of the peak with increasing pressure could be due to many possible effects, including the changes in the background absorption, pressure effects on lattice vibrations, production of lattice defects, or effect from the NaCl matrix in which the CuCl particles are dispersed. A d^{10} to d^9s transition requires a mixing of symmetrical and antisymmetrical states, which is already present in the zincblende structure, but is somewhat increased by lattice vibrations.

For complete understanding of the band structure, a wide variety of measurements would be necessary on each compound. It is hoped that these optical measurements will promote some general understanding of the band arrangement of compounds of the same crystal structure, and of the effects in going from a purely valence crystal to a largely ionic compound.

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Ferromagnetism in Dilute Solutions of Cobalt in Palladium

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Measurements of the magnetic properties of solid solutions of cobalt in palladium show that ferromagnetism exists in solutions as dilute as 0.1 at. % of cobalt, when the cobalt atoms are about 10 at. diam apart. The ferromagnetic Curie point is established in this alloy by three different methods as 7°K. Bohr magneton numbers are determined for the whole series of alloys, and the moment associated with one cobalt atom is found to increase with dilution from 1.7 Bohr units in pure cobalt to a limit of 9 to 10 units in the greatest dilution. Lattice constants measured at room temperature show the effect of the onset of ferromagnetism at about 10 at.% cobalt. A simple model explains the magnitude and variation of the cobalt moment.

CONSTANT,[1] and more recently Gerstenberg,[2] have shown that dilute solutions of cobalt in palladium are ferromagnetic, and that the moment associated with one cobalt atom (the total ferromagnetic moment divided by the number of cobalt atoms) is greater than the atomic moment of pure cobalt. Working at temperatures above 80°K, ferromagnetism was observed[1,2] in alloys as dilute as 5 at. % cobalt. Crangle,[3] working to 20°K, has found ferromagnetism in solutions of iron in palladium as dilute as 1.25 at. % iron. If it is assumed that the total moment is carried by the iron atoms the moment per atom must be more than 7 Bohr magnetons. As Gerstenberg and Crangle point out, it must be concluded that some of the moment resides on the Pd atoms.

The present work was undertaken to find out how dilute the cobalt alloys could be made and still remain ferromagnetic. As shown below, the most dilute alloy studied, 0.1 at. % of Co in Pd, was found to be ferromagnetic even though the distance between Co atoms is about 10 at diam. Interpretation is given of the high moment per cobalt atom, and of ferromagnetic interaction over these long distances.

MATERIALS AND MEASUREMENTS

The palladium used was of 99.999% purity, the greatest impurities being 0.0002% each of Fe and Cu. The purity of the electrolytic Katanga cobalt was 99.91%, the principal impurities being 0.04% Fe and 0.04% Si. The constituents were melted in argon in pure fused silica and raised to about 1800° with high-frequency heating. After cooling they separated from the silica with no sign of corrosion. The loss in weight during melting was usually less than 0.1%. Spectroscopic analysis of the specimen containing 0.1 at. % Co showed a trace of silicon and iron to the extent of less than 0.001%; photometric analysis of Co gave 0.10 at. %.

Magnetic moments were measured in fields up to 12 koe at temperatures down to 1.3°K, as previously described.[4] The moment per atom of alloy was determined by extrapolation to $T=0$, $H=\infty$, except that in the most dilute alloys the paramagnetic moment of pure palladium was subtracted before extrapolation. Curie points were determined by the classical Weiss-Forrer method and also by the method of plotting[5] H/σ_m vs σ_m^2, σ_m being the magnetization per mole.

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[1] F. W. Constant, Phys. Rev. **36**, 1654 (1930).

[2] D. Gerstenberg, Ann. Physik **2**, 236 (1958).

[3] J. Crangle, Phil. Mag. **5**, 335 (1960).

[4] R. M. Bozorth, H. J. Williams, and D. Walsh, Phys. Rev. **103**, 572 (1956).

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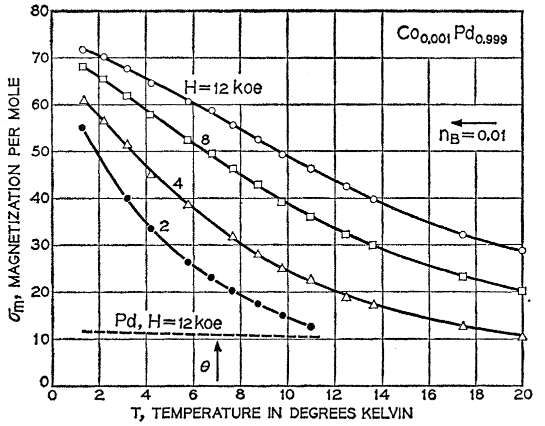

FIG. 1. Magnetic moments per mole (gram-atom) of alloy, at indicated field-strengths and temperatures. The broken line refers to a specimen of pure palladium.

RESULTS

Figure 1 shows as an example the measurements of moment vs temperature for the alloy containing 0.1 at. % Co. In this case the highest measured magnetization per mole is about 73, and in order to find the saturation ferromagnetic moment we have first subtracted the paramagnetic moment of pure Pd, for which the highest σ_m was observed to be 11.5. Similar corrections were made to the moments for various temperatures and field strengths. Hysteresis was observed at 1.3°K; the loop for a maximum applied field of 12 koe was found to have a vertical height of 15% of σ_m at 400 oe.

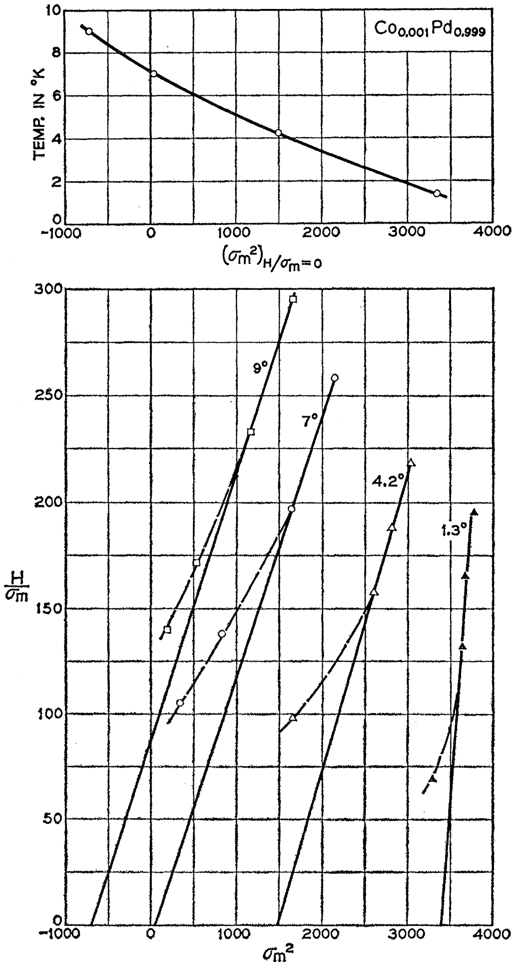

FIG. 2. Determination of Curie point of 0.1 at. % alloy, σ_m having been corrected for moment of pure Pd.

The Curie point of this alloy was determined most accurately by plotting H/σ_m vs σ_m^2, σ_m having been corrected in this case by subtracting the moment of pure Pd. Figure 2 shows that the lines drawn through the high-field points pass through the origin at about 7°K, the same Curie point as that determined by the Weiss-Forrer method.

The magnetization of pure Pd at $H=12$ koe is plotted as a broken line in Fig. 1, and the $1/\chi_m$ curve (at $H=8$ koe) is given in Fig. 3. No ferromagnetism was detected down to 1.3°K. A maximum in susceptibility was observed at about 80°K, in fair agreement with the results of Hoare and Mathews[6] who interpreted the maximum as evidence of antiferromagnetic behavior; the existence of antiferromagnetism is yet to be established. The paramagnetic moment above 85°K is $\mu_{\text{eff}}=1.8$; this corresponds to $S=0.5$ if we put $\mu_{\text{eff}}=2[S(S+1)]^{\frac{1}{2}}$. No appreciable changes in the values result from corrections for diamagnetism of the Pd core.

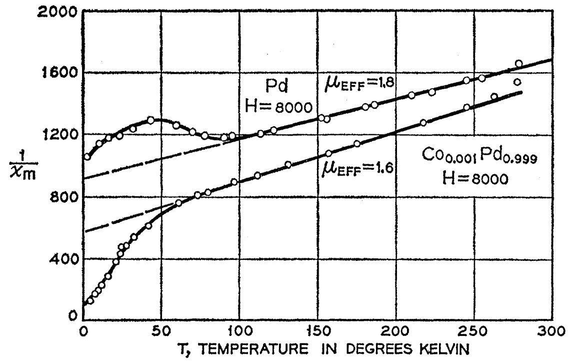

FIG. 3. Reciprocal susceptibility of palladium of high purity, showing maximum in χ at about 85°K, and of $Co_{0.001}Pd_{0.999}$ showing change in slope near the Néel point of Pd.

Average *ferromagnetic* moments per atom of alloy n_B and Curie points θ are given for the series in Figs. 4 and 5. Values of θ for compositions greater than 10 at. % Co are taken from Grube and Winkler.[7] At all compositions the curve of Fig. 4 lies above the straight line based on the idea that only Co atoms of moment 1.7 contribute to the total moment of the alloy. As nearly as can be determined both the moment and the Curie point extrapolate to zero Co, provided we sub-

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[6] F. E. Hoare and J. C. Matthews, Proc. Roy. Soc. (London) 212A, 137 (1952).

[7] G. Grube and O. Winkler, Z. Electrochem. 41, 52 (1935).

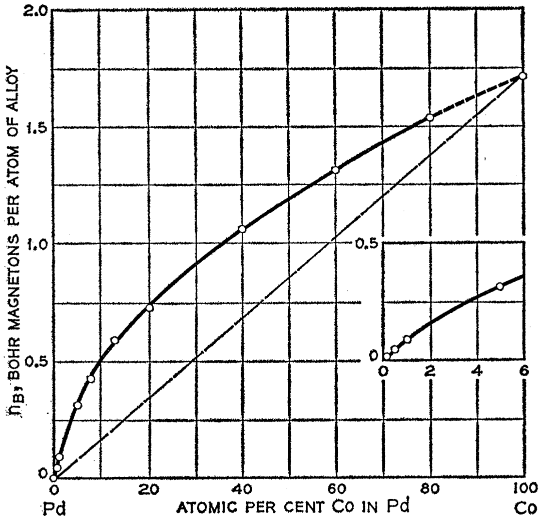

FIG. 4. Ferromagnetic moments per atom of alloy.

tract the paramagnetic moment of Pd as measured in the pure material.

If we divide the total moment by the number of Co atoms we have the moment associated with each Co atom without making any assumption as to whether the moment resides entirely on the Co atom, or partly on the Co, and the rest on some or all of the Pd atoms (see discussion). Such numbers, designated n_c and equal to n_B (fractional content of Co atoms), are plotted in Fig. 6. As the insert shows, n_c appears to approach a limit at zero Co of 9 to 10 Bohr magnetons. The scatter of the points below 1 at. % Co is presumably due to errors in the measurements, corrections, and composition.

From the plot of $1/\chi_m$ vs T for 0.1 at. % Co, given in Figs. 3 and 7 for various values of H, we find for the paramagnetic region that μ_{eff} is 1.6 in the range 80–300°K. The curve shows a marked change in slope at about 40° and approaches the Curie point when extrapolated to the temperature axis (weak field values). This change in slope is consistent with the coexistence of a small number of units of large moment and a larger number of units of small moment (see Discussion).

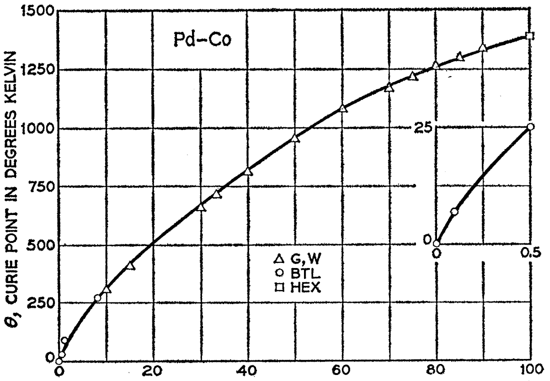

FIG. 5. Curie points of alloys. Data for the higher concentrations of cobalt are due to Grube and Winkler (see footnote 7 in text).

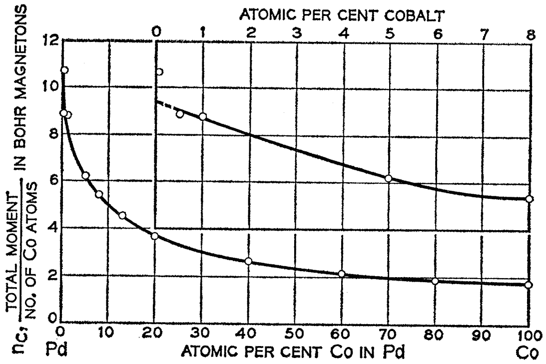

FIG. 6. Moment associated with one cobalt atom at various cobalt concentrations.

Ordinarily the initial susceptibility χ_0 is a maximum at the Curie point. We have determined the susceptibility in weak fields of 10 and 20 oe by placing the specimen in a coil and turning both coil and specimen together through 180°, the ends of the coil being connected to a galvanometer. Previous measurements[8] on the solid solution $Gd_{0.08}Ce_{0.92}Ru_2$ showed that the maximum in χ_0 occurred at 6.2°K while the Curie point as determined by the Weiss-Forrer method was 6.4°K. However, in the alloy of 0.5 at. % Co in Pd χ_0 was found to be a maximum at about 14°K while θ determined by the Weiss-Forrer method was 26°K. In the 0.1 at. % alloy no maximum in χ_0 was observed. We conclude from the agreement between the values of θ determined by three methods [(1) Weiss-Forrer extrapolation; (2) H/σ_m vs σ_m^2 plots; and (3) $1/\chi_m$ vs T extrapolation] that the true Curie point of the 0.1 at. % alloy is 7±1°K and that χ_0 is not a maximum at the Curie point in dilute alloys of this system.

Preliminary examination of cobalt additions to other elements of the Pd and Pt triads indicates that a solution of 1 at. % in Pt is ferromagnetic, and that solutions of several percent in Rh are not ferromagnetic.

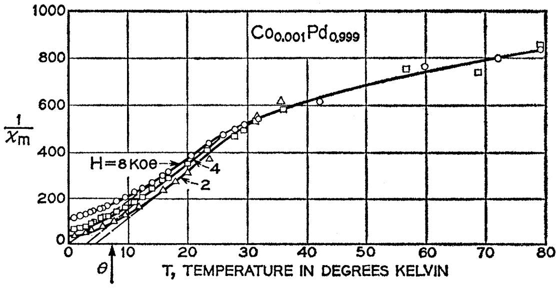

FIG. 7. Reciprocal susceptibility in the lower temperature range, showing dependence on field strength and extrapolation to ferromagnetic Curie point.

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[8] R. M. Bozorth, D. D. Davis, and A. J. Williams, Phys. Rev. **119**, 1570 (1960).

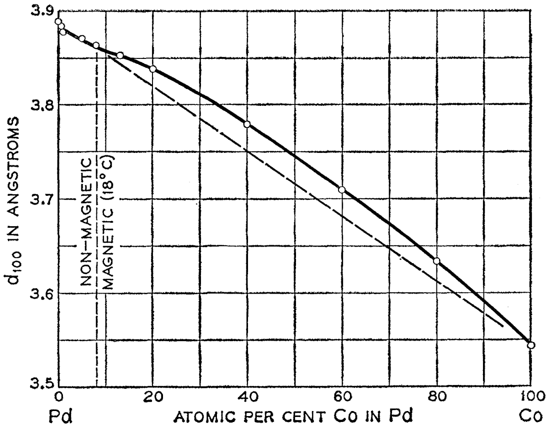

FIG. 8. Lattice constants of Co-Pd alloys.

X-RAY DATA

X-ray diffraction powder photographs of the alloys were taken at room temperature using Co $K\alpha$ radiation ($\lambda = 1.790$A). The lattice constants were calculated from the measured interplanar spacing of the (311) and (222) reflections (see Fig. 8). The samples used were unannealed filings, and gave rather broad lines particularly for the Co-rich alloys. The estimated error is 0.005A for the high-Co alloys, 0.002 for the low-Co alloys.

The form of the lattice constant vs composition curve is of the expected kind (convex upwards) for a system such as this is, which has a solidus that is concave upwards.

The curvature seems to disappear near 8–10 at. % Co. Alloys having less than this amount of Co are not ferromagnetic at room temperature. Qualitatively the change in the position of the curve at the onset of ferromagnetism is in accord with the change in the thermal expansion of Ni as it is heated through the Curie point: Williams[9] observed a contraction of about 1.5% as the magnetization is lost by heating. This is in the same direction, and several times as large, as the change in lattice constant in the Co-Pd alloys as they become nonmagnetic at room temperature with decreasing Co content.

DISCUSSION

In view of previous theoretical work on dilute alloys[10] it was somewhat surprising to find ferromagnetism in the dilute alloy that Crangle studied, 1.25 at. % Fe in Pd, and now it is even more surprising to find it when the concentration of the magnetic atom is 0.1 at. % so that the Co atoms are separated by 10 atomic distances, or somewhat less if their distribution departs from a close-packed arrangement.

A simple model accounts for the moment ($n_c = 9$ to 10) per Co atom, and for its rate of decrease with Co concentration. We assume that the moment on each Co atom is 1.7 (as in pure Co), and that each of its twelve nearest neighbor Pd atoms has a moment of 0.6 (corresponding to complete polarization of the 0.6 hole in the 4*d* band) and, finally, that more distant Pd atoms are nearly unpolarized. The essential feature of the model is the saturation of Pd moment on a shell of atoms surrounding a Co atom. At finite Co concentrations a certain fraction of these shells will overlap one another, and thus reduce the average moment per Co. A straightforward calculation shows that for small Co concentration, n_c decreases by about 1 Bohr magneton per atom percent Co. Both this figure and the total moment are in good agreement with the experimental values.

Polarization of the Pd atoms near a Co atom is caused by exchange interaction between the 4*d* electrons of Pd and the (localized) 3*d* electrons on the Co. However, because of the very large susceptibility and density of states in pure Pd, the exchange integral required for the saturation envisaged above is rather small. A value of a few tenths of an electron volt should be sufficient to saturate the Pd atoms nearest a Co atom.

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We are glad to acknowledge the benefit of discussions with Professor R. Brout, Dr. P. W. Anderson, and Dr. B. T. Matthias.

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[9] C. Williams, Phys. Rev. **46**, 1011 (1934).

[10] For example, H. Sato, A. Arrott, and R. Kikuchi, J. Phys. Chem. Solids **10**, 19 (1959); R. Brout, Phys. Rev. **115**, 824 (1959).