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de Haas–van Alphen Effect in a Zinc Alloy Exhibiting a Resistance Minimum*

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The de Haas–van Alphen effect has been measured using a torque method at magnetic fields up to 8 kOe and temperatures between 4.2 and 1.6°K for both pure zinc and a zinc manganese alloy exhibiting a resistance minimum. Experimentally, it is shown that there is no change in the period of the oscillations although the field and temperature dependence of the amplitude of the oscillations is found to be anomalous. A consideration of the influence of the conduction electron relaxation time on the de Haas–van Alphen effect shows that the observed behavior may be explained if the relaxation time is allowed to approach zero in a small energy interval, Δ, about the Fermi energy. Using the phenomenological theory of the resistance minimum, due to Korringa and Gerritsen, and the value of Δ obtained from the de Haas–van Alphen effect experiments the resistance as a function of temperature was calculated and found to agree within experimental error with the measured values.

INTRODUCTION

In normal metals and alloys the electrical resistance decreases with decreasing temperature and eventually becomes constant at temperatures sufficiently low that the scattering of the conduction electrons is chiefly due to crystal imperfections and impurities. In 1930 Meissner and Voigt[1] observed that in certain metals the electrical resistivity fell to a small value with decreasing temperature and then rose by a few percent as the temperature was further lowered. This effect was studied more closely by de Haas *et al.*[2] who found that the temperatures at which the minimum occurred increased with increasing residual resistance ratio. This established that the minimum in electrical resistance was due to the presence of crystal imperfections and/or impurities. MacDonald and Pearson[3] have shown that along with the resistance minimum there also occurs an anomalous thermo-emf. Large negative values of the thermo-emf are observed at temperatures somewhat higher than the temperature at which the resistance minimum occurs in these alloys. The experimental position as of 1960 is summarized by van den Berg,[4] who points out that the anomalies in the transport properties are now believed to be due to the presence of certain transition element impurities and in fact the ability to produce a resistive anomaly seems to depend on the existence of a localized magnetic moment introduced by the impurity.

Recent extensions of the Schmitt[5] theory of the resistance minimum by Kasuya,[6] Bailyn,[7] and de Vroomen[8] to explain "giant" thermoelectric powers in dilute alloys at low temperatures predict an effective relaxation time which is sharply energy dependent near the Fermi energy.[9] Domenicali[10] in an extension of some early work of Korringa and Gerritsen[11] has shown that such a relaxation time will explain the resistance and thermoelectric power of these alloys over a wide temperature range.

Since the amplitude of the de Haas–van Alphen effect is related to the relaxation time of the conduction electrons, a study of this effect in a zinc manganese alloy, which exhibited a resistance minimum, was made in order to determine whether an energy-dependent relaxation time would account for any anomaly which might be found in the de Haas–van Alphen oscillations.

The experimental study was made on zinc since it was known to exhibit a resistance minimum[12] and a large-amplitude de Haas–van Alphen effect.[13]

Discussion of the Theory of the de Haas–van Alphen Effect for Zinc

The present experiments on the de Haas–van Alphen effect consists of measurements on the field dependence of the torque exerted on a single-crystal sample in a homogeneous magnetic field. The torque C about an axis can be derived from the free energy F of the electron system since

$$C=-\partial F/\partial\psi, \tag{1}$$

where ψ is an angle specifying rotation in a plane normal to the prescribed axis. [See Fig. 1(a).] The large ampli-

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[†] This work has been submitted as partial fulfillment for the degree of Doctor of Philosophy at the University of Ottawa, Canada.

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[9] For a discussion of these effects and the present situation the reader is referred to D. K. C. MacDonald, *Thermoelectricity, and Introduction to Principles* (John Wiley & Sons, Inc., New York, 1962) and also to D. K. C. MacDonald and A. M. Guenault, Phil. Mag. **6**, 1201 (1961).

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[11] J. Korringa and A. N. Gerritsen, Physica **19**, 457 (1953).

[12] Y. Muto, Y. Tawara, Y. Shibuya, and T. Fukuroi, J. Phys. Soc. Japan **14**, 380 (1959).

[13] B. I. Verkin and I. M. Dmitrenko, Izv. Akad, Nauk SSSR, Ser. Fiz. **19**, 409 (1955).

tude long-period de Haas–van Alphen oscillations observed in zinc arise from pieces of Fermi surface which are ellipsoidal in shape[13,14] and are situated as shown in Fig. 1(b). Since the surfaces are ellipsoidal, it is possible to use the expression for the free energy of the conduction electrons derived by Dingle.[15] He showed that the part of the free energy that depends periodically on the magnetic field is given by

$$F_{\text{periodic}}=\frac{2\pi(2m^*)^{3/2}kTV(\beta^*H)^{3/2}}{\sqrt{2}h^3}\sum_{p=1}^{\infty}\left[\frac{(-1)^p\cos(2\pi pE_0/\beta^*H-\pi/4)}{p^{3/2}\sinh 2\pi^2pkT/\beta^*H}\cos p\pi(m^*/m)\exp(-ph/\tau\beta^*H)\right], \tag{2}$$

where $\beta^*=e/m^*c$ is an effective double Bohr magneton, V is the volume of the crystal, T is the absolute temperature E_0 is the Fermi energy measured from the bottom of the ellipsoid, τ is the electron relaxation time, and m^* is the cyclotron effective mass.

This expression can be simplified for zinc since it has been shown experimentally[16] that harmonics are small. Also, the effective mass is of the order of 0.01 of the free electron mass and hence $\cos(\pi m^*/m)$ is unity. Combining Eqs. (1) and (2) and noting that $E_0/\beta^*H\gg 1$, the torque on the sample is given by

$$C=BH^{1/2}T\frac{\sin(2\pi E_0/\beta^*H-\pi/4)}{\sinh(2\pi^2kT/\beta^*H)}e^{-2\pi^2kx/\beta^*H}, \tag{3}$$

where

$$B=\frac{E_0kV}{\pi^3}\left(\frac{e\hbar}{c}\right)^{1/2}\frac{\partial m^*}{\partial\psi} \tag{4}$$

and

$$x=\hbar/\pi k\tau.$$

The quantity x has the dimensions of temperature and is called the collision or Dingle temperature.

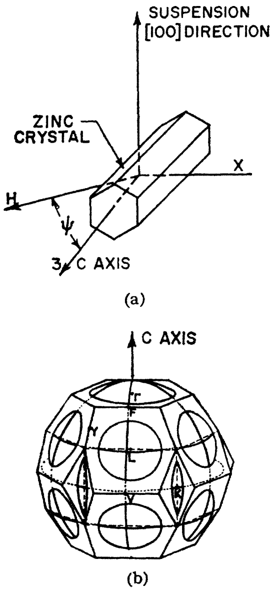

FIG. 1. (a) The orientation of the zinc crystals. (b) The Fermi surface of zinc [after E. Fawcett, J. Phys. Chem. Solids **18**, 320 (1961)]. The surfaces marked K are associated with the long-period de Haas–van Alphen effect.

From Eq. (3) it can be seen that the period P of the oscillations can be written

$$P=\beta^*/E_0=\beta/E_0(m^*/m), \tag{5}$$

where $\beta=e/mc$ is a double Bohr magneton.

The effective mass of the electrons can be determined from the ratio of the amplitude $|C_1|$ of the oscillations at temperature T_1 to the amplitude, $|C_2|$, at temperature T_2.

Assuming that the temperature is low enough that the relaxation time is constant then the ratio of the amplitudes, from Eq. (3), is given by

$$\frac{|C_1|}{|C_2|}=\frac{T_1\sinh[(2\pi^2kT_2/\beta)(m^*/mH)]}{T_2\sinh[(2\pi^2kT_1/\beta)(m^*/mH)]}=W, \tag{6}$$

where m^*/m is the only unknown quantity. Equation (6) can be solved by graphical methods for m^*/m. From the value of m^*/m and the corresponding period the value of the Fermi energy E_0 can be calculated from Eq. (5).

Once the effective mass has been determined the collision temperature x can be evaluated from the field dependence of the amplitude of the oscillations. Excluding the periodic term, Eq. (3) may be written:

$$\alpha=\xi-xH^{-1},$$

where

$$\alpha=\frac{\beta\ln\{(|C|/H^{1/2}T)\sinh[(2\pi^2kT/\beta H)(m^*/m)]\}}{2\pi^2k(m^*/m)} \tag{7}$$

and

$$\xi=\frac{\beta\ln B}{2\pi^2k(m^*/m)}, \tag{8}$$

whence if α is plotted as a function of H^{-1} a straight line should result whose slope is $-x$. The relaxation time, τ, can then be obtained from Eq. (4).

Sample Preparation

The alloys were prepared by melting 99.999% pure zinc, (obtained from the New Jersey Zinc Company) together with 99.97% pure powdered manganese, (obtained from A. D. MacKay, Inc.) in a quartz tube under an inert atmosphere. The maganese was powdered in an agate mortar to avoid the possibility of ferromagnetic contamination. The melt was maintained at a tempera-

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[14] W. A. Harrison, Phys. Rev. **118**, 1190 (1960).

[15] R. B. Dingle, Proc. Roy. Soc. (London) **A211**, 500 (1952).

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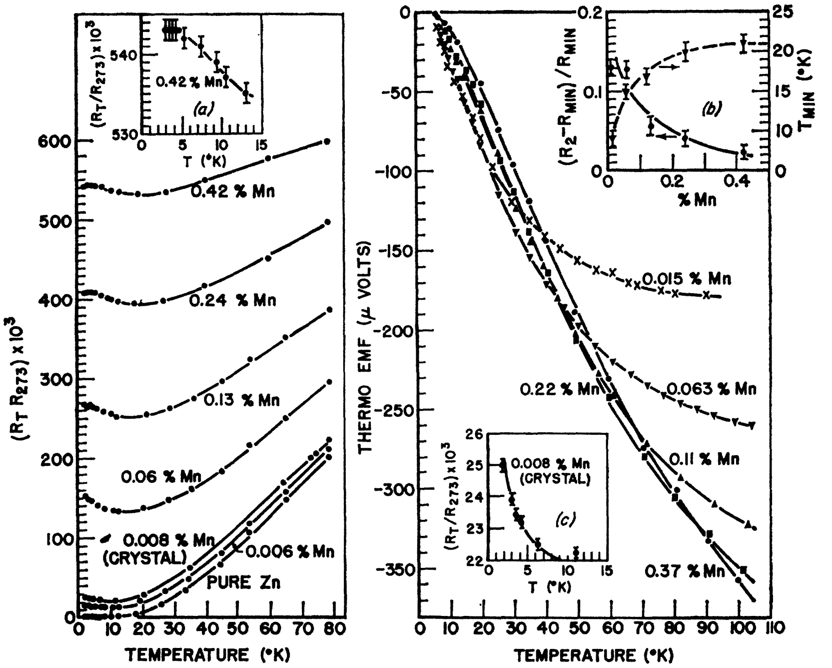

FIG. 2. The electrical resistance and thermo-emf as a function of temperature, Insets *a*, *b*, and *c* are referred to in the text.

ture of 700°C for a period of 2 h, during which time it was agitated vigorously every 15 min. The melt was then quenched in ice water. The concentration of manganese in the alloys was determined from a graph of residual resistance ratio $R_{4.2}/(R_{273}-R_{4.2})$ as a function of nominal concentration obtained from the weights of the components of the alloy. A line giving the best fit was drawn and the concentration of each alloy determined from the graph using the measured resistance ratio.

The resistance and thermo-emf samples were wires of rectangular cross section $\frac{1}{16}$ in. wide made from cold-rolled strips about 0.005 in. thick. After fabrication these samples were etched in a 50% hydrochloric acid solution and given a strain relieving anneal under vacuum at 400°C for 24 h and then quenched in ice water.

The $\frac{5}{16}$-in.-diameter spherical single crystals required for the de Haas–van Alphen effect measurements were grown by Tamman's method in a graphite mold by cooling the sample from 10°C above the melting point to 10°C below the melting point at the rate of about 5°C/h. The crystals were etched in a 50% hydrochloric acid solution which clearly showed any grain boundaries which might be present. The basal plane was determined by cleaving the crystals under liquid nitrogen and the [100] direction found by x-ray diffraction in a Bragg-type spectrometer. The piece removed from the crystal was rolled into a strip and its resistance ratio, and hence its maganese concentration determined. Table I gives the resistance ratio, resistivity, and nominal manganese concentration for all the samples studied.

Experimental Methods and Results

The cryostat and experimental procedure used in making the electrical resistance measurements have been described previously.[17,18] The results of the resistance measurements are shown in Fig. 2. Inset (c) of Fig. 2 shows the resistance of the zinc manganese single crystal used in the de Haas–van Alphen experiments. Inset (a) shows the low-temperature resistance of the most concentrated alloy containing 0.42% manganese. The resistance of this alloy is constant between 1.8 and 5°K and no evidence of a resistance

TABLE I. The resistance ratio, composition, and resistivity of the various samples measured.

Sample	Resistance ratio $[R_{4.2}/(R_{273}-R_{4.2})]\times 10^3$ End 1	End 2	Conc. Mn (wt. %)	Resistivity (10^{-6} Ω cm)
Resistance	1.2		Pure Zn	5.5
	14.7		0.006	5.0
	171		0.06	5.7
	362		0.13	6.7
	396		0.14	6.9
	692		0.24	8.1
	1190		0.42	12.0
Thermo-emf	40.6	42.8	0.015	
	174	1.81	0.063	
	334	300	0.11	
	676	583	0.22	
	1060	1060	0.37	
de Haas–van Alphen crystal	23.8		0.008	

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[17] A. C. Rose-Innes and R. F. Broom, J. Sci. Instr. **33**, 31 (1956).

[18] F. T. Hedgcock, W. B. Muir, and E. E. Wallingford, Can. J. Phys. **38**, 376 (1960).

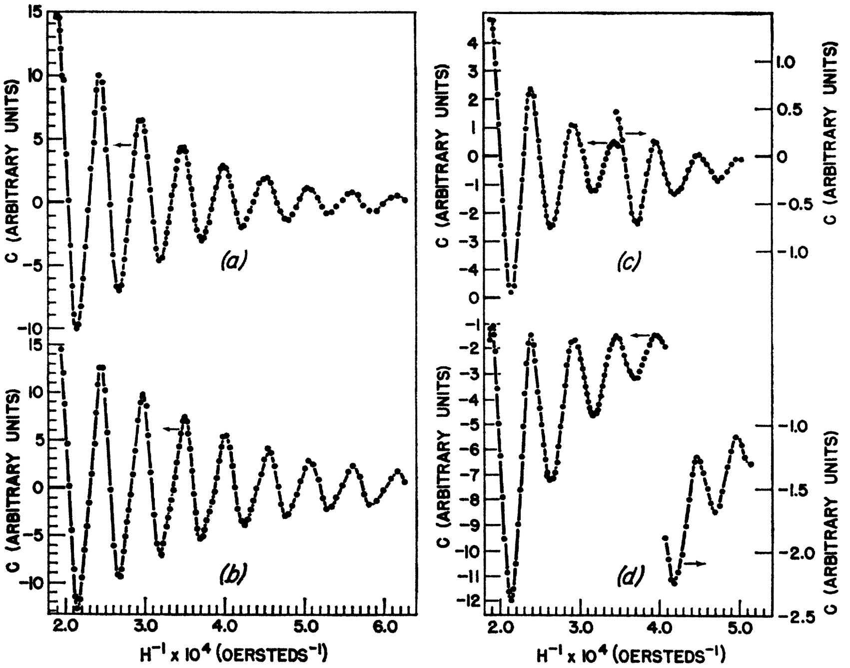

FIG. 3. The experimental results of the de Haas–van Alphen effect measurements. (a) pure zinc $T=4.2°$K, $\psi=34.5°$; (b) pure zinc $T=1.75°$K, $\psi=34.5°$; (c) 0.008 wt. % zinc manganese alloy $T=4.2°$K, $\psi=34.0°$; (d) 0.008 wt. % zinc manganese alloy $T=1.65°$K, $\psi=34.0°$. The vertical asymmetry of the oscillations is probably due to the influence of the anisotropic crystalline environment of the manganese ions and is presently undergoing further investigation.

maximum was found. The temperature at which the minimum occurs and the depth of the minimum D, defined by $D=(R_{2.0}-R_{\min})/R_{\min}$, are plotted as a function of manganese concentration and shown in inset (b) of Fig. 2. These results are similar to those for other alloys showing a resistance minimum.[18,19]

The thermo-emf measurements were made in a cryostat similar to that used by MacDonald and Pearson.[20] The emf of a zinc-zinc manganese thermocouple, having its cold junction at 4.2°K and its hot junction at temperatures varying between 5 and 100°K, was measured using a galvanometer amplifier.[21] To reduce the effects of stray thermo-emf's in the leads a superconducting reversing switch[22] was used which allowed the potential from the thermocouple to be reversed inside the cryostat. The results of these measurements are also shown in Fig. 2. They agree qualitatively at least with other thermo-emf measurements on alloys showing a resistance minimum.[20]

The de Haas–van Alphen effect was measured using a servo torsion balance similar in design to that of Croft, Donahoe, and Love,[23] the only difference being the dc amplifier which, in this case, is identical to one used by the authors in a low-temperature susceptibility servo balance.[24] Arrangements were made for pumping on the liquid-helium Dewar and measurements were made both at 4.2 and about 1.7°K. The temperature was determined by measuring the vapor pressure above the liquid helium. The crystals were oriented in the field as shown in Fig. 1(a). The Typical results obtained for the torque as a function of field are shown in Fig. 3 for both pure zinc and a 0.008 wt. % zinc manganese alloy.

Analysis of the de Haas–van Alphen Effect Measurements

The period of the oscillations is given by the slope of the line obtained by plotting the values of H^{-1} at the extreme values of the torque against half-integers as shown in Fig. 4. As can be seen in Fig. 5, the square of

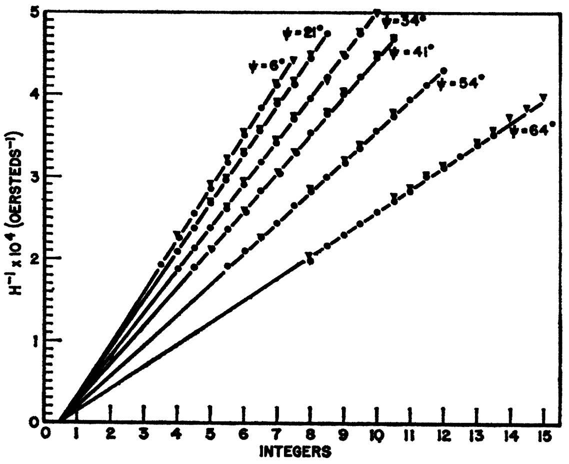

FIG. 4. The values of H^{-1} at extreme values of the torque as a function of half-integers for the 0.008 wt. % zinc manganese alloy. ● indicate data obtained at 4.2°K; ▼ indicate data obtained at 1.7°K.

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[19] A. N. Gerritsen, Physica 25, 489 (1959).

[20] D. K. C. MacDonald and W. B. Pearson, Proc. Roy. Soc. (London) A219, 373 (1953).

[21] D. K. C. MacDonald, J. Sci. Instr. 24, 232 (1947).

[22] I. M. Templeton, J. Sci. Instr. 32, 172 (1955).

[23] G. T. Croft, F. J. Donahoe, and W. F. Love, Rev. Sci. Instr. 26, 360 (1955).

[24] F. T. Hedgcock and W. B. Muir, Rev. Sci. Instr. 31, 390 (1960).

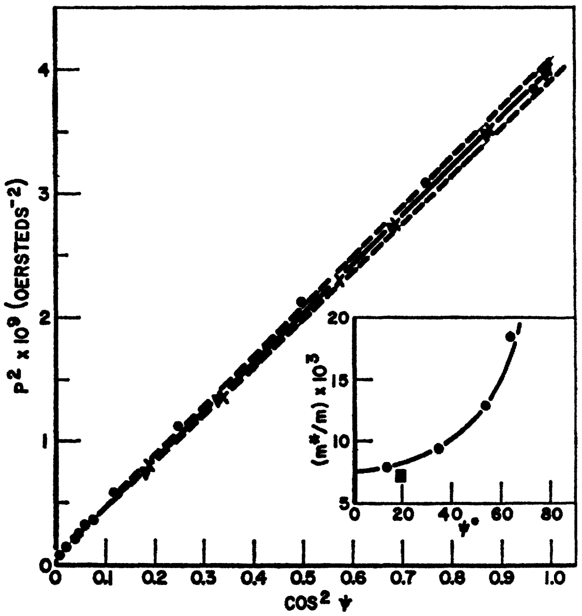

FIG. 5. P^2 as a function of $\cos^2\psi$. ▼ indicate data for pure zinc; ● indicate data for pure zinc obtained by Verkin and Dmitrenko; × indicate data for the 0.008 wt. % zinc manganese alloy; the dotted lines indicate the experimental error; the inset shows m^*/m as a function of orientation for pure zinc; ■ indicates the value obtained by Dhillon and Shoenberg.

the period P is a linear function of $\cos^2\psi$ which is to be expected for an ellipsoidal Fermi surface.[25] Included in Fig. 5 are the data obtained by Verkin and Dmitrenko[13] for pure zinc. The results are seen to be identical within the indicated 1.5% experimental error.

The effective mass of the electrons is determined by plotting W [see Eq. (6)] as a function of m^*/mH for various values of T_1 as shown in Fig. 6(a)[26] using the experimental values of $|C_1|/|C_2|$ and T_1 corresponding values of m^*/mH are read from the graph and m^*/m calculated. The values obtained for the effective mass of pure zinc are plotted as a function of orientation in the inset of Fig. 5. As indicated in the figure, our value is slightly greater than that obtained by Dhillon and Shoenberg,[16] but agree with those of Joseph and Gordon.[27] The value of the Fermi energy of pure zinc, measured from the bottom of the ellipsoid was calculated using Eq. 5 and found to be $(3.8\pm0.2)\times10^{-14}$ erg.

Since the zinc alloy exhibits a low-temperature resistance anomaly, it was anticipated that the relaxation time would not be constant in the temperature range of the de Haas-van Alphen effect measurements. This means that the effective mass of the electrons in the alloy cannot be determined by the above method. In order to carry out the analysis for the collision temperature for the alloy it was assumed that the effective mass of the electrons in the alloy was identical to that of the electrons in pure zinc. This is probably a reasonable assumption considering the extreme dilution (0.01 at. %) of the alloy.[28]

The collision temperature was determined from the slope of the line obtained by plotting α as a function of H^{-1} [see Eq. (7)] as shown in Fig. 7 for pure zinc and in Fig. 8 for the zinc manganese alloy. As has been noted previously[29] the curves are linear only for low fields.[30] The collision temperature was deduced from the linear portion of these curves and is found to be independent of orientation and temperature for pure zinc and has a value of 1.3°K.[31] The collision parameter is apparently a function of both temperature and orientation for the zinc manganese alloy. This dependence will be analyzed further in the next section. All the experimental results obtained from the de Haas-van Alphen effect measurements are summarized in Table II.

DISCUSSION OF RESULTS

Field and Temperature Dependence of the Amplitude

Allowing for a temperature-dependent relaxation time, which might be expected in these alloys, Eq. (7)

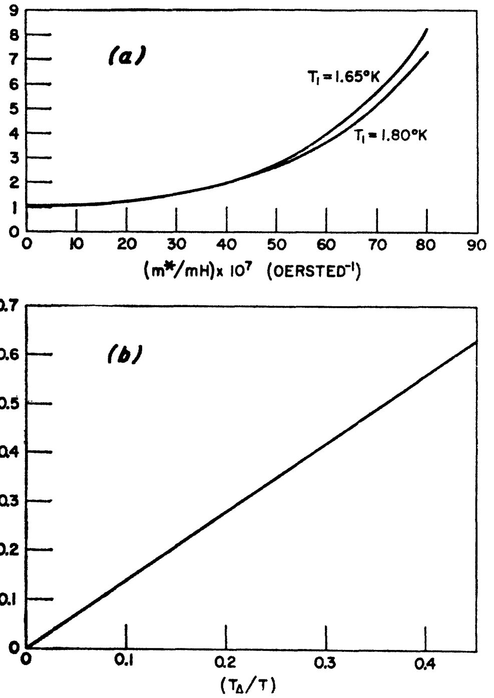

FIG. 6. (a) Calculated values of W as a function of (m^*/mH); (b) the function $I(T_\Delta/T)$ as a function of (T_Δ/T).

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[25] D. Shoenberg, *Progress in Low Temperature Physics* (Interscience Publishers, Inc., New York, 1959), Vol. II.

[26] T_2 remains fixed at 4.2°K.

[27] A. S. Joseph and W. L. Gordon, Phys. Rev. **126**, 489 (1962).

[28] It is shown later that this assumption is consistent with the experimental results.

[29] F. J. Donahoe and F. C. Nix, Phys. Rev. **95**, 1395 (1954).

[30] This is probably due to "magnetic breakdown" between the ellipsoids and the arms of the second zone surface. R. W. Stark, Phys. Rev. Letters **9**, 482 (1962).

[31] This value agrees with the value obtained by Joseph and Gordon (reference 27).

TABLE II. The experimental results obtained from the de Haas–van Alphen effect measurements.

	Period $\times 10^5$ (Oe^{-1})		Effective mass $(m^*/m)\times 10^3$		Collision temperature (°K)			
					Pure zinc	Apparent value, Zn-Mn		
ψ (deg)	Pure Zn	Zn-Mn	Pure Zn	Zn-Mn	4.2+1.7°K	4.2°K	2.6°K	1.7°K
14.5	6.10		7.9	Assumed to be the same as the values for pure zinc	1.3			
21		5.90				5.1		5.9
34		5.22				5.0		5.8
34.5	5.26		9.3		1.3			
41		4.80				5.2	5.7	6.1
54		3.68				4.7		5.6
54.5	3.72		12.8		1.3			
64		2.82				4.3		5.4
64.5	2.74		18.3		1.3			
$E_0=(3.8\pm 0.2)\times 10^{-14}$ erg								

shows that the slope of the lines in Fig. 8 may vary with temperature but their intercept at infinite field should be independent of temperature. The experimental results do not agree with theory and, in fact, a large variation of the intercept with temperature is observed. In order to determine whether or not this anomaly was another manifestation of an energy-dependent relaxation time, the free energy, and hence the amplitude of the de Haas–van Alphen effect, was determined for the case of a simple energy-dependent relaxation time.

Dingle[15] has calculated the free energy of the conduction electrons in a metal in a magnetic field when the relaxation time is independent of energy. He has shown that the part of the free energy giving rise to the de Haas–van Alphen effect can be written

$$F_{\text{periodic}}=\frac{2\pi(2m^*)^{3/2}kTV}{h^3}\left(\frac{\beta^*H}{2}\right)^{1/2}e^{-i\pi/4}$$

$$\times\sum_{p=-\infty,\neq 0}^{\infty}(p)^{-1/2}(-1)^pQ, \quad (9)$$

where

$$Q=\int_{-\infty}^{\infty}e^{-2\pi(a|p|-iE/\beta^*H)}\ln[1+e^{(E_0-E)/kT}]dE, \quad (10)$$

and $a=\hbar/\tau\beta^*H$. If it is assumed that the relaxation time varies with energy such that $\tau=\tau_0$ everywhere except in the narrow energy range $(E_0-\Delta)\leqslant E\leqslant(E_0+\Delta)$ where $\tau=0$. The integral Q can then be written

$$Q=e^{-2\pi a_0|p|}\left\{\int_{-\infty}^{\infty}e^{i2\pi pE/\beta^*H}\ln[1+e^{(E_0-E)/kT}]dE\right.$$

$$\left.-\int_{E_0-\Delta}^{E_0+\Delta}e^{i2\pi pE/\beta^*H}\ln[1+e^{(E_0-E)/kT}]dE\right\}, \quad (11)$$

since the integral is zero when $\tau=0$. The first part of Q when combined with Eq. (9) gives Dingle's expression for the free energy [see Eq. (2)]. It is thus seen, from Eqs. (9) and (11), that the effect of the postulated energy-dependent relaxation time is to add a term to the free energy which is given by combining the second part of Q in Eq. (11) with Eq. (9). This term has been evaluated in Appendix I, and results in an expression for the torque on a single crystal of material exhibiting a resistance minimum, due to the postulated energy-dependent relaxation time, given by

$$C=BH^{1/2}T\frac{\sin(2\pi E_0/\beta^*H-\pi/4)}{\sinh(2\pi^2kT/\beta^*H)}e^{-2\pi^2kx_0/\beta^*H}$$

$$\times\left[1+\frac{kT\sinh(2\pi^2kT/\beta^*H)}{\beta^*H}I\left(\frac{T_\Delta}{T}\right)\right], \quad (12)$$

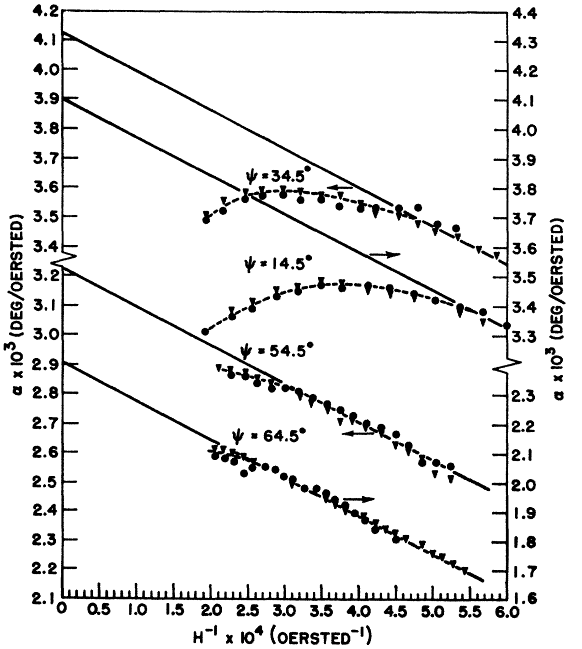

FIG. 7. Field dependence of the amplitude of the oscillations for pure zinc. ● indicates data obtained at 4.2°K; ▼ indicates data obtained at 1.7°K.

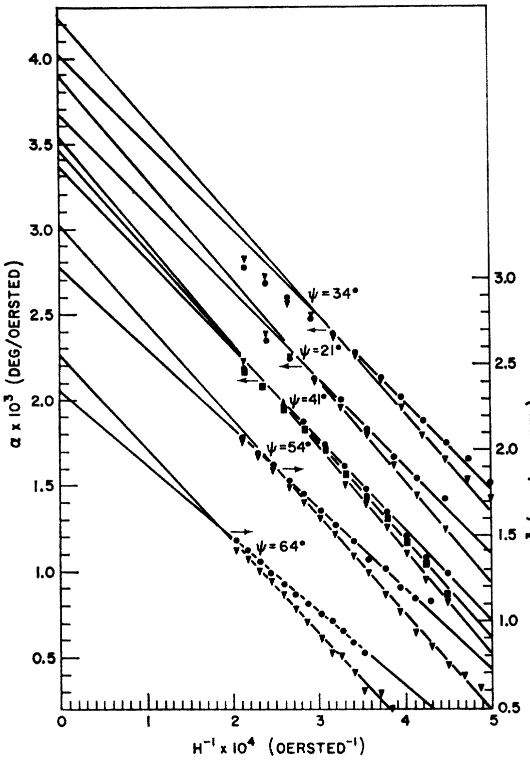

FIG. 8. Field dependence of the amplitude of the oscillations for the 0.008 wt. % zinc manganese alloy. ● indicates data obtained at 4.2°K; ■ indicates data obtained at 2.6°K; ▼ indicates data obtained at 1.7°K.

where $kT_\Delta = \Delta$ and $x_0 = \hbar/\pi k \tau_0$. The function $I(T_\Delta/T)$ is shown in Fig. 6(b). The field dependence of the amplitude of the de Haas-van Alphen oscillations will now be given by

$$\alpha - \eta = \xi - x_0 H^{-1}, \tag{13}$$

where

$$\eta = \beta \ln\left[1 + \frac{kT \sinh(2\pi^2 kT/\beta^* H)}{\beta^* H} I\left(\frac{T_\Delta}{T}\right)\right] \Big/ 2\pi^2 k(m^*/m).$$

Figure 9 shows the results obtained by plotting $\alpha - \eta$ as a function of H^{-1} for $T_\Delta = 0.75$°K. The value of 0.75°K for T_Δ was found by a process of trial and error to give the best fit of Eq. (13) to the experimental data.[32] As would be expected, from equation (13), $\alpha - \eta$ is seen to be a linear function of H^{-1} having a slope $-x_0$ and an intercept ξ at infinite field, both of which are independent of temperature. The collision temperature is now seen to be independent of orientation and has a value of 5.9°K.

In the foregoing analysis it has been assumed that the effective mass of the electrons in the alloy was identical to that of the electrons in pure zinc. If this is the case, then from Eqs. (13), (7), and (4) and the fact that the volume of the samples is the same in both cases, it is seen that $\alpha - \eta$, for the alloy, and α, for pure zinc, should be equal when they are extrapolated to infinite field for any given orientation. As can be seen from Figs. 7 and 9 the values of the intercepts agree to within about 10% thus confirming the correctness of the assumption.

While it is well known that the relaxation time which is measured using the de Haas-van Alphen effect is quite different from that which is measured by electrical resistance it would seem that for alloys exhibiting a resistance minimum the energy range over which the relaxation time was assumed to be zero should be the same in both cases. On this basis the resistance of a sample having a zero relaxation time in the energy range $E_0 - 0.75k$ to $E_0 + 0.75k$ has been computed using the empirical formula given by Korringa and Gerritsen.[11] The result of doing this is shown by the solid line in inset (c) of Fig. 2. As can be seen from the figure agreement within the experimental error of the resistance measurements has been obtained.

CONCLUSIONS

The period of the de Haas-van Alphen oscillations in pure zinc and in the 0.008 wt. % zinc manganese alloy were found to be the same within the 1.5% experimental

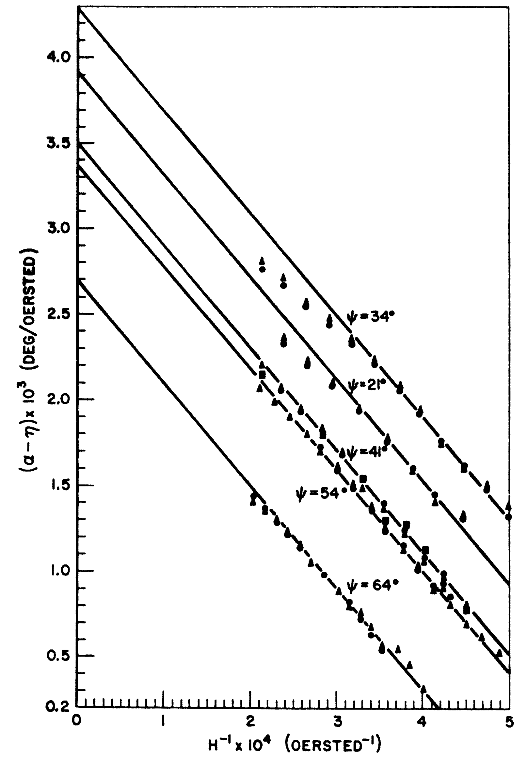

FIG. 9. Field dependence of the amplitude of the oscillations in the 0.008 wt. % zinc manganese alloy allowing for the postulated energy-dependent relaxation time. ● indicates data obtained at 4.2°K; ■ indicates data obtained at 2.6°K; ▲ indicates data obtained at 1.7°K.

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[32] Noticeable misfit could be detected for a change in T_Δ of ±0.2°K.

error. However, the variation of the amplitude of the oscillations with field and temperature was found to be anomalous in the alloy. In order to explain this anomaly, the effect of an energy-dependent relaxation time on the de Haas-van Alphen oscillations was investigated. A relaxation time that was assumed to be zero in the energy range $(E_0-kT_\Delta)\geqslant E\geqslant(E_0+kT_\Delta)$ and constant elsewhere was found to fit the experimental results when $T_\Delta=0.75$°K. The electrical resistance was calculated from the expression given by Korringa and Gerritsen[11] when the relaxation time has the above behavior. Using a value of T_Δ of 0.75°K the calculated and measured resistance were found to agree within experimental error.

It is planned to extend these measurements to other suitable alloy systems in which an energy-dependent relaxation time might be expected to occur.

APPENDIX I

The part of the free energy of the conduction electrons which varies periodically with inverse magnetic field has been shown by Dingle[15] to be

$$F_{\text{periodic}}=-2\pi(2m^*)^{3/2}kTV(\beta^*H/2)^{1/2}\times\sum_{p=-\infty,\neq0}^{\infty}(p)^{-1/2}(-1)^pQ,\quad\text{(A1)}$$

where

$$Q=e^{-i\pi/4}\int_{-\infty}^{\infty}e^{-2\pi(a|p|-ipE/\beta^*H)}\times\ln\{1+e^{(E_0-E)/kT}\}dE,\quad\text{(A2)}$$

$\beta^*=e/m^*c$ an effective double Bohr magneton, $a=\hbar/\tau\beta^*H$, and τ is the conduction electron relaxation time. For alloys having a low-temperature resistance and thermopower anomalies it has been pointed out that the relaxation time might be expected to be sharply energy dependent.

The simplest energy-dependent relaxation time is that assumed by Korringa and Gerritsen[11] in which $\tau=\tau_0$, a constant, except for $(E_0-\Delta)\leqslant E\leqslant(E_0+\Delta)$ when $\tau=0$. Under this condition the integral Q [Eq. (A2)] becomes

$$Q=e^{-(2\pi a_0|p|+i\pi/4)}\left[\int_{-\infty}^{\infty}e^{i2\pi pE/\beta^*H}\ln\{1+e^{(E_0-E)/kT}\}dE-\int_{E_0-\Delta}^{E_0+\Delta}e^{i2\pi pE/\beta^*H}\ln\{1+e^{(E_0-E)/kT}\}dE\right]=Q_1+Q_2,\quad\text{(A3)}$$

since the integral Q is zero when $\tau=0$. A value of $\tau/\tau_0=0.2$ is sufficiently small to make $Q\to0$. Combining Q_1 with Eq. (A1) gives an expression for the free energy identical to that obtained by Dingle[15] which is

$$F_{\text{periodic}}=\frac{2\pi(2m^*)^{3/2}kTV(\beta^*H)^{3/2}}{h^3\sqrt{2}}\sum_{p=1}^{\infty}\left[\frac{(-1)^p\cos(2\pi pE_0/\beta^*H-\pi/4)}{p^{3/2}\sinh(2\pi^2pkT/\beta^*H)}e^{-hp/\tau_0\beta^*H}\right].\quad\text{(A4)}$$

It is thus seen that the effect of an energy-dependent relaxation time is to add a term to the free energy which is determined by combining Q_2 with Eq. (A1).

To evaluate Q_2, consider the two cases (i) $E_0\gg\Delta$, (ii) $E_0\gtrsim\Delta$.

Case (i)

If $E_0\gg\Delta$, then $e^{i2\pi pE/\beta^*H}$ can be put equal to $e^{i2\pi pE_0/\beta^*H}$ and putting $(E-E_0)/kT=x$ with $\Delta=kT_\Delta$, Q_2 may be written

$$Q_2=-kTe^{-[2\pi a_0|p|-i(2\pi pE_0/\beta^*H-\pi/4)]}I(T_\Delta/T),\quad\text{(A5)}$$

where

$$I(T_\Delta/T)=\int_{-T_\Delta/T}^{T_\Delta/T}\ln(1+e^{-x})dx.\quad\text{(A6)}$$

Equation (A6) was integrated by numerical methods and the results are shown in Fig. 6(b). On combining Eq. (A5) with Eq. (A1), the term, f, which must be added to the free energy to account for the energy-dependent relaxation time, is calculated to be

$$f=\frac{2\pi(2m^*)^{3/2}kTV(\beta^*H)^{3/2}}{h^3\sqrt{2}}\sum_{p=1}^{\infty}p^{-1/2}(-1)^p\frac{kT}{\beta^*H}\cos(2\pi pE_0/\beta^*H-\pi/4)e^{-ph/\tau_0\beta^*H}.\quad\text{(A7)}$$

On adding Eq. (A7) to Eq. (A4) the periodic part of the free energy of the conduction electrons, in a metal having a resistance minimum due to the postulated energy-dependent relaxation time, is given by

$$F_{\text{periodic}}=\frac{2\pi(2m^*)^{3/2}kTV(\beta^*H)^{3/2}}{h^3\sqrt{2}}\times\sum_{p=1}^{\infty}\left[\frac{(-1)^p\cos(2\pi pE_0/\beta^*H-\pi/4)}{p^{3/2}\sinh(2\pi^2pkT/\beta^*H)}e^{-ph/\tau_0\beta^*H}\left\{1+\frac{pkT\sinh(2\pi^2pkT/\beta^*H)}{\beta^*H}I(T_\Delta/T)\right\}\right].\quad\text{(A8)}$$

In the present experiments the torque on a single crystal was measured. The torque C will be given by

$$C=-\partial F/\partial\psi,$$

where ψ is an angle denoting rotation in a plane normal to the axis of suspension of the crystal. In the differentiation of (A8), to obtain the torque, the main contribution comes from the cosine term since $E_0/\beta^*H\gg 1$. Thus the torque on the crystal is given by

$$C=-\frac{\partial F}{\partial\psi}=-\frac{\partial F}{\partial(1/\beta^*)}\frac{\partial(1/\beta^*)}{\partial m^*}\frac{\partial m^*}{\partial\psi} \tag{A9}$$

$$=\left(\frac{e\hbar}{c}\right)^{1/2}\frac{E_0kTV}{\pi\hbar^3}H^{1/2}\frac{\partial m^*}{\partial\psi}\sum_{p=1}^{\infty}\left[\frac{(-1)^p\sin(2\pi pE_0/\beta^*H-\pi/4)}{p^{1/2}\sinh(2\pi^2pkT/\beta^*H)}\right.$$
$$\left.\times e^{-ph/\beta^*\tau_0H}\left\{1+\frac{pkT\sinh(2\pi^2pkT/\beta^*H)}{\beta^*H}I(T_\Delta/T)\right\}\right], \tag{A10}$$

which reduces to Eq. (12) of the main part of the paper by using the arguments following Eq. (2) in the main part of the paper.

Case (ii)

If $E_0\gtrsim\Delta$, then $e^{i2\pi pE/\beta^*H}$ cannot be put equal to $e^{i2\pi pE_0/\beta^*H}$ in the expression for Q_2. Instead, put $(E-E_0)/kT=x$ and the expression for Q_2 becomes

$$Q_2=-kTe^{-[2\pi a_0|p|-i(2\pi pE_0/\beta^*H-\pi/4)]}\int_{-\Delta/kT}^{\Delta/kT}e^{i[2\pi p(kTx/\beta^*H)]}\ln(1+e^{-x})dx. \tag{A11}$$

Since it is desired mainly to know the qualitative effect of the energy-dependent relaxation time on the period of the oscillations, Eq. (A11) can be simplified at the cost of accuracy in the value of Q_2 by putting

$$(1+e^{-x})=2,$$

whence

$$Q_2=-kT\ln 2e^{-[2\pi a_0|p|-i(2\pi pE_0/\beta^*H-\pi/4)]}\int_{-\Delta/kT}^{\Delta/kT}e^{i2\pi pkTx/\beta^*H}dx$$
$$=\frac{\beta^*H\ln 2}{2\pi p}e^{-2\pi(a_0|p|)}\{ie^{i[2\pi p(E_0-\Delta)/\beta^*H-\pi/4]}-ie^{i[2\pi p(E_0+\Delta)/\beta^*H-\pi/4]}\}. \tag{A12}$$

Taking the real part of Eq. (A12), Q_2 becomes

$$Q_2=\frac{\beta^*H\ln 2}{2\pi p}e^{-2\pi a_0|p|}\cos(2\pi pE_0/\beta^*H-\pi/4)\sin(2\pi p\Delta/\beta^*H). \tag{A13}$$

Combining Eq. (A13) with Eq. (A1) and adding it to Eq. (A4), the periodic part of the free energy of the condition electrons in a metal exhibiting a resistance minimum due to the postulated energy-dependent relaxation time is

$$F_{\text{periodic}}=\frac{2\pi(2m^*)^{3/2}kTV(\beta^*H)^{3/2}}{h^3\sqrt{2}}\sum_{p=1}^{\infty}\left\{\frac{(-1)^p\cos(2\pi pE_0/\beta^*H-\pi/4)}{p^{3/2}\sinh(2\pi^2pkT/\beta^*H)}\right.$$
$$\left.\times e^{-ph/\tau_0\beta^*H}\left[1+\frac{2\sinh(2\pi^2pkT/\beta^*H)}{\pi}\sin(2\pi p\Delta/\beta^*H)\right]\right\}. \tag{A14}$$

It is thus seen that the effect of τ being equal to zero, in an energy range Δ about the Fermi energy, is to add a periodic term to the free energy whose amplitude is sinusoidally modulated. The period of the modulation, P_{mod}, is given by

$$P_{\text{mod}}=\beta^*/p\Delta.$$

The ratio of the period of the modulation to the period of the oscillations is

$$P_{\text{mod}}/P=(\beta^*/p\Delta)(pE_0/\beta^*)=E_0/\Delta.$$

For the zinc 0.008 wt. % zinc manganese alloy which has been measured, E_0 and Δ are, respectively, 3.8×10^{-14}

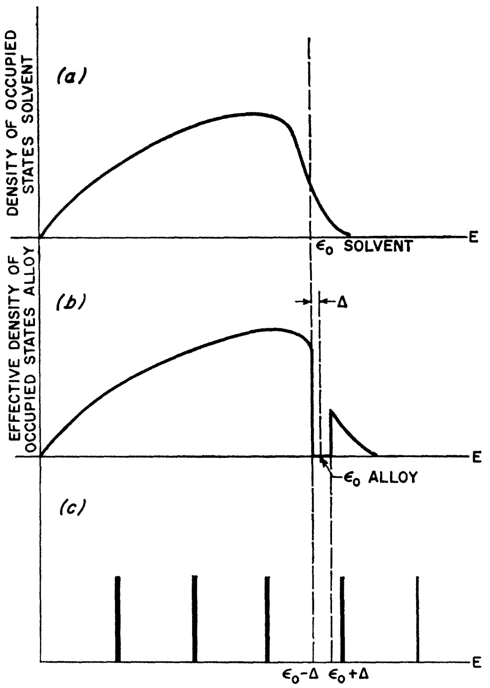

FIG. 10. (a) The density of populated states as a function of energy for the pure metal. (b) The effective density of states as a function of energy for an alloy having the postulated energy dependent relaxation time. (c) A schematic representation of the magnetic energy levels which give rise to the de Haas-van Alphen effect. Populated levels are indicated by heavy lines.

erg and 1.0×10^{-16} erg. Whence $P_{\text{mod}}/P\sim400$ and the effect of the modulation will be unnoticeable.

The above theory suggests the following physical model. Any state existing in the energy interval in which $\tau=0$ must, by the uncertainty principle, be very broad. As a consequence the transition probability between this state and any other unoccupied state will be large and thus the net effect of the energy-dependent relaxation time will be to induce a gap in the effective density of states[33] [Fig. 10(b)]. If a rigid band model is assumed for the alloy and the electron-to-atom ratio remains unchanged on alloying,[34] then the Fermi energy of the alloy must increase by an amount Δ in order to accomodate all the electrons[35] [*cf.* Figs. 10(a) and (b)]. This increase in the Fermi energy leads to a decrease in the period which is given by

$$P_{\text{alloy}}=(\beta^*/E_0)(1-\Delta/E_0)=P_{\text{pure}}(1-\Delta/E_0),$$

where E_0 is the Fermi energy of the solvent. In the present case $\Delta/E_0\sim1/400$ and hence a decrease in the period of 0.25% would be expected. This is well within the present experimental accuracy of 1.5%.

The effect of the gap in the density of states on the de Haas-van Alphen oscillations can be seen from Fig. 10(c). As the field increases the magnetic levels move to the right. At energy $E_0-\Delta$ they depopulate rapidly giving rise to oscillations of period $\beta^*/(E_0-\Delta)$. At energy $E_0+\Delta$ they repopulate and give rise to a second set of oscillations having period $\beta^*/(E_0+\Delta)$. Since this pair of oscillations have nearly the same period, they will beat and give rise to a set of modulated oscillations having period β^*/E_0 and a modulation period of β^*/Δ. [*cf.* Eq. (A14)] From Fig. 10(b) it is seen that another consequence of the gap in the density of states is that the transition from populated to unpopulated states is more abrupt than would normally be expected. This results in an increase in the amplitude of the oscillations in manner which is analogous to a reduction in temperature. As can be seen from Eq. (A10), this is the expected behavior.

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[33] Equation (2.3) in Dingle's (reference 15) paper also leads to this conclusion. It should be pointed out that in either case the concept of a "density of states" may not be permissible for states which have such a poorly defined energy.

[34] In the present case zinc and manganese are both assumed to have valence 2.

[35] This effect was not predicted by the detailed analysis given earlier because, for mathematical simplicity, the analysis was carried out under the assumption that E_0 was constant.