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Magnetostriction of Paramagnetic Transition Metals. I. Group 4 - Ti and Zr; Group 5 - V, Nb, and Ta; Group 6 - Mo and W

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The longitudinal magnetostriction of transition metals of groups 4, 5, and 6 was measured with a capacitance dilatometer at low temperature 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 Ti, −0.34; Zr, −1.6; V, 1.2; Nb, 1.7; Ta, 1.1; Mo, 14; W, 6.5. The contribution from the spin paramagnetism is obtained from the volume dependence of the density of states, which is estimated from the electronic Grüneisen coefficient with a correction for the electron-phonon coupling. The resultant values of the volume dependence of the orbital susceptibility for V, Nb, and Ta are physically reasonable. The negative magnetostriction of Ti and Zr is not inconsistent with their thermal expansion, but the large positive magnetostriction of Mo and W is difficult to understand. The samples of Mo and W exhibit oscillatory de Haas–van Alphen magnetostriction at 4.2 °K.

I. INTRODUCTION

It is notoriously difficult to separate experimentally the several contributions to the magnetic susceptibility of transition metals. We have attempted to do this by determining their magnetostriction, which provides a measure of the strain dependence of the susceptibility. We describe here the results for transition metals of groups 4, 5, and 6. Preliminary results were reported in Ref. 1, but most of the measurements have been repeated in larger magnetic fields to achieve greater accuracy. We defer until a later paper the results for group-8 metals and alloys.

We employ a differential capacitance dilatometer to measure the longitudinal magnetostriction, which is very small even in fairly strongly paramagnetic metals, typically between one and ten parts in 10^8 in a field of 100 kOe; the experimental problems associated with differential thermal expansion of the sample and the capacitance cell are obviated by performing the measurement at low temperature. Normally, a liquid-helium bath is used, but the Mo and W samples were sufficiently pure to exhibit oscillatory de Haas–van Alphen magnetostriction at 4.2 °K, and their monotonic magnetostriction was measured at liquid-hydrogen temperature.

In Sec. II we describe the apparatus and the experimental procedure for correcting the observed differential length change for the small magnetostriction of the copper capacitance cell. We describe rather carefully this measurement and a typical measurement on a Ta sample to illustrate how we deal with experimental problems such as drift and hysteresis of the apparatus. In Sec. III we present experimental data taken in fields up to 100 kOe, which supersede the lower-field data up to 37 kOe reported in Ref. 1. We describe also the lower-field data for Mo and W, since these metals show anomalous linear field dependence of the magnetostriction, which we attribute tentatively to physical defects, of the samples. The frequencies and amplitudes of the de Haas–van Alphen magnetostriction in Mo and W are also given, but these should be regarded only as very preliminary results pending a thorough study of oscillatory magnetostriction in these metals. We attempt in Sec. IV to explain the observed monotonic magnetostriction, which is expressed as the logarithmic volume dependence of the magnetic susceptibility $\partial \ln\chi/\partial \ln V$. The values of $\partial \ln\chi/\partial \ln V$ for the group-5 metals are of the expected sign and order of magnitude. But the negative sign of the magnetostriction for the group-4 metals, and particularly the large positive values of $\partial \ln\chi/\partial \ln V$ for the group-6 metals, are difficult to explain.

II. EXPERIMENTAL METHOD

The most demanding requirement of an experimental technique to measure magnetostriction in paramagnetic metals is high sensitivity. This follows from the small magnitude of the magnetostriction for a typical "nonmagnetic" metal. For example, Ta in a field of 100 kOe has a magnetostriction,

$$\frac{l(H)-l(0)}{l(0)}=\frac{\Delta l}{l_0}\simeq 125\times 10^{-10} \quad .$$

This is smaller than the magnetostriction of most transition metals, but nontransition metals may be expected to have a still smaller magnetostriction. We employ a differential capacitance dilatometer

which is capable of measuring fractional length changes of a few parts in 10^{10} in a sample about 4 cm long. The magnetostriction of Ta can therefore be measured with an accuracy of about 10%.

Instrumentation

The success of the capacitance dilatometer in high-sensitivity magnetostriction (and thermal-expansion) measurements depends directly on the recent development of precision methods of measuring small capacitances. White[2] described the first capacitance bridge designed specifically for this purpose, basing his design on the method of comparison of three-terminal capacitors in a bridge circuit with transformer ratio arms due to Thompson.[3] For several years, commercial bridges of this type have been available, and we employ a General Radio type 1615 instrument. The bridge is driven by a 5-kHz 100-V supply (these values are not critical), with the output fed to a phase-sensitive detector. For relatively large magnetostriction the magnetic field is swept at a uniform rate and the out-of-balance signal from the phase-sensitive detector is fed to the Y axis of a recorder, the X axis being fed from the field-measuring device. Because of the eddy currents in the walls of the capacitance cell and in the sample, this method is unsatisfactory for high-sensitivity measurements, and the data described here are taken in constant field after allowing the apparatus to settle down after changing the field. The earlier measurements described in Ref. 1 were made in a Westinghouse superconducting solenoid of niobium zirconium providing a 37-kOe field, while most of the measurements described here were made in an RCA superconducting solenoid of niobium tin providing 100 kOe.

Capacitance Cell

The construction of the capacitance cell illustrated in Fig. 1 follows closely White's[2] design. The body of the cell is a cylinder of oxygen-free high-conductivity (OFHC) copper, which after machining is annealed for 24 h in an inert atmosphere at about 500 °C to avoid creep and hysteresis on thermal cycling. The ends of the cylinder are surface ground and lapped flat and parallel to 0.0001 in. (0.1 mil), then gold plated and relapped. The length of the cylinder is about 1.5 in. (more precisely 1.4958 in.), and the 0.5-in.-diam sample is about 3 mil shorter. Since the required gap between the end of the sample and the capacitor plate should be about 3 mil *at low temperature*, the sample is made slightly longer or shorter according to whether its thermal expansion is larger or smaller than that of copper. The magnitude of the gap is not critical and reference to

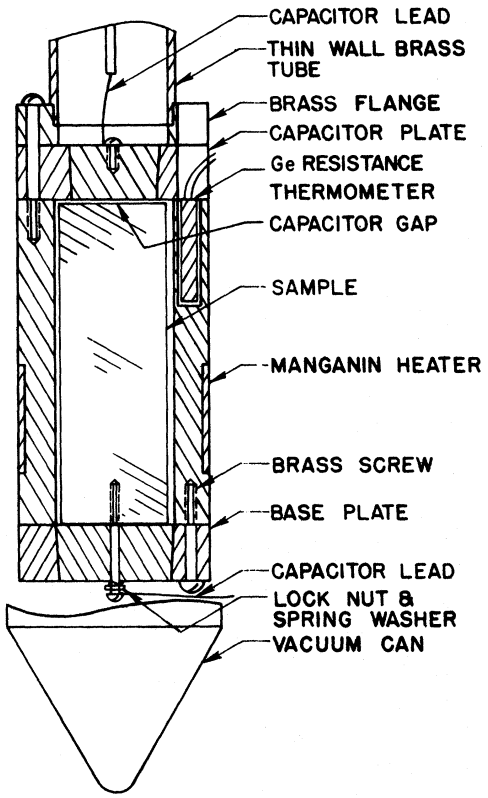

FIG. 1. Differential capacitance dilatometer for measuring magnetostriction and thermal expansion.

a compendium of thermal-expansion measurements[4] from room temperature to liquid-nitrogen temperature or below provides an accurate enough estimate of this correction.

The top end of the sample constitutes one plate of the capacitor, the other being a plug of OFHC copper which is surrounded by a guard ring of OFHC copper from which it is insulated by a fillet of Epoxy. Like the cylinder, the OFHC copper parts are annealed after machining, and the plug is then glued with Epoxy into the guard ring with a jig to prevent relative motion during hardening of the Epoxy. We used an Epoxy Scotch-weld-type EC-2186 made by the Minnesota Mining Co., which is cured at 350 °F for 1 h. The lower surface (narrow end of the taper) is ground and lapped flat and parallel to 0.1 mil, then gold plated and relapped. The gold plating of the cylinder, the capacitor plate, and guard ring, and the base plate, which is constructed in a similar manner, serves to improve their thermal contact at low temperatures and to prevent corrosion. There is some difficulty when lapping these plates, especially after gold plating, in avoiding shorting across the Epoxy insulator by metallic slurry, but this can be removed by agitation in an ultra-

sonic bath of solvent. The diameters of the center plug of the base plate and the capacitor plate are, respectively, $\frac{9}{16}$ and 0.4 in., and the annular gap between the center plug and the surrounding ring is 8 mil, the plug and the ring having a matching 2° taper. The lower lapped end of the sample is held firmly onto the lapped surface of the base plate by means of an 0-80 brass screw and spring washer. The base plate and capacitor plate are securely screwed to the cylinder by three 2-56 brass screws. The capacitance cell is enclosed within a 1-in.-diam vacuum can filled with about 10^{-1}-Torr helium exchange gas, which is immersed in liquid helium at 4.2 °K (or liquid hydrogen at 20.4 °K for some measurements). To change the sample the vacuum can is unsoldered and the three screws which attach the base plate to the cylinder are removed.

For thermal-expansion measurements the liquid-helium bath is pumped to a temperature below 1.5 °K and, with the vacuum can evacuated, the temperature may be rapidly controlled by means of the manganin heater at any value up to about 30 °K, indicated by the germanium resistance thermometer shown in Fig. 1.

Sample Preparation

Since the end plates of the capacitance cell are flat to 0.1 mil and the ends of the cylinder are flat and parallel to the same accuracy, the deviation from parallelism of the center plug of the base plate on which the sample sits and the center plug of the capacitor plate is not more than 0.2 mil over the diameter of the sample. The end faces of the sample are ground and lapped flat and parallel to about the same accuracy, so that variation of the capacitor gap should not be more than about 0.3 mil. The gap is usually about 3 mil, so that the maxiumum error in the formula connecting change in capacitance with change in gap, which arises in the unlikely event that the gap over one-half of the sample is 10% smaller than the other half, is also about 10%. For a given deviation from parallelism the accuracy can obviously be improved by the use of a copper gasket under the cylinder to give a larger gap, but the error only decreases inversely as the gap whereas the sensitivity decreases inversely as the square of the gap.

The end of the sample is drilled and tapped to accommodate the 0-80 brass screw which secures it to the base of the capacitance cell. If the sample is too small to make a 1.5-in.-long by 0.5-in.-diam cylinder, it is soldered or glued with Epoxy to two 0.5-in.-diam OFHC copper slugs to make up a total length of about 1.5 in. The ends of the slugs are then ground and lapped flat and parallel with the total desired length. If Epoxy is used to secure the sample to the slugs, electrical continuity must be ensured by painting over the joint with air-drying silver paint.

Performance

To convert measurements of magnetostriction relative to the copper walls of the cell into absolute magnetostriction we need to know the magnetostriction of the cell. We determine this by measuring a sample of high-purity Si, since having no free carriers at low temperature the magnetization of Si is very small and it is reasonable to assume its magnetostriction to be much smaller than that of Cu. We find that the magnetostriction of the copper cell is only about 10^{-9} in a 100-kOe field, an order of magnitude smaller than that of Ta. We describe the calibration of the cell against Si and the determination of the magnetostriction of Ta in some detail since these experiments serve to demonstrate the performance and limitations of the apparatus in measurements requiring as high sensitivity as possible.

The Si sample was made from a pulled rod of p-type material with a room-temperature resistivity ρ_{RT} about 1000 Ω cm and a dislocation density about 100 cm^{-2}. After grinding and lapping to the required length, the sample was metal coated by evaporation of a thin layer of Al to provide a conducting end face which constitutes one capacitor plate, electrically connected to the base plate and so to the capacitor lead. Since it was anticipated that the magnetostriction would be small, the length was chosen so that after allowance for differential thermal expansion relative to the cell from room temperature to 4.2 °K the gap would be only about 1 mil, giving a higher sensitivity than in less critical measurements.

The experimental data are shown in Fig. 2. The first set of measurements were made in the Westinghouse solenoid in fields up to about 35 kOe and the data in Fig. 2(a) show that this field is barely sufficient to achieve a meaningful result for such a small magnetostriction. Because of drift the data points for field increasing diverge from those for field decreasing, and on completion of the set of measurements, which takes about 20 min., the zero-field value of the capacitance has changed by 23×10^{-6} pF, which is equivalent to a fractional length change of the sample of 10×10^{-10}. Drift of this order of magnitude is usually observed independently of whether or not the field is changed, and may be of either sign though usually the capacitance decreases with time. We are uncertain of the cause of this effect, which may be due to very slow creep of the Epoxy in the end plates of the cell.

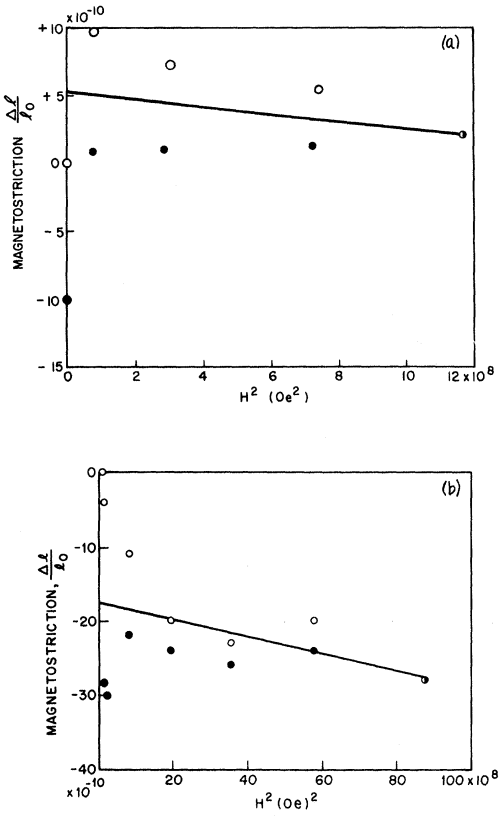

FIG. 2. Magnetostriction of silicon relative to copper cell: (a) up to 35 kOe; (b) up to 94 kOe. ○ – field increasing; ● – field decreasing; straight line – least-squares fit to average of field-increasing and field-decreasing data points.

Another effect of unknown origin is the apparent *increase* in length of about 10×10^{-10} between zero field and the second data point at 8.7 kOe, which is also observed in decreasing field. An effect of the same order of magnitude but of either sign is observed in many samples: The higher-field data quadratic in field give a positive or negative intercept with the length axis when extrapolated to zero field. The sign and magnitude of the zero-field intercept seem to be unrelated to the sign and magnitude of the higher-field magnetostriction. We do not know the cause of this effect, and choose to regard it as spurious and to ignore the zero-field data points when determining the coefficient of the quadratic field dependence of the magnetostriction. In Fig. 2(a) when we discount the pair of zero-field data points, the least-squares fit to the averages of field-increasing and field-decreasing points has a slope, $\Delta l/l_0H^2=(-0.3\pm0.3)\times10^{-18}$. We give a large standard deviation since repeated sets of measurements in some cases showed somewhat more scatter than appears in Fig. 2(a).

The measurements up to near 100 kOe made with a new copper cell and cryogenic assembly, which fits the RCA solenoid, are plotted in Fig. 2(b). They show more scatter than the lower-field measurements and a *negative* zero-field intercept. The least-squares fit to the averages of field-increasing and field-decreasing points (again discounting the lowest-field pair of data points, which in this solenoid correspond to a trapped field of about 5 kOe) agrees in order of magnitude with the lower-field data, giving $\Delta l/l_0H^2=(-0.12\pm0.03)\times10^{-18}$. We adopt this value, with its sign reversed, as the magnetostriction of Cu, which is used to correct all magnetostriction measurements in the apparatus.

The magnetostriction data for Ta are shown in Fig. 3. The behavior in low fields in Fig. 3(a) is again irregular and in making the least-squares fit both the lowest-field pair of data points (which are made in a field of a few hundred oersteds since tantalum is superconducting at 4.2 °K in zero field) and the pair of data points at $H^2=0.8\times10^8\,\mathrm{Oe}^2$ are discounted. The resultant slope is $\Delta l/l_0H^2=(1.38\pm0.09)\times10^{-18}\,\mathrm{Oe}^{-2}$, and for the higher-field measurements shown in Fig. 3(b) the corresponding value with the lowest-field pair of data points discounted is $\Delta l/l_0H^2=(1.13\pm0.02)\times10^{-18}\,\mathrm{Oe}^{-2}$. We adopt the latter value since the higher-field data give about an order of magnitude better accuracy than the lower-field data because of the quadratic variation of the magnetostriction with field. The resultant value for the magnetostriction of Ta after correction for the magnetostriction of the copper cell is $\Delta l/l_0H^2=(1.25\pm0.04)\times10^{-18}\,\mathrm{Oe}^{-2}$.

The measurements on Si and Ta illustrate the problems encountered in measuring other metals. Because of drift in the capacitance, measurements are made at equal time intervals in increasing followed by decreasing field, and the average of the pair of data points at each field value is used for calculation. The data taken in the high-field solenoid up to 100 kOe are used in preference to the low-field data presented in Ref. 1, since the latter are about an order of magnitude less accurate because of the quadratic field dependence of the magnetostriction. The irregular behavior at low fields illustrated in Figs. 2 and 3 is observed in some other metals, and as a general rule we include only data taken at 10 kOe and higher fields in making the least-squares fit. In Figs. 4–8 the data corrected for magnetostriction of the copper cell are shown with an arbitrary reference point from which length changes are measured, which is chosen so that the least-squares fit goes through the origin. This procedure eliminates the nonzero intercept at zero field observed typically, but the results for Si and Ta indicate that this is not an

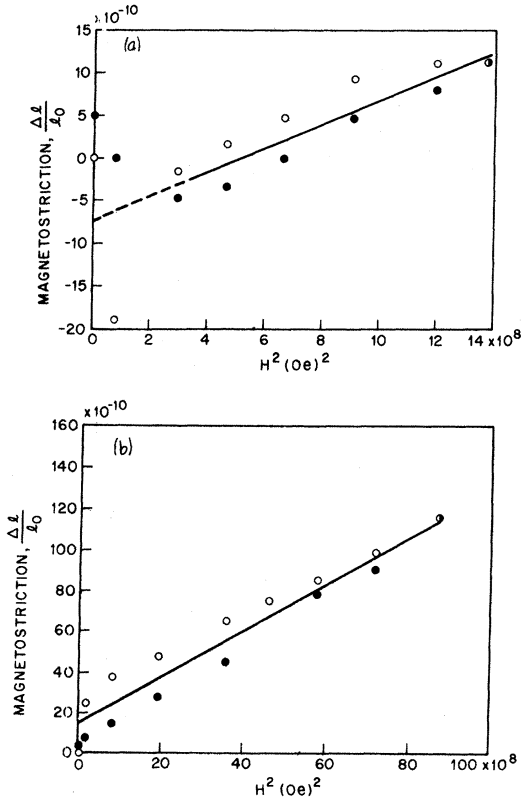

FIG. 3. Magnetostriction of tantalum: (a) up to 37 kOe; (b) up to 94 kOe. ○ – field increasing; ● – field decreasing; straight line – least-squares fit to average of field-increasing and field-decreasing data points.

intrinsic property of the sample since its sign is reversed between Figs. 2(a), 2(b) and 3(a), 3(b).

Data Reduction

The longitudinal magnetostriction of a metal single crystal is related thermodynamically to

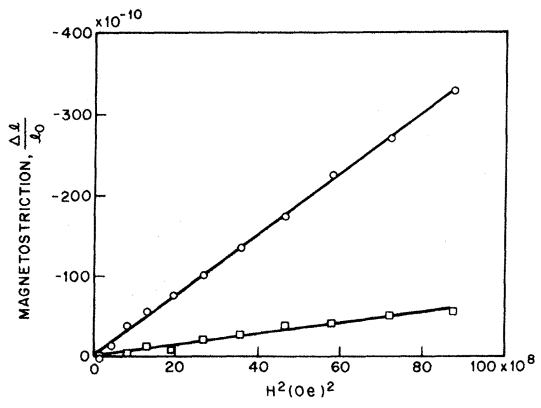

FIG. 4. Magnetostriction of Ti (□) and Zr (○) at 4.2 °K.

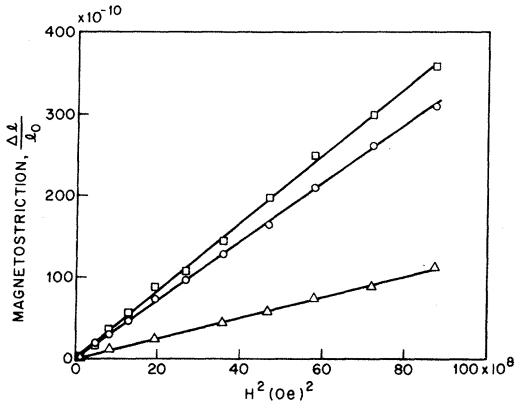

FIG. 5. Magnetostriction of V (□), Nb (○), and Ta (△) at 4.2 °K.

the uniaxial stress derivative of the magnetization M per g atom in the field direction,

$$\Omega \frac{\partial \epsilon_i}{\partial H_i} = \frac{\partial M_i}{\partial \sigma_i} = S_{ij} \frac{\partial M_i}{\partial \epsilon_j} \quad , \tag{1}$$

where Ω is the atomic volume and S_{ij} are the compliance coefficients of the crystal. We make the assumption that

$$\frac{\partial M_1}{\partial \epsilon_1} = \frac{\partial M_1}{\partial \epsilon_2} = \cdots = \frac{\partial M_1}{\partial \ln V}, \quad \frac{\partial M_1}{\partial \epsilon_{4,5,6}} = 0, \tag{2}$$

and it follows that

$$\frac{\partial \epsilon_1}{\partial H_1} = \frac{(S_{11}+2S_{12})}{\Omega} \frac{\partial M_1}{\partial \epsilon_1} = \frac{\kappa}{3\Omega} \frac{\partial M_1}{\partial \ln V} \quad , \tag{3}$$

where κ is the compressibility. We make this assumption to facilitate comparison of our experimental results for the longitudinal magnetostriction with the electronic term in the linear thermal expansion, which in a cubic crystal gives the volume derivative of the electronic specific heat. However, it would be desirable to check the validity of the assumption for some metals by transverse magnetostriction measurements on single crystals, or even on the polycrystalline samples we normally use.

The assumption of isotropy is valid for the Pauli spin paramagnetism so long as there is not strong exchange enhancement of the susceptibility, which may result in moderate anisotropy of the g factor (and therefore probably of $\partial M_i/\partial \epsilon_j$) as in Pd or Pt.[5] The assumption may not be correct for metals in which the orbital paramagnetism is the dominant term in the susceptibility, though Denbigh and Lomer's[6] calculation of the orbital paramagnetism in paramagnetic Cr suggests that the anisotropy of $\partial M_i/\partial \epsilon_j$ would be small.

We substitute χH for M_1 in Eq. (3), χ being the susceptibility per g atom, and omit the subscripts,

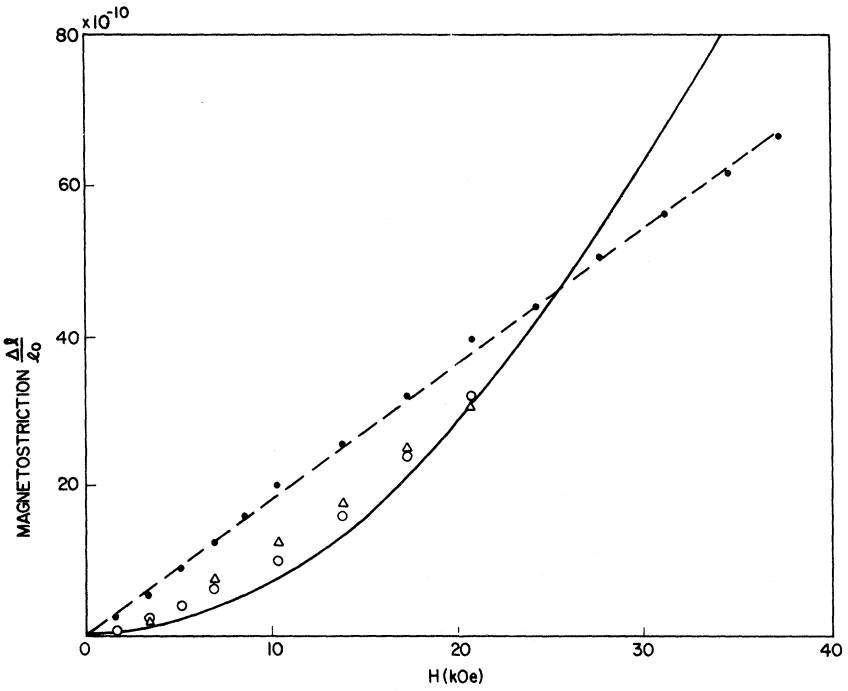

FIG. 6. Low-field magnetostriction of Mo. ● – Mo*A*; ○ Mo*B* at 4.2 °K; △ – Mo*B* at 1.5 °K: continuous line – extrapolation to zero field of quadratic magnetostriction of Mo*B* at 20.4 °K shown in Fig. 8.

to obtain

$$\frac{\partial \epsilon}{\partial H} = \frac{\kappa\chi}{3\Omega}\frac{\partial \ln\chi}{\partial \ln V} H \quad , \tag{4}$$

which gives on integration

$$\frac{\partial \ln\chi}{\partial \ln V} = \frac{6\Omega}{\kappa\chi}\frac{l(H)-l(0)}{l(0)H^2} = \frac{6\Omega}{\kappa\chi}\frac{\Delta l}{l_0 H^2} \quad . \tag{5}$$

Thus, for a field-independent susceptibility the fractional length change $\Delta l/l_0$ should be quadratic in the field with a coefficient which is a measure of the volume dependence of the magnetic susceptibility.

III. EXPERIMENTAL RESULTS

The samples described in Table I were measured previously in fields up to 37 kOe and several seemed to show a magnetostriction linear in field as described briefly in Ref. 1. The more recent measurements in fields up to near 100 kOe show that the magnetostriction of all these metals is quadratic in field at higher fields. We describe both the lower-field and the higher-field data for Mo and W, since the linear magnetostriction at lower fields is clearly evident and reproducible in samples of those metals.

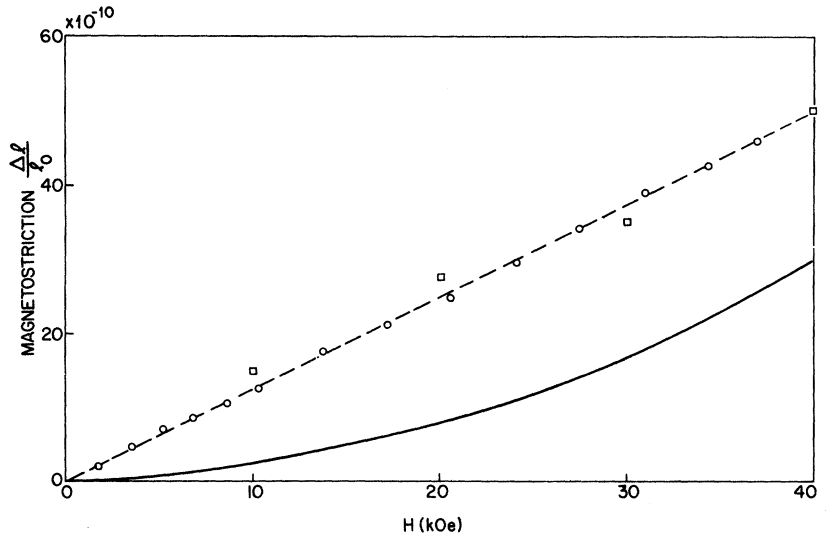

FIG. 7. Low-field magnetostriction of W. ○ – data up to 37 kOe in Westinghouse solenoid at 4.2 °K; □ – data up to 40 kOe in RCA solenoid at 20.4 °K; continuous line – extrapolation to zero field of quadratic magnetostriction at 20.4 °K shown in Fig. 8.

TABLE I. Magnetostriction samples.

Group	Metal	Size (in.)	Source[a]	Preparation and purity
•••	Si	$1\frac{1}{2}\times\frac{1}{2}$	B. T. L.	pulled from melt, $\rho_{RT}\simeq 1000\ \Omega$ cm
4	Ti	$\frac{3}{4}\times\frac{1}{8}$	M. R. C.	3-pass electron-beam float-zoned
	Zr	$\frac{3}{4}\times\frac{1}{8}$	M. R. C.	no metallic impurities except < 10 ppm Fe and Cu
5	V	$1\times\frac{2}{16}$	B. T. L.	melted on silica boat, RRR$\simeq 50$[b]
	Nb	$1\frac{1}{2}\times\frac{1}{2}$	M. R. C.	3-pass electron-beam float-zoned
	Ta	$1\frac{1}{2}\times\frac{1}{2}$	M. R. C.	
6	Mo	$1\frac{1}{2}\times\frac{1}{2}$	M. R. C.	3-pass electron-beam float-zoned
	W	$1\times\frac{3}{16}$	West.	multiple-pass electron-beam float-zoned

[a]B. T. L. – Bell Telephone Laboratories; M. R. C. – Materials Research Corp., Orangeburg, N. Y.; West. – Westinghouse, Bloomfield, N. J.

[b]RRR is the estimated residual resisivity ratio.

In the case of Ti and Zr, which were also reported to have a linear magnetostriction in Ref. 1, the experimental data up to 37 kOe were unsatisfactory because of low sensitivity resulting from use of too large a capacitor gap. The higher-field data are considerably more accurate and the magnetostriction has a quadratic field dependence as shown in Fig. 4. Both metals have a negative magnetostriction, and the positive linear magnetostriction ascribed to Ti in Ref. 1 is now thought to be incorrect. The coefficients of the quadratic magnetostriction are given in Table II.

The data for V, Nb, and Ta are shown in Fig. 5. The magnetostriction is quadratic and the coefficients given in Table II are in reasonably good agreement with those given in Ref. 1, though the higher-field data are considerably more accurate because of the greater field range.

Samples of Mo and W measured up to 37 kOe were found to exhibit a magnetostriction which appears to be linear (though positive for both signs of field), as shown in Figs. 6 and 7 and reported in Ref. 1. Sample Mo*A* was prepared from a float-zoned rod by cutting off the ends with a diamond-impregnated cutting wheel and grinding and lapping the end faces. It was suspected that the linear magnetostriction may be associated with lattice defects introduced by this process, and a second sample Mo*B* was prepared from another ingot by spark cutting off the ends and spark planing the end faces. Mo*B* was sufficiently pure and strain free to exhibit oscillatory de Haas–van Alphen magnetostriction at 4.2 °K, so the high-field measurements were done in liquid hydrogen at 20.4 °K where thermal scattering reduces the oscillations to a negligibly small amplitude. The resultant data in Fig. 8 exhibit a quadratic magnetostriction which is shown extrapolated back to zero field in Fig. 6. We also show in Fig. 6 low-field measurements on Mo*B* at 4.2 and 1.5 °K up to 20 kOe (at higher fields the oscillatory magnetostriction is too large in amplitude to measure the monotonic magnetostriction), which are in reasonably good agreement with the extrapolated quadratic magneto-

TABLE II. Magnetostriction of group-4, -5, and -6 transition metals.

Group	Metal	$\Delta l/l_0H^2$ (10^{18} Oe^{-2})	χ[a] (10^6 g-at.$^{-1}$)	Ω/k[b] (10^{-13} dyn cm)	$\frac{\partial \ln\chi}{\partial \ln V}$
4	Ti	-0.69 ± 0.05	157	1.29	−0.34
	Zr	-3.79 ± 0.06	114	0.78	−1.6
5	V	4.18 ± 0.06	297	1.38	1.2
	Nb	3.60 ± 0.04	240	1.88	1.7
	Ta	1.25 ± 0.04	157	2.21	1.1
6	Mo	7.12 ± 0.08	81	2.61	14
	W	1.83 ± 0.03	53	3.15	6.5

[a]Room-temperature values of χ from S. A. Nemnonov, Fiz. Metal. i Metalloved. 19, 550 (1965) [Phys. Metals Metallog. USSR 19, 66 (1965)], with corrections to low temperature from N. V. Volkenshteyn and E. V. Galoshina, Fiz. Metal. i Metalloved. 20, 368 (1965) [Phys. Metals Metallog. USSR 20, 48 (1965)]; R. Kohlhaas and W. D. Weiss, Z. Angew, Phys. 28, 16 (1969); H. Suzuki and S. Migahara, J. Phys. Soc. Japan 20, 2102 (1965).

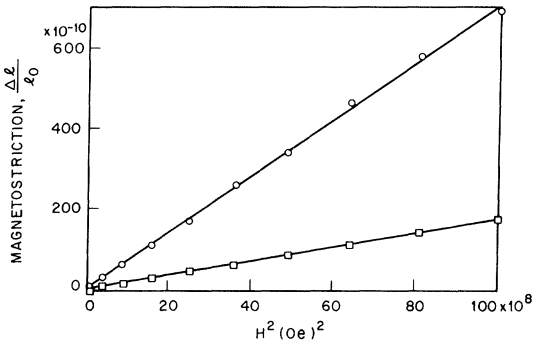

FIG. 8. Magnetostriction of Mo (○) and W (□) at 20.4 °K.

striction. We do not understand the unusual low-field behavior of MoA but characterize Mo in Table II by the coefficient of the normal quadratic magnetostriction observed for the more carefully prepared sample MoB.

The W sample was also prepared like MoA. As shown in Fig. 8 its high-field magnetostriction measured at 20.4 °K is quadratic, with the coefficient given in Table II. This sample also exhibits de Haas–van Alphen oscillations at 4.2 °K in high fields, but their amplitude is negligibly small up to 37 kOe. At low fields the magnetostriction is linear as shown in Fig. 7. We believe this linearity to be associated with sample imperfections, as in the case of Mo. The high value of the residual resistivity ratio (see Table III) indicates that the W sample is almost free from chemical impurities, which typically cause large-angle scattering with a large contribution to the residual resistivity. But the small amplitude of the oscillatory de Haas–van Alphen magnetostriction relative to that of sample MoB, whose residual resistivity ratio is an order of magnitude smaller (see Table III), provides indirect evidence that the W sample contains physical defects. These defects might be thought to cause small-angle scattering and thereby dephase the cyclotron motion and reduce the amplitude of the de Haas–van Alphen oscillations, while contributing little to the residual resistivity. A field-independent magnetization associated with such defects could give a linear magnetostriction if the magnetization were stress dependent. However the stress dependence would have to be large, since a careful measurement of the magnetic susceptibility[7] showed no sign of such a field-independent magnetization. The magnetic susceptibility of the W sample was found to be 55×10^{-6} emu/mole, independent of temperature between 6 and 10 °K and independent of field up to 50 kOe.

In Table II the standard deviation of the coefficient $\Delta l/l_0H^2$ refers to the scatter of the experimental data about the least-squares fit in Figs. 4, 5, and 8. The systematic errors in the magnetostriction (for example, due to nonparallelism of the sample with the capacitor plate), and in the susceptibility, probably exceed these random errors, and the values of $\partial \ln\chi/\partial \ln V$ in the last column of Table II are given to only two significant figures.

The frequencies and amplitudes of the de Haas–van Alphen magnetostriction and further sample information for Mo and W are given in Table III. The sample MoB consisted of several crystals, but from the range of observed frequencies we were able to identify the oscillations as arising from the electron lens situated on the line in reciprocal space connecting the Brillouin-zone center Γ and the corner H, according to the assignment first given by Brandt and Rayne[8] and later confirmed by Sparlin and Marcus.[9] The W sample was a single crystal with its axis in a nonsymmetry direction, and we give only the range of frequencies observed, which enable an identification with the hole pocket of the center of the zone face N.

IV. DISCUSSION

The main contributions to the magnetic susceptibility in a transition metal are the Pauli spin paramagnetism and the orbital paramagnetism, and in our discussion of the volume dependence of the susceptibility we neglect the other contributions. The spin-orbit terms in the susceptibility are smaller than the spin term by a factor $\sim\lambda/\Delta$, with λ the spin-orbit coupling energy and Δ of the order of the bandwidth, and are therefore quite negligible. The orbital diamagnetism of the filled core is both small and likely to have a weak volume dependence. The orbital diamagnetism of the outer d electrons may have an appreciable volume dependence, but is still smaller than the core diamagnetism. The Landau diamagnetism of the conduction electrons is necessarily much smaller than the spin paramagnetism in those transition metals in which the spin paramagnetism is the dominant contribution to the susceptibility, since such metals have a large band mass concomitant with the high density of states responsible for the dominance of the spin paramagnetism. When the orbital paramagnetism dominates the spin paramagnetism we can again neglect the Landau diamagnetism, since it is still unlikely to exceed one-third the spin paramagnetism in any transition metal.

TABLE III. Oscillatory de Haas–van Alphen magnetostriction in Mo and W.

Sample	Range of frequencies[a] MOe	Amplitude[b] (10^8)	RRR[c]	Orientation	Sheet of Fermi surface
MoB	5–7	~30	~300	$\gtrsim$3 crystals	Electron lens on ΓH
W	6–8	~2	~20 000	near ⟨112⟩	Hole pocket at N

[a] Three or more frequencies were observed in both Mo and W in the given ranges of frequencies.

[b] The longitudinal strain amplitude at 100 kOe and 4.2 °K.

[c] RRR is the estimated residual resistivity ratio.

The spin susceptibility with enhancement due to Coulomb interactions is[10]

$$\chi_s = \frac{2\mu_B^2 N(0)}{1 - N(0)V_C} \quad , \tag{6}$$

where μ_B is the Bohr magneton, $N(0)$ is the density of states at the Fermi surface, and V_C is the screened Coulomb interaction between the conduction electrons. The volume dependence of χ_s is

$$\frac{\partial \ln \chi_s}{\partial \ln V} = \frac{\partial \ln N(0)}{\partial \ln V} + \frac{N(0)V_C}{1 - N(0)V_C}\left(\frac{\partial \ln N(0)}{\partial \ln V} + \frac{\partial \ln V_C}{\partial \ln V}\right). \tag{7}$$

The volume dependence of the density of states may be obtained from the thermal expansion of the metal, with a small correction for the volume dependence of the electron-phonon coupling constant λ. The electronic Grüneisen coefficient γ_e obtained from the electronic terms in the thermal expansion and the specific heat[11] may be written

$$\gamma_e = \frac{\partial \ln[N(0)(1+\lambda)]}{\partial \ln V} = \frac{\partial \ln N(0)}{\partial \ln V} + \frac{1}{1+\lambda}\frac{\partial \lambda}{\partial \ln V} . \tag{8}$$

The correction term may be evaluated from the pressure dependence of the ratio T_c/Θ of the superconducting transition temperature to the Debye temperature. McMillan[12] writes

$$\ln\left(\frac{T_c}{\Theta}\right) \simeq \frac{-(1+\lambda)}{\lambda - \mu^*} \quad , \tag{9}$$

and finds that the Coulomb coupling constant μ^* is roughly constant and equal to 0.13 for transition metals. We obtain from Eq. (9), when we assume $\partial \mu^*/\partial \ln V = 0$, the expression

$$\frac{\partial \ln(T_c/\theta)}{\partial \ln V} = \frac{1+\mu^*}{(\lambda - \mu^*)^2}\frac{\partial \lambda}{\partial \ln V} \quad , \tag{10}$$

which, with Eq. (8), gives

$$\frac{\partial \ln N(0)}{\partial \ln V} = \gamma_e - \frac{(\lambda - \mu^*)^2}{(1+\lambda)(1+\mu^*)}\frac{\partial \ln(T_c/\Theta)}{\partial \ln V} . \tag{11}$$

In strongly exchange-enchanced metals and alloys there may be an additional term in the electronic specific heat[10] and thermal expansion[13] associated with spin fluctuations, but this effect is negligible in the transition metals of groups 4, 5, and 6.

The orbital susceptibility is given by[14]

$$\chi_0 = \mu_B^2 \sum_{nn'} \int \frac{d^3k}{(2\pi)^3} \frac{f(E_{n\vec{k}}) - f(E_{n'\vec{k}})}{E_{n\vec{k}} - E_{n'\vec{k}}} \times \langle n\vec{k}\,|L_z|\,n\vec{k}'\rangle\langle n'\vec{k}\,|L_z|\,n\vec{k}\rangle \quad , \tag{12}$$

where n, n' are band indices and $E_{n\vec{k}}$, $E_{n'\vec{k}}$ are the corresponding band energies at wave vector $\vec{k}$. L_z is the angular momentum operator about the field direction z, and the product of matrix elements, which we denote in abbreviated form by $\langle L_z\rangle^2$, contributes to the integral only between occupied and unoccupied states because of the term involving the difference between Fermi functions $f(E_{n\vec{k}})$. The energy denominator is of the order of the bandwidth Δ and we can crudely approximate the orbital susceptibility by

$$\chi_0 \simeq \mu_B^2 \frac{N_e N_h}{N_e + N_h}\frac{\langle L_z\rangle^2}{\Delta} \quad , \tag{13}$$

where N_e and N_h are the numbers of electrons and holes per g atom, respectively. The volume dependence of χ_0, from Eq. (13), is

$$\frac{\partial \ln \chi_0}{\partial \ln V} = \frac{\partial \ln \langle L_z\rangle^2}{\partial \ln V} - \frac{\partial \ln \Delta}{\partial \ln V} \simeq \frac{\partial \ln \langle L_z\rangle^2}{\partial \ln V} + \frac{\partial \ln N(0)}{\partial \ln V} , \tag{14}$$

since $\Delta \simeq 1/N(0)$.

From Eqs. (7) and (14) we obtain an expression for the volume dependence of the total susceptibility χ (neglecting contributions other than the spin and orbital susceptibilities),

$$\frac{\partial \ln \chi}{\partial \ln V} = \frac{\partial \ln N(0)}{\partial \ln V} + \frac{\chi_0}{\chi}\frac{\partial \ln \langle L_z\rangle^2}{\partial \ln V} + \frac{\chi_s}{\chi}\frac{N(0)V_C}{1 - N(0)V_C}\left(\frac{\partial \ln N(0)}{\partial \ln V} + \frac{\partial \ln V_C}{\partial \ln V}\right), \tag{15}$$

with $\partial \ln N(0)/\partial \ln V$ given by Eq. (11).

The only metal for which the spin and orbital susceptibilities have been experimentally separated is V, for which measurements of the gyromagnetic ratio[15] show that $\chi_0 \simeq 2\chi_s$. We can assume that χ_0 and χ_s are of the same order of magnitude also for the group-4 metals Ti and Zr and the other group-5 metals Nb and Ta, so that $\chi_0/\chi \sim \frac{1}{2}$. The exchange-enhancement factor $1/[1 - N(0)V_C]$ in these metals is thought to be close to unity, since if $N(0)V_C$ were large their superconducting temperatures would be depressed by the strong Coulomb interaction.[16] We therefore neglect the last term in Eq. (15), and when we compare $\partial \ln \chi/\partial \ln V$ with $\partial \ln N(0)/\partial \ln V$ as in Table IV we

TABLE IV. Comparison of magnetostriction with thermal expansion.

Group	Metal	$\frac{\partial \ln(T_c/\theta)}{\partial \ln V}$ [a]	λ [b]	$\frac{1}{(1+\lambda)}\frac{\partial \lambda}{\partial \ln V}$ [c]	γ_e [d]	$\frac{\partial \ln N(0)}{\partial \ln V}$	$\frac{\partial \ln \chi}{\partial \ln V}$
4	Ti	−13.9	0.38	−0.6	1.9	2.5	−0.34
	Zr	−23.4	0.41	−1.2	0.0	1.2	−1.6
	V	−1.8	0.60	−0.2	1.65	1.85	1.2
5	Nb	1.7	0.82	0.4	1.5	1.1	1.7
	Ta	3.0	0.65	0.4	1.3	0.9	1.1
	Mo	4.7	0.41	0.2	1.5	1.3	14
6	W	···	0.29	···	0.2	~0.2	6.5

[a] From Ref. 17.

[b] From Ref. 12.

[c] Calculated from Eq. (10) with $\mu^* = 0.13$.

[d] Values of γ_e and γ_G from Ref. 9 except fot Ti and Zr: J. A. Cowan, A. Pawlowicz, and G. K. White, Cryogenics 8, 155 (1968).

see that the difference $(\chi_0/\chi)\partial \ln\langle L_z\rangle^2/\partial \ln V$ is near zero for the group-5 metals and about 3 for the group-4 metals. The volume dependence of the matrix elements in the orbital susceptibility would be very difficult to calculate, but values of $\partial \ln\langle L_z\rangle^2/\partial \ln V$ of order unity seem physically reasonable.

Kushida and Murphy[18] have measured the pressure dependence of the Knight shift in V. Their estimate of the volume dependence of the orbital contribution to the Knight shift is $\partial \ln K_0/\partial \ln V = -0.5$. This value should be compared with our estimate of the volume dependence of χ_0, $\partial \ln\chi_0/\partial \ln V = 0.95$, which we obtain by substituting $\partial \ln N(0)/\partial \ln V$ for $\partial \ln\chi_s/\partial \ln V$ and putting $\chi_0 = 2\chi_s = \frac{2}{3}\chi$ in the expression

$$\frac{\partial \ln\chi_0}{\partial \ln V} = \frac{\chi}{\chi_0}\frac{\partial \ln\chi}{\partial \ln V} - \frac{\chi_s}{\chi_0}\frac{\partial \ln\chi_s}{\partial \ln V} \quad . \tag{16}$$

The relation of K_0 to χ_0 is

$$K_0 = 2\chi_0\langle r^{-3}\rangle \quad , \tag{17}$$

where the average of r^{-3} is taken over all states contributing to the orbital susceptibility, giving $\partial \ln\langle r^{-3}\rangle/\partial \ln V \simeq 2$.

When we turn to the group-6 metals Mo and W for which the spin susceptibility is considerably smaller than the orbital susceptibility because of the small value of the density of states, we are at a loss to explain the very large values of $\partial \ln\chi/\partial \ln V$. As shown in Table IV, $\partial \ln\chi/\partial \ln V$ is much greater than $\partial \ln N(0)/\partial \ln V$, and yet there is no reason to expect $\partial \ln\langle L_z\rangle^2/\partial \ln V$ to be much greater for the group-6 metals than for the group-5 metals. We can see no way to explain why in particular the magnetostriction of Mo is larger than that of any group-5 metal (see Table II), though its susceptibility is several times smaller.

In conclusion, we find that our expectation of separating the several contributions to the susceptibility of the transition metals by determining their magnetostriction is not fulfilled in the metals of groups 4, 5, and 6. The magnetostriction of the group-4 and -5 metals is consistent with estimates of the volume dependence of the density of states obtained from the thermal expansion if we make physically reasonable assumptions about the volume dependence of the orbital susceptibility. But the large positive magnetostriction of the group-6 metals remains unexplained.

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