invar effects in FeNi are though to result from an antiferromagnetic direct Fe-Fe exchange interaction occurring in the fcc structure,^{84,85} and it has been observed that pressure tends to strengthen this antiferromagnetic interaction at the expense of ferromagnetic interactions.^{85,86} Thus T_C is suppressed by pressure in a ferromagnetic Invar-type alloy, or the Néel temperature T_N is enhanced if the alloy is antiferromagnetic. This effect has been observed in the fcc Fe-rich alloys $FePd^{87}$ and is consistent with the data of Möller and Drickamer in the fcc Pd-rich system PdFe; i.e., relative to the strongly *positive* pressure dependence of $T_c(p)$ in PdCo, the pressure dependence of $T_{c}(p)$ in PdFe is small or weakly negative. Conceivably Invar-type Fe-Fe interactions in the nondilute PdFe alloys tend to force T_c down with pressure, suppressing dT_c/dp below the positive values appearing in PdCo where such interactions are not present.⁸⁸

In the dilute alloys the pressure derivatives $dT_c/$ dp appear to be negative: Fawcett et al.³³ have found $dT_c/dp = -(4 \pm 4) \times 10^{-3}$ °K/kbar for $Pd_{0.997}Fe_{0.003}$ and $-(0.10\pm0.04)$ °K/kbar for Pd_{0.97}Fe_{0.03}, while Christoe et al.⁸⁹ have measured $dT_C/dp = -(0.09 \pm 0.01)$ °K/kbar for Pd_{0.97}Fe_{0.03} (averaged from 0 to 60 kbar). Fawcett et al.33 have also found $dT_c/dp = (0.0 \pm 0.1)$ °K/kbar for $\mathrm{Pd}_{0.\,97}\mathrm{Co}_{0.\,03}.$ If, as expected, the dilute alloys behave similarly with pressure, then dT_c/dp is negative in dilute PdCo. The positive dT_c/dp seen in the higher-concentration PdCo alloys is then similar to the situation in PdNi, where $dT_c/dp < 0$ for the dilute alloys and then increases with x, becoming positive for $x \gtrsim 0.20$ ⁴⁰ According to the above arguments involving the differences between the systems PdCo and PdFe at moderate concentrations, the behavior observed for $T_C(p)$ of PdCo in Ref. 44 must be characteristic of the nondilute regime, hence involving direct impurity-impurity interactions which are not treated by the model used in Ref. 44. Thus the fit afforded by the dilute-alloy model in Ref. 44, although sufficient, may not be necessary, and we note that a treatment involving directly interacting impurities^{15,71,90-93} might be more appropriate.

Before concluding we briefly present the pressure-dependent Fe^{57} isomer shifts for the current fcc *Pd*Co alloys, at 297 °K, in Fig. 9. The data of Ingalls *et al.*⁹⁴ for Fe^{57} in pure Pd (fcc) and Co (hcp) are also indicated. The *Pd*Co results are seen to be composition-independent and coincident with the Pd and Co data within experimental accuracy. The similarity of the pressure dependences of Fe^{57} isomer shifts in close-packed transition metals, noted by Ingalls *et al.*,⁹⁴ is maintained here. A more complete discussion of the effects of pressure on Fe^{57} isomer shifts in transition metals is given in Ref. 75.



FIG. 9. Pressure and volume dependences of Fe^{57} isomer shifts ϵ in *PdC*o alloys at 297 °K. Dashed and dotted lines are from Ref. 94.

V. CONCLUSION

In this work we have shown that the dramatic effects observed for the pressure-dependent Fe⁵⁷ hyperfine fields at 297 °K in a series of Pd_{1-r}Co_r alloys (with $x \simeq 0.08$, 0.09, 0.12, and 0.15) are due partially to the positively pressure-dependent Curie temperatures (cf. Fig. 4), but not entirely. Account must also be taken of the pressure dependences of the zero-temperature hyperfine field and of the host-impurity coupling constant. This coupling constant was first introduced by Jaccarino et al.⁶⁰ in a molecular-field treatment and is expected to be physically meaningful when the impurity has a localized well-formed moment (as seems to be the case for Fe^{57} in $PdCo^{5, 6, 72, 16}$) which is not too strongly coupled to the host magnetization.⁶² We have shown that the present data can be fitted semiquantitatively in the molecular-field approximation with two composition-independent parameters: $d \ln H_0 / dp \approx + (1.0 \pm 0.5) \times 10^{-3} / \text{kbar}$ and $d \ln \zeta / dp \approx -(3 \pm 1) \times 10^{-3}$ /kbar, and have noted that this fit is unique if the composition independence is assumed to be necessary, as seems reasonable. To our knowledge, a pressure-dependent host-impurity coupling constant has not been seen before in any metal. It was observable here only through the consistency requirements set by the series of alloys investigated.

Although it is not impossible that the effects seen here are related to Fe-clustering phenomena as described by Ferrando *et al.*²⁹ and Rubenstein³⁰ for Fe⁵⁷ in ferromagnetic PdNi alloys, this pos-

sibility can be regarded as unlikely for several reasons: (i) The Fe⁵⁷-clustering effects in PdNi were observed to disappear after long annealing times of several days. The annealing period here was still longer and at comparable temperatures. (ii) Since the alloy systems PdCo, PdFe, and CoFe are all random substitutional alloys, it is unlikely that the present ternary system PdCo(Fe) would tend to segregate under long annealing periods. (iii) The two distinct sets of hyperfine field patterns observed by Ferrando et al. as indicative of clustered and nonclustered Fe⁵⁷ were not seen here. Another possibility that the pressure effects observed in this work are related to demagnetizing effects of the foil samples and thus are not true microscopic phenomena can also be discounted. Although the foil samples are plastically deformed in the course of a pressure run (mainly they are squeezed thinner), the effects observed here are completely reversible, as noted earlier, and thus cannot be a function of the sample shape.

In parametrizing the finite-temperature impurity hyperfine-field problem for the present case of Fe^{57} in PdCo, we have shown that the positive pressure dependence of $|H_0|$ is probably due mainly to the positive pressure dependence of the hyperfine coupling constant |A|. The negative pressure dependence of $|\xi|$ indicates that the Fe^{57} impurity moment becomes progressively uncoupled from the host magnetization as the pressure increases. Comparison of the PdCo data with PdFe indicates that the positive pressure dependence of the Curie temperatures in this concentration regime is due, at least partially, to direct impurity-impurity interactions.

An important result of this work is the demonstration of the importance of impurity effects in measurements of the pressure dependence of impurity hyperfine fields in metals, particularly at finite temperatures. A similar importance of impurity effects has recently been discussed in relation to the pressure dependence of Fe⁵⁷ isomer shifts in transition and noble metals.75 Thus although one might expect to gain information on the pressure-dependent properties of the PdCo alloys via the magnitudes of the Fe⁵⁷ hyperfine fields, it is apparent here that one observes mainly the pressure-dependent properties of the Fe⁵⁷ impurity state itself and of its interaction with the host, through the pressure dependences of the coupling constants A and 5.95

ACKNOWLEDGMENTS

The authors wish to acknowledge the cooperation and skill of G. DePasquali in the preparation of the Mössbauer sources. We also thank J. G. Booth of the Battelle Memorial Institute for synthesizing samples, P. A. Beck for help with the metallurgy, and M. Cohen and K. R. Reddy for stimulating discussions. One of us (J. A. C.) performed essentially all of the analysis while at the Department of Physics, University of Pennsylvania.

APPENDIX

It seems not to be generally appreciated that the Brillouin-related molecular-field spontaneousmagnetization functions can be easily calculated to any desired degree of accuracy without recourse to graphical solutions or computers, if only the Brillouin functions themselves are available with sufficient accuracy. The procedure is simply to calculate the quantity

$$r(x) = \frac{3S}{S+1} \frac{B_S(x)}{x}$$
 (A1)

from the given $B_S(x)$. $\tau(x)$ here is just T/T_C , and a plot of $B_S(x)$ vs $\tau(x)$ is exactly the spontaneousmagnetization function $\sigma(T)/\sigma_0$ vs T/T_C for spin S, i.e., the function $f(T/T_C)$. The price paid for this ease of calculation is that the independent variable is x (implicitly) instead of T/T_C , which is a minor inconvenience.

The impurity response function $g(T/T_C)$ of Eq. (5) can also be calculated simply, by an extension of the above implicit method, *if* the host spontaneous-magnetization function $f(T/T_C)$ is expressed within the molecular-field theory. $g(T/T_C)$ is then given exactly by a plot of

$$B_{S'}\left(\frac{S+1}{3S}\zeta x\right) \mathrm{vs} \ \tau(x) , \qquad (A2)$$

where $\tau(x)$ is the same as in Eq. (A1). Here S is the effective spin/atom of the host, S' is the impurity spin, and ξ is the impurity-host coupling parameter of Eq. (5). Note that when S' = S and ξ = 3S/(S+1) the impurity's response is just that of the host itself, so that $g(T/T_C) = f(T/T_C)$.

In some situations it is desirable to generate a family of the ζ -dependent functions $g(T/T_c)$ from a given experimental $g(T/T_c)$, the host function $f(T/T_c)$ being unknown. For example, as mentioned in the text, a temperature-dependent measurement of the Fe⁵⁷ hyperfine field in a given alloy at p = 0 would give a zero-pressure function, say, $g_0(T/T_c)$, from Eq. (4). In order to investigate the behavior of the parameter $\zeta(p)$ it is then necessary to obtain the family of curves $g(T/T_c)$ related to $g_0(T/T_c)$ by simple variation of the parameter ζ , as in Fig. 7. From Eq. (5), this can be done according to

$$g(T/T_{c}) = B_{S'}\left(\frac{\xi}{\xi_{0}} B_{S'}^{-1}(g_{0}(T/T_{c}))\right), \qquad (A3)$$

where ζ_0 is the (unknown) value of ζ in $g_0(T/T_C)$, S' is the impurity spin, and B_S^{-1} is an inverse Bril-

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