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Magnetostriction of Dilute Magnetic Alloys

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Measurements of the magnetostriction and magnetization of two ferromagnetic *Pt*Fe alloys and a paramagnetic *Pd*Ni alloy are presented. The Belov equation for the free energy of a weak itinerant ferromagnet including magnetoelastic terms is used to estimate the volume dependence of the Curie temperature T_C. For the alloy $Pt_{0.99}Fe_{0.01}$, the resultant value is $\partial \ln T_C/\partial\omega = -47$, where ω is the volume strain. The volume dependence of the magnetization M, determined from the magnetostriction, is field dependent and decreases monotonically from $\partial \ln M/\partial\omega = -1.6$ at 35 kOe to $\partial \ln M/\partial\omega = -37$ at 2 kOe, where it is still decreasing rapidly. This behavior is in disagreement with the *s-d* interaction model, which was found to explain satisfactorily the behavior of *Pd*Fe alloys. The model predicts that $\partial \ln M/\partial\omega$ should be field independent and of the same order of magnitude as $\partial \ln T_C/\partial\omega$. In the alloy $Pt_{0.97}Fe_{0.03}$, it is not possible to estimate $\partial \ln T_C/\partial\omega$ from the Belov plots, because of domain effects. The value of $\partial \ln M/\partial\omega$ is constant and equal to -0.5 above about 15 kOe, but increases considerably at lower fields, as in $Pt_{0.99}Fe_{0.01}$, before domain effects intervene. The Belov equation is modified to describe the magnetostriction and magnetization of the paramagnetic alloy $Pd_{0.9811}Ni_{0.0189}$, and thereby to estimate the value, $\partial \ln \chi_A/\partial\omega = -19$, of the volume dependence of its susceptibility χ_A. The Belov equation and its modification for a strongly paramagnetic metal describe satisfactorily the field dependence of the magnetostriction, but not the magnetization, both for the ferromagnetic *Pt*Fe alloys and the *Pd*Ni alloy.

I. INTRODUCTION

Magnetostriction is the change of dimensions of a magnetic sample in a field. In a paramagnet, or in a ferromagnet for a field high enough to have overcome all effects of domain wall motion and domain rotation, the magnetostriction is of interest since, when combined with the magnetization, it measures the strain dependence of the interactions responsible for the magnetic properties of the sample.

We have measured the magnetostriction and magnetization of dilute alloys of iron in platinum (*Pt*Fe) and nickel in palladium (*Pd*Ni).[1] We compare the behavior of the *Pt*Fe alloys with similar results for *Pd*Fe alloys reported previously.[2] *Pt* Fe and *Pd*Fe alloys are ferromagnetic[3] and may be described phenomenologically by the free-energy expression for weak itinerant ferromagnetism,[4] which Wohlfarth[5] amended by adding volume-dependent terms introduced by Belov.[6] We find that the field dependence of the magnetization and the magnetostriction of *Pt*Fe alloys well below and through the Curie temperature T_C is consistent with the Belov equation for the free energy. Our resultant estimate of the volume dependence of T_C is very large and negative, in contrast with the small positive values measured directly for *Pd*Fe alloys.[2] The volume dependence of the magnetization of the *Pt*Fe alloys is field dependent even well below T_C, unlike that of the *Pd*Fe alloys, and decreases with increasing field to a value at high fields much smaller than the volume dependence of T_C. This behavior is not consistent with the predictions of the *s-d* interaction model, which was found to explain satisfactorily the behavior of the *Pd*Fe alloys.[2]

Small quantities of nickel in palladium rapidly increase the exchange-enhanced paramagnetic susceptibility until at a concentration of about 2 at.% the alloy becomes ferromagnetic. We find that the alloy $Pd_{0.9811}Ni_{0.0189}$ is paramagnetic when suitably annealed, though it shows clear indications of ferromagnetism when measured after remelting with no subsequent anneal. The Belov equation may be modified to describe the magnetostriction and magnetization of this strongly paramagnetic alloy, and so determine the volume dependence of its susceptibility.

II. EXPERIMENTAL

The magnetostriction was measured in longitudinal fields up to 35 kOe at various temperatures up to 20 °K by a capacitance method. The temperature was measured and controlled by reference to a germanium resistance thermometer, with corrections applied for its magnetoresistance. The magnetization was measured in fields up to 15 kOe by means of a pendulum magnetometer.

The alloy samples were prepared by fusion of the elements in an argon arc furnace. The starting materials were all of spectrochemical purity 99.999%. The platinum was in the form of wire, the palladium sponge, and the iron and nickel electrolytic. Each sample was melted several times to achieve uniformity of composition. The *Pd*Ni sample was annealed for 70 h at 1100°C at pressures below 10^{-6} Torr. This sample was remelted and measured again without annealing to investigate the effect of annealing.

III. MAGNETOSTRICTION OF DILUTE FERROMAGNETIC ALLOYS

In Figs. 1 and 2, we show the magnetization and the longitudinal magnetostriction of the dilute ferromagnetic alloy $Pt_{0.99}Fe_{0.01}$ as functions of the magnetic field at various temperatures in the neighborhood of the Curie temperature. Neither property is linear in the field and to discuss the observed behavior we employ the Belov equation for the free energy per unit volume, which we write, including higher-order magnetization and magnetoelastic terms,

$$F = F_{00} - \frac{1}{4\chi_0}\left(1 - \frac{T^2}{T_C^2}\right) M^2 + \frac{1}{8\chi_0 M_{00}^2} M^4 + O(M^6) + \cdots - HM + (1/2\kappa)\,\omega^2 - C(T)\,\omega(M^2 - M_0^2) + O(\omega M^4) + \cdots \quad (1)$$

We follow Wohlfarth's[5] notation, with ω as the relative volume change, $F = F(M, \omega)$, $F_{00} = F(0, 0)$, $M = M(H, T)$, $M_{00} = M(0, 0)$, $M_0 = M(0, T)$, $\chi_0 = [\partial M(H, 0)/\partial H]_{H\to 0}$, and κ as the compressibility, but generalize the lowest-order magnetoelastic term to accommodate temperature dependence of the coefficient $C(T)$. The relation between the

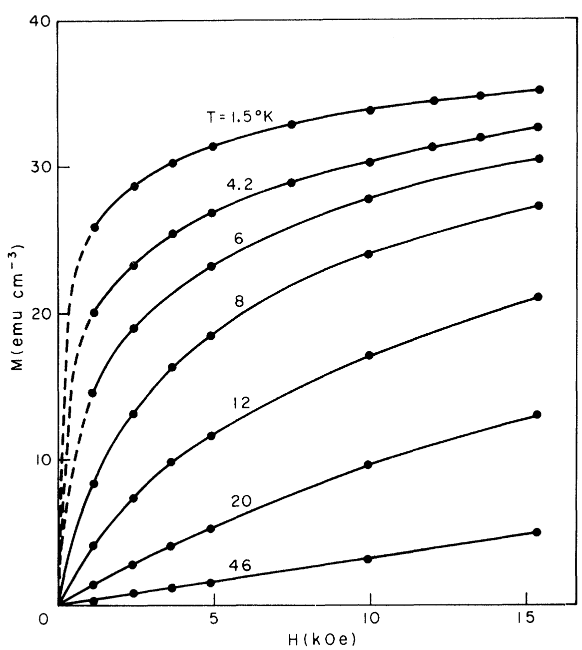

FIG. 1. Magnetization of $Pt_{0.99}Fe_{0.01}$ as a function of field at various temperatures.

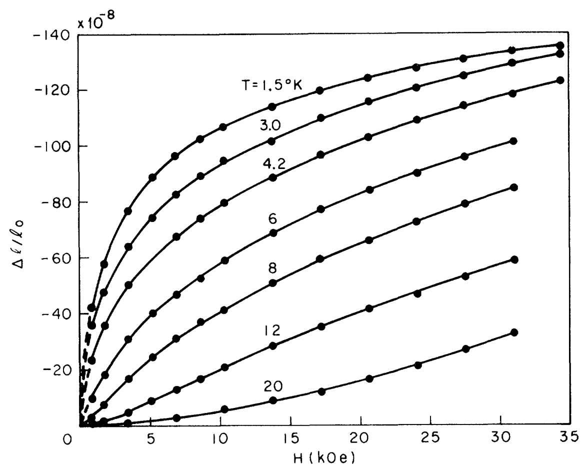

FIG. 2. Magnetostriction of $Pt_{0.99}Fe_{0.01}$ as a function of field at various temperatures.

magnetization and the field is obtained by minimizing F with respect to M in Eq. (1) with $\omega = 0$,

$$H = -\frac{1}{2\chi_0}\left(1 - \frac{T^2}{T_C^2}\right) M + \frac{1}{2\chi_0 M_{00}^2} M^3 + O(M^5) + \cdots . \quad (2)$$

Equation (2) suggests the use of an Arrott plot[7] of H/M versus M^2 to describe the magnetization data. The resultant curves shown in Fig. 3 are linear when H/M is small, but at the lower tem-

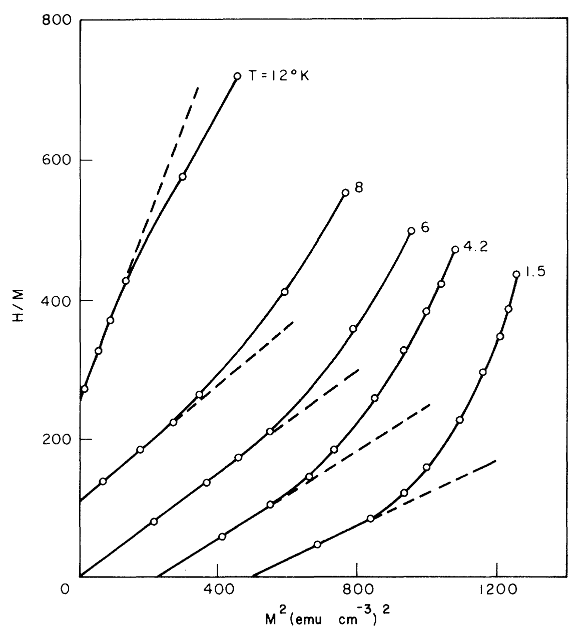

FIG. 3. Arrott plot for $Pt_{0.99}Fe_{0.01}$.

peratures the curves turn upwards to approach the saturation magnetization at higher values of H/M. We attribute this behavior formally to the effect of terms of order M^5 and higher in Eq. (2) [and therefore terms of order M^6 and higher in Eq. (1)]. We note further that the coefficients of all terms appear to be temperature dependent, whereas the Belov equation implies temperature dependence of only the first term in Eg. (2).

However, despite these deficiencies we can still employ Eq. (2) to deduce from the experimental data in Fig. 3 the Curie temperature, $T_C = 6\,^\circ\mathrm{K}$, from the criterion that the best linear fit to the data at low fields intersect the origin; the susceptibility, $\chi_0 = 3.6\times 10^{-3}\ \mathrm{cm}^{-3}$, from a plot (Fig. 4) of the limiting value of H/M at zero M versus $(1 - T^2/T_C^2)$; the magnetization, $M_{00} = 23.4$ emu cm^{-3} (corresponding to $3.8\,\mu_B$ per Fe atom), from the slope of the low-field linear fit to the data at the lowest measuring temperature, $T = 1.5\,^\circ\mathrm{K}$.

The magnetostriction is obtained by minimizing F with respect to ω in Eq. (1),

$$\omega = \kappa C(T)(M^2 - M_0^2) + O(M^4) + \cdots \quad . \qquad (3)$$

The data shown in Figs. 1 and 2 are combined to give in Fig. 5 a Belov plot of volume magnetostriction ω (assumed to be three times the longitudinal magnetostriction) versus the square of the magnetization at various temperatures, with magnetic field up to 15 kOe the implicit parameter. Evidently, at all temperatures a linear fit to the experimental data is possible, although the best linear fit at the Curie temperature, $T_C = 6\,^\circ\mathrm{K}$, having a

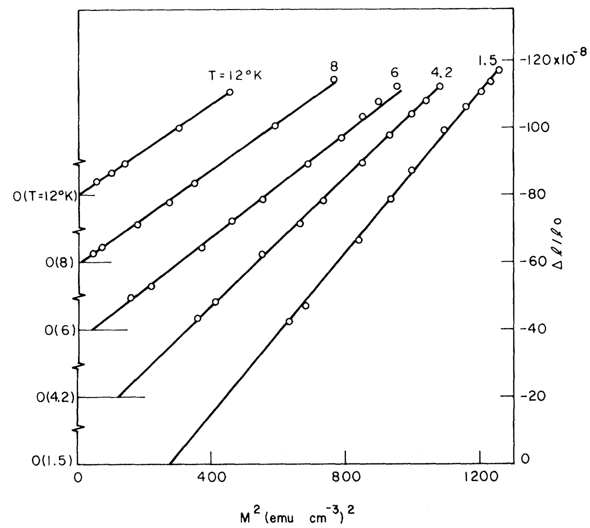

FIG. 5. Belov plot for $Pt_{0.99}Fe_{0.01}$.

slope $-1.8\times10^{-9}\ (\mathrm{emu/cm^3})^{-2}$, makes a positive intercept with the magnetization axis. It is clear from a comparison of Figs. 3 and 5 that in Eq. (1) the higher-order magnetoelastic terms are less important than the higher-order magnetization terms. It seems therefore a reasonable procedure to deduce the volume dependence of the magnetization parameters from the Belov plot.

The equation for the volume dependence of the Curie temperature may be obtained by equating to zero the volume derivative of the coefficient of M^2 in Eq. (1) at $T = T_C$, $M_0 = 0$, and $\omega = 0$, which gives

$$\frac{\partial \ln T_C}{\partial \omega} = 2C(T_C)\chi_0 \quad . \qquad (4)$$

From Eq. (3), we have $\kappa C(T_C) = \omega/M^2 = -1.8\times 10^{-9}$ $(\mathrm{emu/cm^3})^{-2}$, and substituting the measured susceptibility, $\chi_0 = 3.6\times 10^{-3}\ \mathrm{cm}^{-3}$, and the compressibility of platinum, $\kappa = 3.52\times10^{-13}$ cgs, we obtain $\partial \ln T_C/\partial\omega = -47$. This very large negative value of the volume derivative of the Curie temperature of $Pt_{0.99}Fe_{0.01}$ is in marked contrast with the small positive values measured directly for alloys of iron in palladium.[2] The latter was shown to be consistent with the small negative values of $\partial \ln M(H,0)/\partial\omega$ obtained from the negative magnetostriction, which in *Pd*Fe alloys is linear in field when $H \gtrsim 5$ kOe at temperatures well below the Curie temperature.[8]

It is instructive to estimate likewise the value of $\partial \ln M(H,0)/\partial\omega$ for $Pt_{0.99}Fe_{0.01}$ by determining the magnetostriction coefficient $l^{-1}\partial l/\partial H$ from the tangent to the magnetostriction curve in Fig. 2 for several fields H at the lowest measuring temperature, $T = 1.5\,^\circ\mathrm{K}$, which we assume to be essentially zero in writing $M = M(H,0)$. We take the corresponding values of the magnetization $M(H,0)$ from

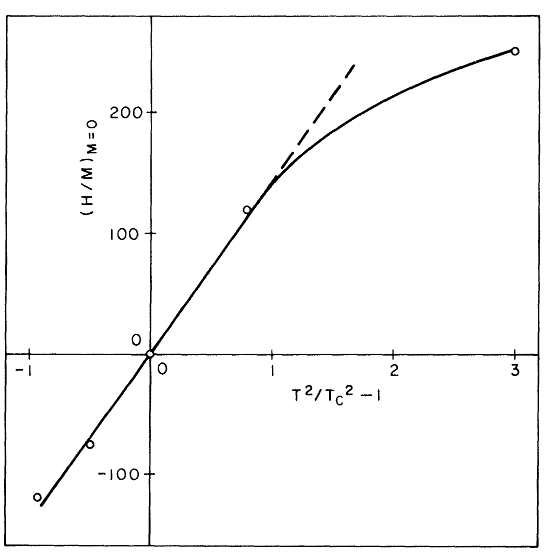

FIG. 4. Plot to determine χ_0 of $Pt_{0.99}Fe_{0.01}$ from Arrott plot.

Fig. 1, thus obtaining

$$\frac{\partial \ln M(H,0)}{\partial \omega} = \frac{3}{\kappa M(H,0)} \frac{1}{l} \frac{\partial l}{\partial H} , \qquad (5)$$

which is shown as a function of H up to 35 kOe in Fig. 6. The volume derivative of the magnetization is small and negative at large fields, but its magnitude increases rapidly with decreasing field and at low fields becomes comparable with the large negative value of $\partial \ln T_C/\partial\omega$. We note that this behavior is not associated with domain effects, since neither the magnetization nor the magnetostriction in Figs. 1 and 2 is hysteretic, and the magnitude of the magnetostriction coefficient, $|l^{-1}\partial l/\partial H|$, increases smoothly and monotonically as zero field is approached.

In contrast with the field variation of $\partial \ln M(H,0)/\partial\omega$ in $Pt_{0.99}Fe_{0.01}$, this quantity is essentially independent of field in *Pd*Fe alloys well below the Curie temperature T_C, until at low enough fields the magnetization and magnetostriction become nonlinear in field owing to domain effects.[8] Near T_C, which is roughly the same in $Pd_{0.997}Fe_{0.003}$ and $Pt_{0.99}Fe_{0.01}$, the field variation of the magnetostriction coefficient is qualitatively different in these two alloys. In $Pt_{0.99}Fe_{0.01}$, $|l^{-1}\partial l/\partial H|$ *decreases* monotonically as zero field is approached, whereas in $Pd_{0.997}Fe_{0.003}$, $|l^{-1}\partial l/\partial H|$ *increases* monotonically with decreasing field near T_C.[8]

In $Pt_{0.97}Fe_{0.03}$, whose magnetization and magnetostriction at several temperatures up to 20 °K are shown in Figs. 7 and 8, the magnitude of the magnetostriction coefficient at low temperature increases as field decreases as in $Pt_{0.99}Fe_{0.01}$. But in the former alloy, domain effects occur at low fields, as is clearly indicated in Fig. 9 by the change in sign of the magnetostriction coefficient $l^{-1}\partial l/\partial H$ at about 200 Oe. There is also some evidence of hysteresis, not shown in Fig. 9. Because of this behavior, the Arrott plots from the data of Fig. 7 become nonlinear at low fields, and it is not possible to estimate $\partial \ln T_C/\partial\omega$ from the Belov plots. However, it appears from the magnetostriction curves shown in Figs. 8 and 9 that $\partial \ln M(H,0)/\partial\omega$, which is constant with a value -0.5 for fields greater than about 15 kOe at 4.2 °K, does increase considerably at lower fields, as in $Pt_{0.99}Fe_{0.01}$, before domain effects intervene. At 16 °K and 20 °K the magnetostriction coefficient appears to increase again at higher fields.

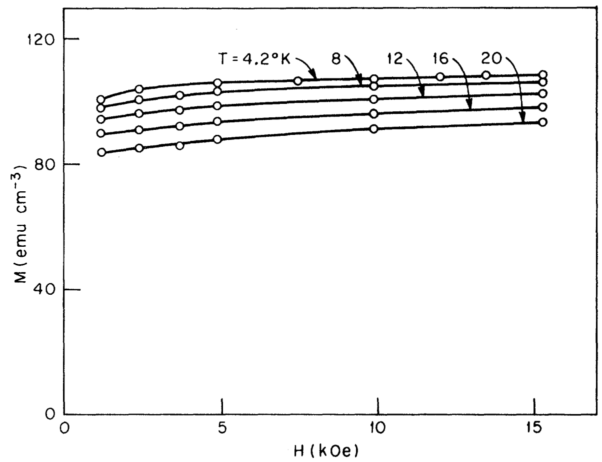

FIG. 7. Magnetization of $Pt_{0.97}Fe_{0.03}$ as a function of field at various temperatures.

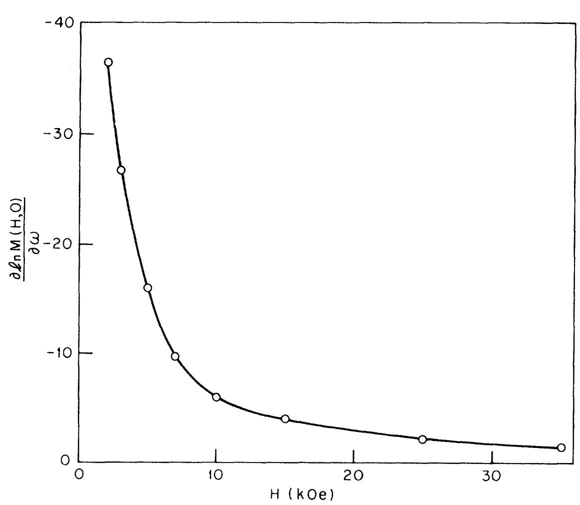

FIG. 6. Volume dependence of magnetization of $Pt_{0.99}Fe_{0.01}$ as a function of field at 1.5 °K.

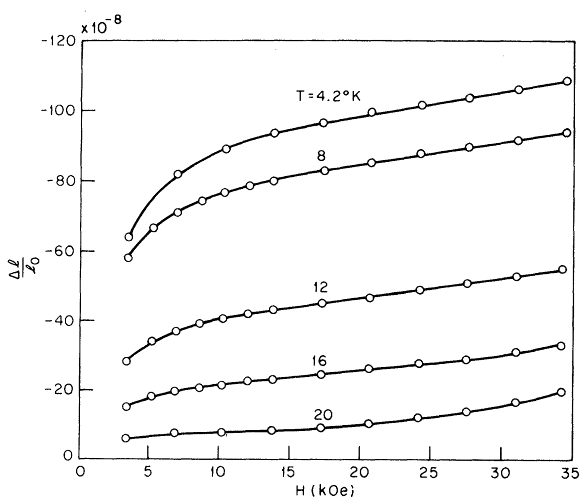

FIG. 8. Magnetostriction of $Pt_{0.97}Fe_{0.03}$ as a function of field at various temperatures.

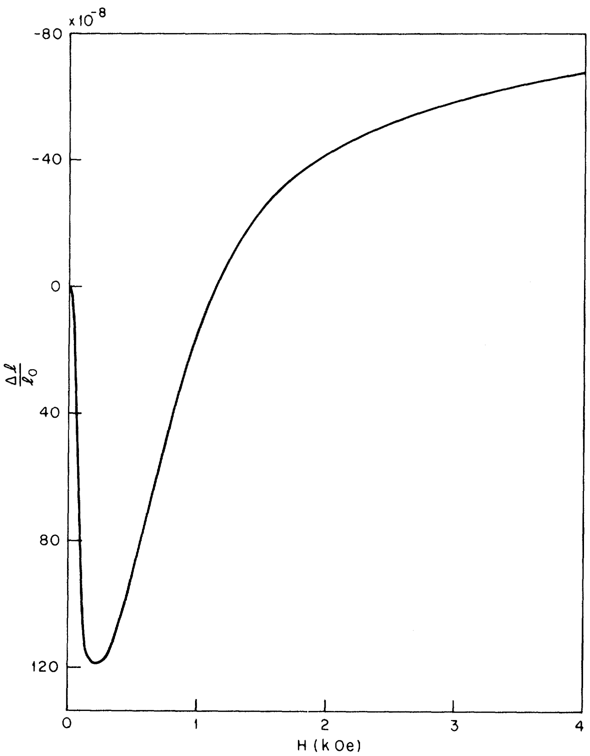

FIG. 9. Low-field magnetostriction of $Pt_{0.97}Fe_{0.03}$ at 1.5 °K.

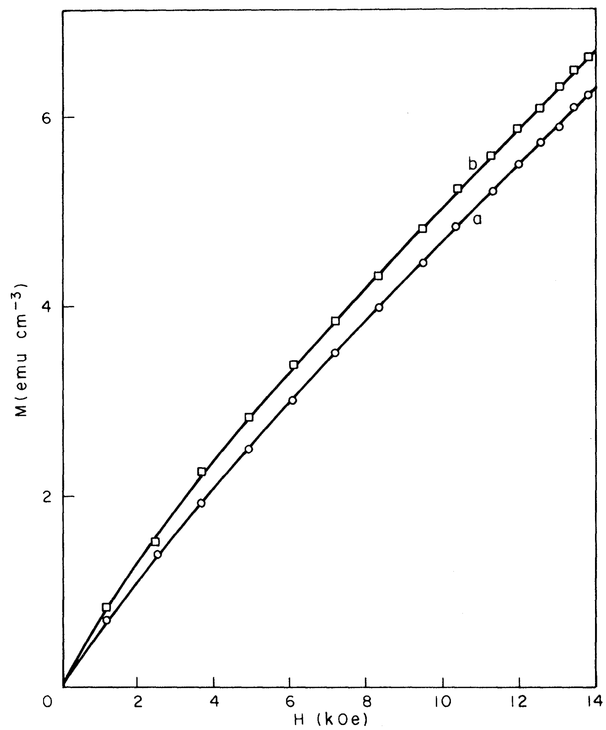

FIG. 10. Magnetization of $Pd_{0.9811}Ni_{0.0189}$ as a function of field at 1.4 °K.

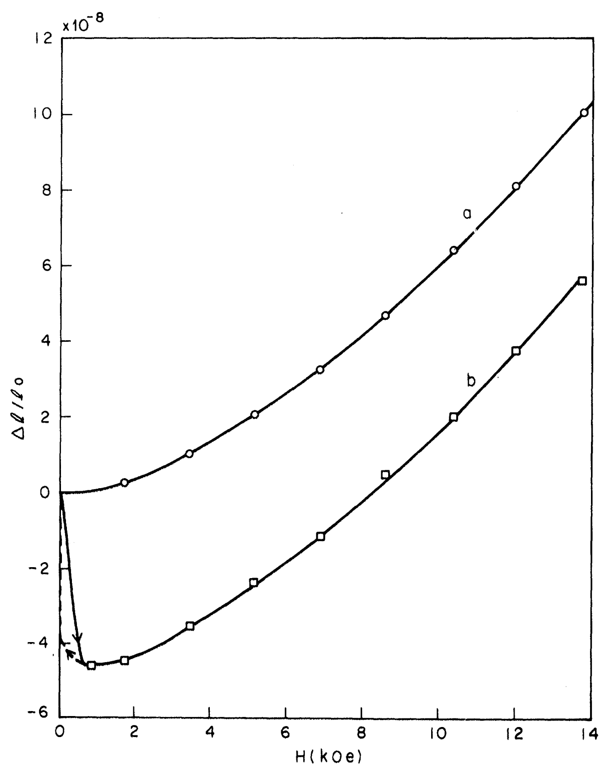

FIG. 11. Magnetostriction of $Pd_{0.9811}Ni_{0.0189}$ as a function of field at 1.4 °K.

IV. MAGNETOSTRICTION OF A DILUTE PARAMAGNETIC ALLOY

We assume that the free energy per unit volume of a strongly paramagnetic metal may be written in a form analogous to Eq. (1) as an expansion in even powers of the magnetization with coefficients which include the magnetoelastic energy

$$F = F_{00} + [1/2\chi(T)]\,M^2 + O(M^4) + \cdots - HM + (1/2\kappa)\,\omega^2 - C(T)\,\omega M^2 + O(\omega M^4) + \cdots \quad . \qquad (6)$$

The zero-field susceptibility, $\chi(T) = [\partial M(H, T)/\partial H]_{H\to 0}$, is now not assumed to have a specific temperature dependence as in the Belov equation, for which in the limit of zero field,[4] $\chi(T) = 2\chi_0[T^2/T_C^2 - 1]^{-1}$ when $T > T_C$. The expressions for the magnetization and the magnetostriction corresponding to Eqs. (2) and (3) are

$$H = M/\chi(T) + O(M^3) + \cdots \qquad (7)$$

and

$$\omega = \kappa C(T) M^2 + O(M^4) + \cdots \quad . \qquad (8)$$

We show in Figs. 10 and 11 the magnetization and the magnetostriction of the dilute alloy $Pd_{0.9811}Ni_{0.0189}$ as functions of the field. This alloy is strongly exchange enhanced, having a low-field low-temperature susceptibility about an order of magnitude greater than that of pure palladium, so that it may aptly be described as nearly ferromagnetic. Since it is a disordered alloy it is important to ensure that there are no locally Ni-rich regions which may be ferromagnetic. The magnetostriction of the annealed sample (Fig. 11, upper curve a) is a roughly quadratic function of field as one expects for a paramagnetic metal which has a roughly field-independent susceptibility (Fig. 10, lower curve a). But the sample which was arc melted and cooled rapidly with no subsequent anneal (Fig. 11, lower curve b) shows at fields up to about 0.7 kOe a large negative hysteretic magnetostriction, which at higher fields again resembles the behavior of the annealed sample. We attribute this behavior at low fields to the existence of ferromagnetic clusters of nickel atoms in the unannealed sample. The absence of such behavior in the annealed sample lends confidence to our interpretation of its magnetostriction as characteristic of a macroscopically homogeneous nearly ferromagnetic alloy. It is interesting to note that the effect of ferromagnetic clusters is much less pronounced in the susceptibility than in the magnetostriction; the differential susceptibilities of the two samples in Fig. 10 are almost identical above about 4 kOe like the differential magnetostriction in Fig. 11, but at low fields there is no evidence for spontaneous magnetization corresponding to the spontaneous magnetostriction seen in the unannealed sample. The Arrott plot for the magnetization (Fig. 12) shows that the higher-order terms in the Belov equation are so large as to make its use as an expansion for the free energy of doubtful value. However, the Belov plot for the magnetostriction (Fig. 13) shows that a linear fit to the experimental data is possible up to about 5 kOe, and the effect of higher-order terms at higher fields is much smaller than for the magnetization. It seems

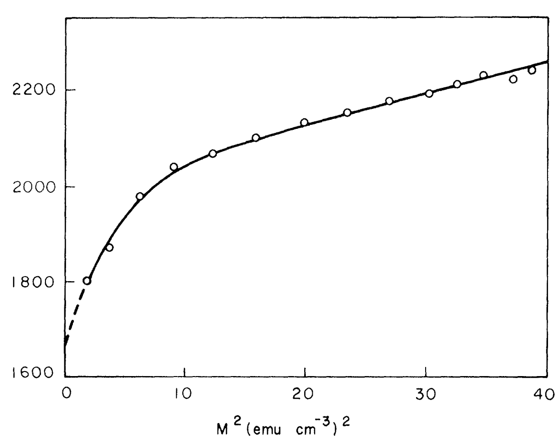

FIG. 12. Arrott plot for $Pd_{0.9811}Ni_{0.0189}$ at 1.4 °K.

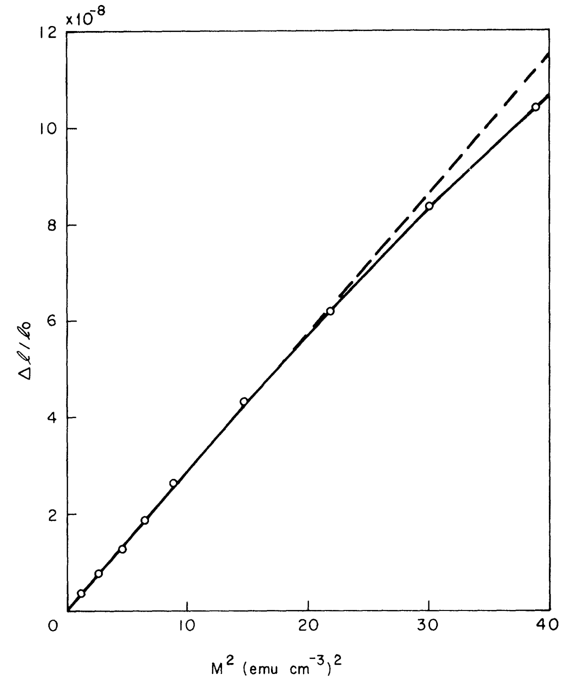

FIG. 13. Belov plot for $Pd_{0.9811}Ni_{0.0189}$ at 1.4 °K.

that in this nearly ferromagnetic alloy, just as in the ferromagnetic alloy, the higher-order magnetoelastic terms are somewhat smaller than the higher-order magnetization terms.

The equation for the volume dependence of the susceptibility of a paramagnetic metal may be obtained by equating to zero the volume derivative of the coefficient of M^2 in Eq. (6), which gives [cf. Eq. (4)]

$$\frac{\partial \ln\chi}{\partial\omega} = 2C(T)\chi(T) \quad . \tag{9}$$

For the paramagnetic alloy $Pd_{0.9811}Ni_{0.0189}$ we obtain from Fig. 13 and Eq. (8) the value, $\kappa C(1.5) = 8.63\times10^{-9}$ $(\mathrm{emu/cm^3})^{-2}$, with $\kappa = 5.42\times10^{-13}$ cgs, the compressibility of pure palladium. Extrapolation of the curve in Fig. 12 to zero magnetization gives $\chi(1.5) = 6.0\times10^{-4}$ $\mathrm{cm^{-3}}$. For these values of the experimental parameters we obtain the value $(\partial \ln\chi/\partial\omega)_{T=1.4\,^\circ\mathrm{K}} = 19$. This is somewhat greater than the value 15.3 given in Ref. 2, which was determined by a less satisfactory fitting procedure.

V. DISCUSSION

The dilute alloy systems *Pd*Fe and *Pt*Fe have been discussed by Takahashi and Shimizu,[9] who employ an s-d interaction model to describe their static magnetic properties. They show that if the $3d$ electrons of the iron atom impurity carries a local moment $g\beta S$ and the exchange interaction with the s electrons of the conduction band is J, the alloy will be ferromagnetic with a Curie temperature

$$T_C = N_{\mathrm{Fe}}\,[g^2\beta^2 S(S+1)/3k_B]\,J^2\chi \;, \tag{10}$$

where N_{Fe} is the concentration of iron and χ is the susceptibility of the host. In the low-concentration limit, the saturation magnetization is[10]

$$M(H\to\infty, 0) = N_{\mathrm{Fe}}\, g\beta S\,(1+\hat{J}\chi) \;, \tag{11}$$

where $\hat{J}$ is a normalized exchange interaction proportional to J.

From Eqs. (10) and (11), we expect the volume dependence of the Curie temperature and the saturation magnetization to be closely related, with

$$\frac{\partial \ln T_C}{\partial\omega} = 2\,\frac{\partial \ln J}{\partial\omega} + \frac{\partial \ln\chi}{\partial\omega} \tag{12}$$

and

$$\frac{\partial \ln M(H\to\infty, 0)}{\partial\omega} = \frac{\hat{J}\chi}{1+\hat{J}\chi}\left(\frac{\partial \ln J}{\partial\omega} + \frac{\partial \ln\chi}{\partial\omega}\right). \tag{13}$$

In the *Pd*Fe system,[2] the magnetostriction coefficient, at temperatures well below T_C and in high magnetic fields where it is constant, gives a value of $\partial \ln M/\partial\omega$ which is consistent according to Eqs. (12) and (13) with the directly measured pressure dependence of T_C, yielding $\partial \ln J/\partial\omega = +2.4\pm 0.5$.

However, the magnetostriction coefficient of the system *Pt*Fe appears not to be consistent with this formulation, since the very large negative volume derivative of T_C deduced from the Belov plots cannot be reconciled with the small negative magnetostriction coefficient at high fields. For example, in $Pt_{0.99}Fe_{0.01}$ we found a value, $\partial \ln T_C/\partial\omega = -47$, which when combined in Eq. (12) with the volume dependence of the susceptibility of platinum,[11] $\partial \ln\chi/\partial\omega = -12$, gives $\partial \ln J/\partial\omega = -17.5$. These values are far greater than the high-field value of $\partial \ln M(H, 0)/\partial\omega$ (see Fig. 6), and therefore are inconsistent with Eq. (13). The monotonic increase with decreasing field of the magnitude of the magnetostriction coefficient of $Pt_{0.99}Fe_{0.01}$, and therefore of $\partial \ln M(H, 0)/\partial\omega$ which eventually approaches the large value of $\partial \ln T_C/\partial\omega$, is qualitatively different from the behavior of the *Pd*Fe alloys and is not explained by the *s-d* interaction model.

The progressive increase of the volume dependence of the susceptibility in *Pd*Ni alloys with increasing nickel concentration was described in Ref. 1. The volume dependence of the susceptibility of the alloy, $\partial \ln\chi_A/\partial\omega$, was found to increase linearly with the exchange enhancement relative to palladium, $\chi_A/\chi_{\mathrm{Pd}}$. The present analysis of the experimental data for the most concentrated alloy $Pd_{0.9811}Ni_{0.0189}$ gives a value, $\partial \ln\chi_A/\partial\omega = -19$, which agrees well with a linear extrapolation of the data from lower concentrations.[1]

It is interesting to note that the Belov equation and its modification for a strongly paramagnetic metal describe satisfactorily the magnetostriction behavior both for the weakly ferromagnetic alloys and the strongly paramagnetic *Pd*Ni alloy, whereas the higher-order terms in the magnetization M make the equations of doubtful value to describe the field dependence of the magnetization for large values of M.

ACKNOWLEDGMENTS

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