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Magnetostriction of Paramagnetic Transition Metals. II. Group-VIII Metals Ru, Rh, Pd, Ir, Pt, and Their Alloys

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The longitudinal magnetostriction of group-VIII transition metals and alloys was measured with a capacitance dilatometer at 4.2 °K in fields up to 100 kOe. The resultant values of the logarithmic volume dependence of the magnetic susceptibility, $\partial\ln\chi/\partial\ln V$, are Ru, −4.8; Rh, 9.6; Pd, −3.4; Ir, 22; Pt, −15; $Rh_{50}Ir_{50}$, 15; $Rh_{50}Pd_{50}$, 8; $Ir_{40}Pd_{40}$, 14; $Pd_{67}Pt_{33}$, −4; and $Pd_{33}Pt_{67}$, −24. Pd, Pt, and their alloys have a negative magnetostriction, which indicates a negative volume dependence of the Coulomb interaction responsible for the exchange enhancement of their spin susceptibility. Rh, Ir, and their alloys with each other and with Pd have a positive magnetostriction, and the resultant large volume dependence of the susceptibility, particularly that of Ir, is difficult to understand. Float-zoned samples of Rh and Ir exhibit oscillatory de Haas–van Alphen magnetostriction at 4.2 °K.

I. INTRODUCTION

In this paper we describe longitudinal magnetostriction measurements on several group-VIII metals and alloys. The experimental procedure was described in a previous paper,[1] where we reported similar measurements on group-IV, -V, and -VI transition metals. The magnetostriction provides a measure of the volume dependence of the magnetic susceptibility, which in Pd and Pt is dominated by the exchange-enhanced Pauli paramagnetism. In these metals and their alloys the magnetostriction is negative, which indicates a negative volume dependence of the Coulomb interaction. In Rh and Ir and their alloys with each other and with Pd, the volume dependence of the susceptibility is large and positive. The very large value for Ir is particularly difficult to understand. Pure samples of Rh and Ir exhibited oscillatory de Haas–van Alphen magnetostriction, which we describe briefly pending a thorough study of the effect in these metals.

II. EXPERIMENTAL

The experimental techniques for measuring the magnetostriction were described in Ref. 1. The samples are described in Table I. Because traces of Fe can affect the low-temperature susceptibility of several of these metals to a marked degree, we give the Fe content when it is available.

The magnetostriction of the group-VIII metals up to 100 kOe at a temperature 4.2 °K is shown in Figs. 1 and 2. The samples Rh*A* and Ir*A* were

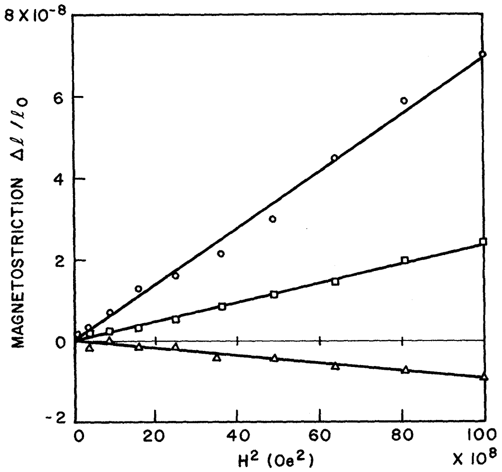

FIG. 1. Magnetostriction of Ru, Rh, and Ir: △, Ru; ○, Rh; □, Ir.

TABLE I. Group-VIII magnetostriction samples.

Period	Metal	Size (in.)	Source[a]	Preparation	Purity
4*d*	Ru	$1\times\frac{3}{16}$	INCO	float zoned	
	Rh*A*	$1\times\frac{3}{16}$	INCO	float zoned	
	Rh*B*	$1\times\frac{1}{4}$	Engelhard	arc melted	$<$10-ppm Fe
	Pd*A*	$1\frac{1}{2}\times\frac{1}{2}$	Materials Research Corp.	float zoned	70-ppm Fe
	Pd*B*	$1\times\frac{1}{4}$	Engelhard	arc melted	$\gtrsim$10-ppm Fe
	Pd*C*	$1\times\frac{1}{4}$	Matthey-Bishop	arc melted	4-ppm Fe
5*d*	Ir*A*	$\frac{3}{4}\times\frac{3}{16}$	INCO	float zoned	
	Ir*B*	$1\times\frac{1}{8}$	Sigmund Cohen	rolled bar	
	Pt	$1\frac{1}{2}\times\frac{1}{2}$	Sigmund Cohen	swaged bar	$\lesssim$ 1-ppm Fe
Alloys	$Rh_{50}Ir_{50}$	$\frac{1}{2}\times\frac{1}{4}$	Bell Telephone Labs	arc melted	
	$Rh_{50}Pd_{50}$	$\frac{1}{2}\times\frac{1}{4}$			
	$Ir_{60}Pd_{40}$	$\frac{1}{2}\times\frac{1}{4}$			
	$Pd_{67}Pt_{33}$	$1\times\frac{1}{4}$			
	$Pd_{33}Pt_{67}$	$1\times\frac{1}{4}$			

[a] We are indebted to the International Nickel Company for the extended loan of samples designated INCO; the alloy samples were prepared by E. Corenzwit and checked to ensure low Fe content.

sufficiently pure to show large de Haas–van Alphen magnetostriction oscillations at 4.2 °K. This makes measurement of the monotonic magnetostriction difficult and the results shown in Fig. 1 were measured on the less pure samples which did not show oscillatory magnetostriction. (The sample Ir*B* made from rolled bar was of course highly polycrystalline.) The magnetostriction in all cases is a quadratic function of the magnetic field and the coefficients are given in Table II. The values for Rh, Pd, and Pt are in reasonably good agreement with those obtained in previous measurements up to 37 kOe.[2]

The higher-field measurements show that Ir has a quadratic magnetostriction like the other metals, and the earlier measurements which indicated a linear magnetostriction[2] are now believed to be incorrect. This error was due to the anomalous behavior often observed at low fields,[1] which sometimes results in a nonzero intercept when the magnetostriction is plotted versus H^2, and may suggest a quasilinear region at low fields.

The nonzero intercept in Pd is of opposite sign to the high-field magnetostriction, as shown in Fig. 3. This behavior was found to be roughly the same and reproducible in the three Pd samples for which the value of the intercept varied from $+10$ to $+20$ $\times 10^{-10}$, a typical size. The explanation of this anomalous low-field behavior is not known. In Figs. 1 and 2 the zero of length is shifted so that the least-squares fit to the experimental points goes through the origin.

The values of the coefficient $\Delta l/l_0H^2$ for the higher-purity samples Pd*B* and Pd*C* were found to be in good agreement, but the magnetostriction coefficient of Pd*A* which contained 70-ppm Fe had the somewhat higher value $\Delta l/l_0H^2 = 24\times10^{-18}$. The susceptibility of Pd*A* was also found to be very temperature dependent at low temperature and rose to the value $\chi_g = 11.2\times10^{-6}$ emu g^{-1}, whereas the values for Pd*B* and Pd*C* at 4.2 °K were $\chi_g = 7.5$ and 6.7×10^{-6} emu g^{-1}, respectively.[3] The data shown in Figs. 2 and 3 were taken on the sample of Pd*C*.

The magnetostriction of the alloy samples is shown in Fig. 4. In most cases the intercept with the ordinate axis is nonzero. The high-field magnetostriction is quadratic in field, and the linear magnetostriction of $Ir_{60}Pd_{40}$ reported in Ref. 2 is now believed to be incorrect. The coefficients $\Delta l/l_0H^2$ are given in Table II. The resultant values of $\partial\ln\chi/\partial\ln V$ for all samples calculated from the formula[1]

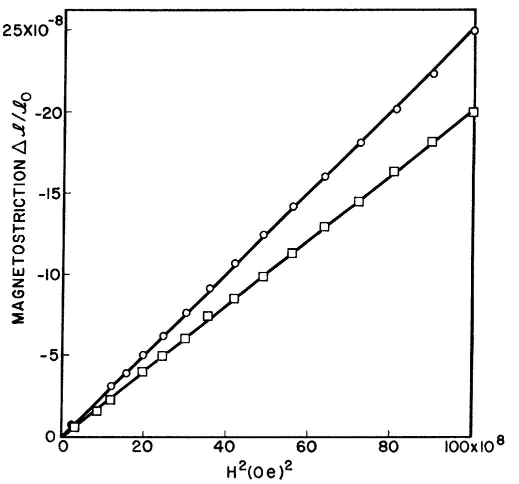

FIG. 2. Magnetostriction of Pd and Pt. ○, Pd; □, Pt.

TABLE II. Magnetostriction of group-VIII transition metals and alloys.

Period	Metal	$\Delta l/l_0H^2$ (10^{-18} Oe^{-2})	χ[a] (10^{-6} g at.$^{-1}$)	Ω/κ[b] (10^{+13} dyn cm)	$\frac{\partial \ln\chi}{\partial \ln V}$
4*d*	Ru	-0.9 ± 0.1	30	2.67	-4.8
	Rh	7.0 ± 0.3	100	2.29	9.6
	Pd	-25.0 ± 0.5	715	1.64	-3.4
5*d*	Ir	2.4 ± 0.1	20	3.09	22
	Pt	-20.0 ± 0.3	211	2.58	-15
Alloys	$Rh_{50}Ir_{50}$	6.0 ± 1	63	2.63	15
	$Rh_{50}Pd_{50}$	17.0 ± 1	247	1.90	8
	$Ir_{60}Pd_{40}$	8.5 ± 1	85	2.27	14
	$Pd_{67}Pt_{33}$	-11.0 ± 0.5	310	1.87	-4
	$Pd_{33}Pt_{67}$	-50.0 ± 3	270	2.17	-24

[a] Values of χ at 20 °K for Ir and Pt from D. W. Budworth, F. E. Hoare, and J. Preston, Proc. Roy. Soc. (London) A257, 250 (1960); χ for Ru from the room-temperature value 35×10^{-6} g at.$^{-1}$ given by H. Kojima, R. S. Tebble, and D. E. Williams, *ibid.* A260, 237 (1961), and corrected to 20 °K by assuming it to have the same temperature dependence as Ir; χ at 4.2 °K for Rh and Pd measured for our samples (see text); χ at 20 °K for the alloys from K. Andres and M. A. Jensen (Ref. 6).

[b] K. A. Schneider, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic, New York, 1964), Vol. 16, pp. 308, 320; for the alloys the values of Ω and κ are assumed to be the averages of the values for the constituent elements weighted according to composition.

$$\frac{\partial \ln\chi}{\partial \ln V} = \frac{6\Omega}{\kappa\chi}\,\frac{\Delta l}{l_0H^2} \tag{1}$$

are given in the last column of Table II.

The frequencies and amplitudes of the de Haas–van Alphen magnetostriction in the samples Rh*A* and Ir*A* at 4.2 °K in a 100-kOe field are given in Table III. The residual-resistivity ratio of these samples is estimated to be ~1000. The frequency 2.6 MOe near a ⟨110⟩ direction in Rh coincides with a branch of the de Haas–van Alphen spectrum, which Coleridge[4] identified with hole pockets at the center of the hexagonal face of the face-centered Brillouin zone.

III. DISCUSSION

It is difficult to account for the very large magnetostriction shown by some of the group-VIII metals and alloys. The Pauli-spin paramagnetism χ_s is thought to be the main contribution to the magnetic susceptibility of Rh.[5] When we write

$$\chi_s = \frac{2\mu_B^2 N(0)}{1 - N(0)V_c}\,, \tag{2}$$

the expression for the volume dependence of the susceptibility becomes

$$\frac{\partial \ln\chi_s}{\partial \ln V} = \frac{\partial \ln N(0)}{\partial \ln V} + \frac{N(0)V_c}{1-N(0)V_c}\left(\frac{\partial \ln N(0)}{\partial \ln V} + \frac{\partial \ln V_c}{\partial \ln V}\right)\,, \tag{3}$$

where $N(0)$ is the density of states at the Fermi surface and V_c is the screened Coulomb interaction between the conduction electrons. The exchange-enhancement factor $[1-N(0)V_c]^{-1}$ may be estimated by comparing the susceptibility and specific-heat densities of state in Table IV; and allowing for some phonon enhancement of N_γ, we estimate a value ~2. With $\partial \ln N(0)/\partial \ln V \equiv \gamma_e = 2.8$ we obtain by substitution in Eq. (3) a value $\partial \ln V_c/\partial \ln V = 0.6$. This value seems reasonable, but no such simple explanation of the large magnetostriction of Ir is apparent. Since for this metal $N_\gamma > N_\chi$ (see Table IV), both the exchange enhancement of the spin

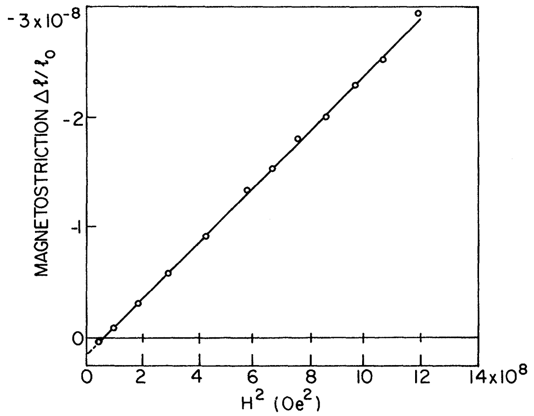

FIG. 3. Magnetostriction of Pd up to 37 kOe.

TABLE III. Oscillatory de Haas–van Alphen magnetostriction in Rh and Ir.

Metal	Frequencies (MOe)	Amplitude (10^{-8})
Rh	2.6	15
	0.8	5
Ir	8.5	25
	7.3	25

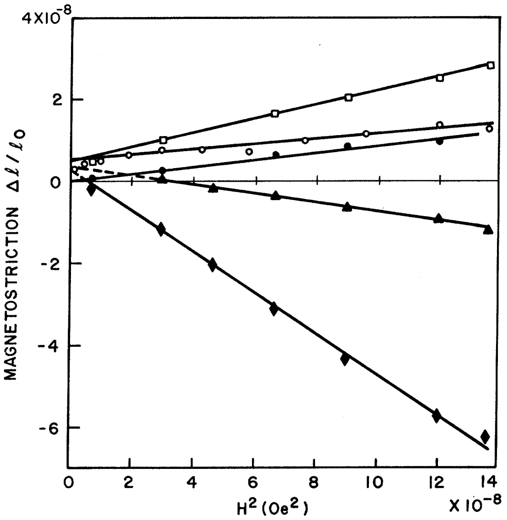

FIG. 4. Magnetostriction of group-VIII alloys. ○, $Rh_{50}Ir_{50}$; □, $Rh_{50}Pd_{50}$; ●, $Ir_{60}Pd_{40}$; ▲, $Pd_{67}Pt_{33}$; ♦, $Pd_{33}Pt_{67}$.

TABLE IV. Electronic Grüneisen parameter γ_e and densities of state for group-VIII transition metals.

Metal		γ_e^a	N_χ [b] (states/eV atom)	N_γ [b] (states/eV atom)
4*d*	Ru	• • •	0.5	0.7
	Rh	2.8	1.48	0.98
	Pd	2.2	12.1	1.96
5*d*	Ir	2.7	0.31	0.69
	Pt	2.4	3.27	1.38

[a] Grüneisen parameter for Rh, Pd, Ir from G. K. White, and A. T. Pawlosicz, J. Low Temp. Phys. (to be published); and for Pt from K. Andres, Physik Kondensierten Materie 2, 294 (1964).

[b] N_χ and N_γ from Ref. 6 except for Ru, whose susceptibility is given by H. Kojima, R. S. Tebble, and D. E. Williams, Proc. Roy. Soc. (London) A260, 237 (1961); and specific heat by F. Heiniger, E. Bucher, and J. Muller, Physik Kondensierten Materie 5, 243 (1966).

susceptibility and the orbital contribution to the susceptibility must be small, and there must be a significant diamagnetic contribution to the susceptibility. Thus the volume dependence of χ_s is roughly equal to the electronic Grüneisen parameter $\partial \ln \chi_s / \partial \ln V \simeq \gamma_e = 2.7$, and the large volume dependence of the total susceptibility, $\partial \ln \chi / \partial \ln V = 22$, must be due either to the orbital contribution χ_0 or to the diamagnetic contribution χ_{dia}. It is difficult to understand why either χ_0 or χ_{dia} should have such a large volume dependence.

In Pd the only significant contribution to the susceptibility is χ_s and the exchange-enhancement factor is large, $[1 - N(0)V_c]^{-1} \simeq 10$. Substitution of γ_e and $\partial \ln \chi / \partial \ln V$ in Eq. (3) gives $\partial \ln V_c / \partial \ln V = -2.7$. The value for Pt with an exchange-enhancement factor of about 4 is $\partial \ln V_c / \partial \ln V \simeq -6$. We have no explanation for the more rapid volume dependence of the Coulomb interaction in Pt than in Pd. The Pd-Pt alloys have negative magnetostriction like the elements Pd and Pt, but there appears to be little systematic variation of the magnitude of $\partial \ln \chi / \partial \ln V$ with alloy composition.

The alloys of Ir and Rh with themselves and with Pd have large positive values of $\partial \ln \chi / \partial \ln V$ like Ir and Rh. It is interesting to note that the systematic increase of susceptibility with electron density observed in a large number of group-VIII alloys[6] would indicate *negative* values of $\partial \ln \chi / \partial \ln V$ for all the group-VIII metals and alloys we have measured except Pd. Andres and Jensen themselves remark (see Fig. 9 of Ref. 6 and also Fig. 1 of Ref. 2) that the magnetostriction results show that the electron density is not an intrinsically important parameter in determining the susceptibility.

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