnetic behavior at low temperatures as indicated by the results for $(\text{Pd}_{0.9}\text{Ag}_{0.1})_{0.9}\text{Gd}_{0.1}$ in Fig. 3.

Magnetic susceptibility data at room temperature for Pd-Ag-Gd alloys are given in Fig. 4, which contains also the susceptibilities for the Pd-Ag system. In Pd-Ag alloys the $4d$ holes are filled up at the silver concentration $X_{\text{Ag}} = 0.55$. In an alloy doped with gadolinium

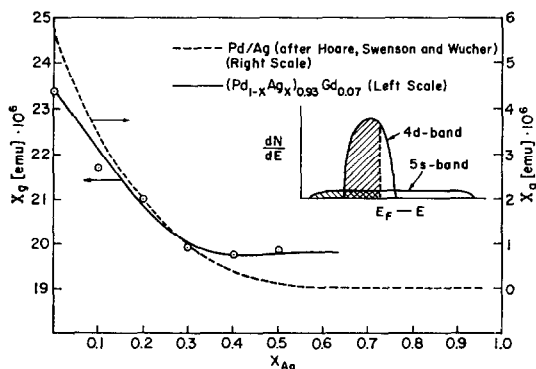
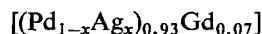


FIG. 4. Magnetic susceptibility data of Pd-Ag-Gd alloys and of Pd-Ag alloys. The inset gives a schematic representation of the band structure of Pd. Data for the broken curve are taken from Ref. (14).

on the other hand, the filling occurs at a silver concentration of about $X_{\text{Ag}} = 0.35$. The gadolinium therefore has donated 0.2 electrons. The assumption that the three valence electrons of gadolinium enter the conduction band of the alloy appears to be valid since the gadolinium concentration of 0.07 corresponds to an electron concentration of $3 \times 0.07 = 0.21$.

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