Effect of Pressure on the Curie Temperatures of *Pd*Co Alloys*

W. B. HOLZAPFEL,† J. A. COHEN,‡ AND H. G. DRICKAMER
Department of Physics, Department of Chemistry and Chemical Engineering, and Materials Research Laboratory, University of Illinois, Urbana, Illinois 61801

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Curie temperatures of *Pd*Co alloys having cobalt concentrations between 5 and 15 at.% are determined by thermal scanning of Mössbauer absorption at pressures up to 175 kbar. The results are discussed in terms of the models of Takahashi and Shimizu and of Kim.

I. INTRODUCTION

THE magnetic properties of alloys of Pd containing Co or Fe impurities have been investigated recently in a variety of experimental[1–12] and theoretical[13–18] papers. It is well established that the paramagnetic impurities induce large localized moments in the Pd host ($\sim 10\mu_B$/impurity in very dilute cases) and that the impurity spins couple ferromagnetically to one another indirectly through the Pd medium at long range (~ 10 Å). The static properties of these alloys are generally discussed in terms of the interaction of the impurity moments with the host's itinerant electrons and of the effective electron-electron interaction and high density of states in the pure host. Such models must account for both the composition and pressure dependence of the Curie temperature, which is a measure of the strength of the magnetic interactions in the host-impurity system.

The "thermal scanning of γ-ray resonance absorption"[8] provides a new tool for Curie-temperature measurements and has been used to determine the composition dependence of T_c in the *Pd*Co alloy system.[8] In the present work, this technique was adapted to high-pressure measurements in the 100-kbar range. The results are discussed in terms of the models of Takahashi and Shimizu[3] and of Kim.[14]

II. SAMPLE PREPARATION

The *Pd*Co alloys were fabricated at the Battelle Memorial Institute, Columbus, Ohio, by arc melting,[19] after which they were homogenized at 1200°C for 212 h in an Ar atmosphere. The resulting buttons were then cold-rolled to 0.001-in. thickness and cut into 0.120 ×0.014-in. rectangular strips. Each strip was electroplated with 1.5 mCi of Co^{57}, which was diffused into the sample bulk at 800°C for 12 h. After being annealed at 900°C for 1 h, the samples were slowly cooled over a period of 10–25 days. This treatment, which has been fully described elsewhere,[20] resulted in reproducible Mössbauer spectra for all samples. A conservative estimate of the uncertainty of the nominal Co contents of the alloys, after all heat treatment, is ±0.5-at.% Co.

III. EXPERIMENTAL TECHNIQUE

The high-pressure Mössbauer technique used in this work differs from earlier descriptions[21] only by the fact that both the radioactive source and the absorber are fixed, and that the counting rate is measured directly by a single-channel analyzer, ratemeter, and X-Y recorder as a function of the sample temperature. The temperature of the sample is measured by a thermocouple which is attached to one of the high-pressure anvils. Calibration measurements showed the value of the temperature gradients between the reference thermocouple and sample to depend on the heating rate. However, constant heating in all measurements ensured that this correction remain approximately constant and smaller than 1°K.

Thermal scanning of recoil-free γ-ray absorption has been used by earlier authors to determine Curie tem-

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† Present address: Physik-Department der Technischen Hochschule München, Munich, Germany.

‡ Present address: Department of Physics, University of Pennsylvania, Philadelphia, Pa.

[1] R. M. Bozorth, P. A. Wolff, D. D. Davis, V. B. Compton, and J. H. Wernick, Phys. Rev. **122**, 1157 (1961).

[2] B. W. Veal and J. A. Rayne, Phys. Rev. **135**, A442 (1964).

[3] T. Takahashi and M. Shimizu, J. Phys. Soc. Japan **20**, 26 (1965).

[4] G. G. Low and T. M. Holden, Proc. Phys. Soc. (London) **89**, 119 (1966).

[5] T. H. Geballe, B. T. Matthias, A. M. Clogston, H. J. Williams, R. C. Sherwood, and J. P. Maita, J. Appl. Phys. **37**, 1181 (1966).

[6] T. A. Kitchens and P. P. Craig, J. Appl. Phys. **37**, 1187 (1966).

[7] W. L. Trousdale, G. Longworth, and T. A. Kitchens, J. Appl. Phys. **38**, 922 (1967).

[8] B. D. Dunlap and J. G. Dash, Phys. Rev. **155**, 460 (1967).

[9] M. D. Wilding, Proc. Phys. Soc. (London) **90**, 801 (1967).

[10] D. M. S. Bagguley, W. A. Crossley, and J. Liesegang, Proc. Phys. Soc. (London) **90**, 1047 (1967).

[11] G. Longworth, Phys. Rev. **172**, 572 (1968).

[12] E. Fawcett, D. B. McWhan, R. C. Sherwood, and M. P. Sarachik, Solid State Commun. **6**, 509 (1968).

[13] T. Moriya, Progr. Theoret. Phys. (Kyoto) **34**, 329 (1965).

[14] D. J. Kim, Phys. Rev. **149**, 434 (1966).

[15] S. Doniach and E. P. Wohlfarth, Proc. Roy. Soc. (London) **A296**, 442 (1967).

[16] A. M. Clogston, Phys. Rev. Letters **19**, 583 (1967).

[17] N. Kumar and K. P. Sinha, Proc. Phys. Soc. (London) **92**, 426 (1967).

[18] I. A. Campbell, J. Phys. **C1**, 687 (1968).

[19] The alloys were kindly supplied by Dr. J. G. Booth of the Metal Science group, Battelle Memorial Institute, Columbus, Ohio.

[20] J. A. Cohen, thesis, University of Illinois, 1968 (unpublished).

[21] P. Debrunner, R. W. Vaughan, A. R. Champion, J. A. Cohen, J. A. Moyzis, and H. G. Drickamer, Rev. Sci. Instr. **37**, 1310 (1966).

peratures in *Pd*Co alloys at atmospheric pressure.[8] The known constant-temperature behavior of the Fe^{57} Mössbauer hyperfine parameters in *Pd*Co alloys under pressure[20] was used here to calculate the shape of the thermal-scanning curves. It was found that, within the present experimental accuracy, the change of the Curie temperature with pressure corresponded to the shift of the half-height point of the thermal-scanning curve. Two typical curves are shown in Fig. 1.

IV. EXPERIMENTAL RESULTS

The effect of pressure on the Curie temperatures of *Pd*Co alloys with Co concentrations between 5 and 15 at.% is shown in Fig. 2. The curves labeled I refer to fresh samples which have had the normal heat treatment outlined above. The curves labeled II have been reannealed after a first pressure run and show results comparable to the fresh samples.

The absolute Curie temperatures of the present alloys at atmospheric pressure are compared with the literature values in Fig. 3 and show good agreement.

V. DISCUSSION

Takahashi and Shimizu[3] have derived, by use of a molecular-field model, an expression for the Curie temperatures of Pd alloys containing low concentrations of Co or Fe. They obtain

$$T_c=\tfrac{4}{3}xJ^2[S(S+1)/Nkg^2\mu_B{}^2]\chi_0(T_c), \quad (1)$$

where χ_0 is the molar (temperature-dependent) paramagnetic susceptibility of the pure Pd host, x is the atomic fraction of Co or Fe impurities, J is an exchange energy representing the strength of the impurity moment—itinerant electron interaction—S is the impurity spin, N is the number of atoms per mole of sample, k is Boltzmann's constant, g is the electronic g factor, and μ_B is the Bohr magneton. Kim[14] has given a more rigorous quantum-statistical derivation of Eq. (1), in which the approximations involved are clarified.

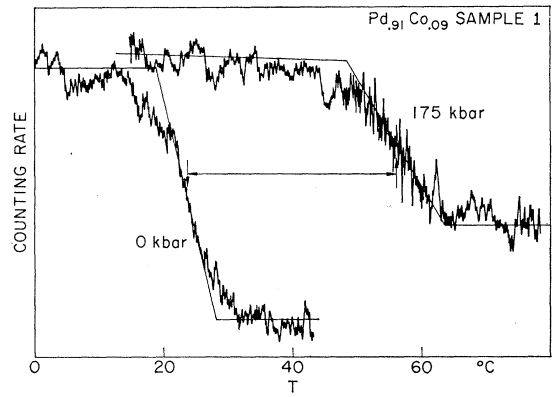

FIG. 1. Effect of pressure on thermal-scanning curves.

In order to solve Eq. (1) explicitly for T_c, we use the fact that, in the temperature range of interest here (between 150 and 450°K), the temperature-dependent paramagnetic susceptibility of pure Pd[1,3] can be well approximated by the empirical relation

$$\chi_0(T)=C/(T+\theta), \quad (2)$$

with $\theta=300$°K and $C=0.33$ emu deg/mole. From Eqs. (1) and (2),

$$T_c=\tfrac{1}{2}\theta[(1+Ax^{1/2})-1], \quad (3)$$

for $150<T_c<450$°K, where

$$A=(4C/B^2)4J^2S(S+1)/3Nkg^2\mu_B{}^2.$$

The best fit of Eq. (3) to the experimental data of the composition dependence of T_c is obtained with $A=88$ and gives the solid curve in Fig. 3. Using $S=1$,[3] this value of A corresponds to $J=0.16$ eV, which is the value of J found by several authors for the *Pd*Fe system.[14,15]

Differentiation of Eq. (3) yields

$$dT_c/dp=C_1[(1+Ax)^{1/2}-1][C_2-(1+Ax)^{-1/2}], \quad (4)$$

where C_1 and C_2 are constants expressible in terms of the pressure derivatives of J, C, and θ. The experimental data of the composition dependence of dT_c/dp are fitted well by Eq. (4) with $C_1=0.62$°K/kbar and $C_2=0.54$. The solid curve in Fig. 4 shows this fit; the dashed curve represents an extrapolation of Eq. (4). The ranges of uncertainty of the fitted parameters are C_1 (−0.2 to +0.1) and C_2 (+0.11 to −0.04).

Equations (1) and (2) can also be used to predict the relative volume dependences of the exchange parameters J in the *Pd*Co and *Pd*Fe alloy systems. From Eqs. (1)

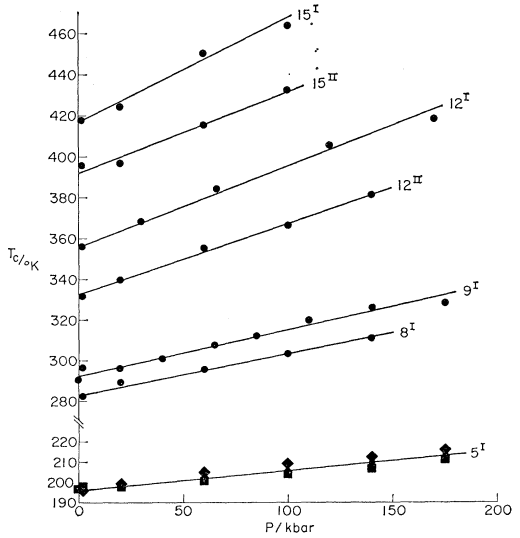

FIG. 2. Effect of pressure on Curie temperatures of *Pd*Co alloys with 5–15-at.% Co.

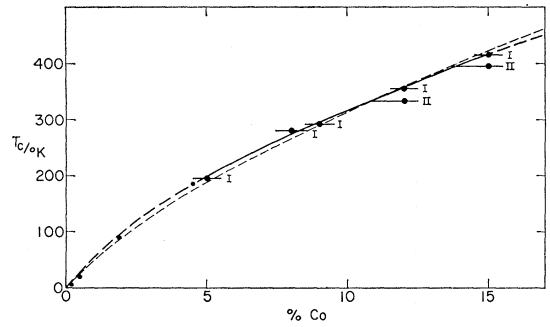

FIG. 3. Curie temperature of *Pd*Co alloys: light dashed line, values of Bozorth *et al.* (Ref. 1); closed circle, values of Dunlap and Dash (Ref. 8); closed circle on horizontal line, present data; solid line, best fit by Eq. (3); dark dashed line, extrapolation of Eq. (3).

and (2) it can be seen that

$$\frac{d\ln T_c}{d\ln V}=K_1-K_2\frac{T_c}{2T_c+\theta} \tag{5}$$

in the temperature range $150<T_c<450$°K, where

$$K_1=2\frac{d\ln J}{d\ln V}+\frac{d\ln C}{d\ln V}-\frac{d\ln\theta}{d\ln V}$$

and

$$K_2=2\frac{d\ln J}{d\ln V}+\frac{d\ln C}{d\ln V}-2\frac{d\ln\theta}{d\ln V}.$$

Thus, at a given T_c,

$$\left[\left(\frac{d\ln T_c}{d\ln V}\right)_{PdCo}-\left(\frac{d\ln T_c}{d\ln V}\right)_{PdFe}\right]_{T_c}=2\frac{d\ln(J_{Co}/J_{Fe})}{d\ln V}\frac{T_c+\theta}{2T_c+\theta}, \tag{6}$$

which is nearly independent of T_c in the range of validity of Eq. (5). Existing data on the volume dependences of T_c in *Pd*Co and *Pd*Fe[12] alloys do not cover overlapping

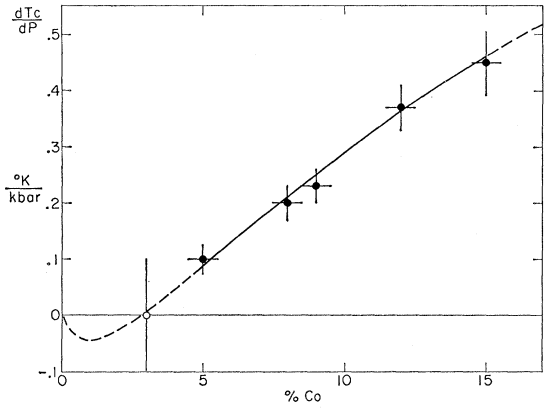

FIG. 4. Pressure coefficient dT_c/dP of *Pd*Co alloys: closed circle on two crossed lines, present data; solid line, best fit by Eq. (4); open circle on two crossed lines, value of D. C. McWhan and M. P. Sarachik [Bull. Am. Phys. Soc. **12**, 504 (1967)]; dark dashed line, extrapolation of Eq. (4).

ranges of T_c; however, extrapolations indicate that, from Eq. (6),

$$\frac{d\ln(J_{Co}/J_{Fe})}{d\ln V}\sim -0.8. \tag{7}$$

In conclusion, it has been shown that the models of Takahashi and Shimizu[3] and of Kim[14] are compatible with the present data on the pressure dependence of the Curie temperatures in *Pd*Co alloys. Further measurements over wider concentration ranges, of both *Pd*Co and *Pd*Fe, and also of the Pt alloys, would be desirable for further tests of the theory. In this conjunction, measurements of the pressure dependence of the susceptibility of pure Pd as a function of temperature would be extremely useful.

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