One must therefore conclude that the nonlinear spin-wave theory for the antiferromagnet, although accurate at low temperatures, does not appear to give a good estimate of the transition temperature for $\eta \neq 1$.

SUMMARY

A single analytical expression for the magnetization was obtained, which is valid for all temperatures. The demonstrated technique of evaluating certain temperature-dependent sums and integrals was employed without necessitating the use of various series approximations or entensive numerically computed summations. Other thermodynamic quantities, such as specific heat, can be calculated in the same manner.

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Magnetic Susceptibility of Dilute Al-Mn Alloys

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The temperature dependence of the magnetic susceptibility of pure aluminum and three aluminum alloys containing 0.045, 0.21, and 0.35 at.% manganese has been measured between 2 and 300 °K. All of the susceptibility results can be fitted to an equation of the form $A + BT^2$. The experimental values of the coefficients A and B for pure aluminum are $19.2 \pm 0.1 \times 10^{-7}$ emu/cc and $3.7 \pm 0.1 \times 10^{-12}$ emu/cc/(°K^2), which are in good agreement with theoretical values derived from the known band structure of aluminum. An additional susceptibility component is observed in th Al-Mn alloys, and the experimental results can be characterized by the equation $\Delta K_{\mathrm{Mn}}(T)/C$ emu/cc at.% Mn $= 13.8 \pm 0.8 \times 10^{-7} - (14 \pm 3 \times 10^{-13})T^2$. The experimentally determined coefficients can be explained by considering an exchange enhancement of the Pauli paramagnetism within the framework of a Hartree-Fock approximation. Values of the exchange enhancement factor η, and the width of the virtual bound d states, Δ, can be uniqiely determined and have the values 4.4 ± 1 and 0.33 ± 0.05 eV, respectively.

It has been known for some time that a transition-metal impurity added to a monovalent metal gives rise to a Curie-Weiss law at high temperatures, e.g., for Cu-Mn $\mu_{\mathrm{eff}} = 4.9\ \mu_B$.[1]

In a divalent host, the higher electron density may result in greater mixing of the conduction electron and d states with a resulting decrease in the moment carried on the manganese, e.g., for Zn-Mn $\mu_{\mathrm{eff}} = 3.9\ \mu_B$.[1] Both of the above systems exhibit a Kondo effect, i.e., a ln-T term in the low-temperature resistivity. In going to a trivalent solvent such as aluminum with a still higher electron density, the manganese ion does not obey a Curie-Weiss law and no Kondo effect is observed.

The present investigation reports on some measurements of the low-temperature static volume susceptibility, $K(T)$ of Al-Mn alloys and pure aluminum. A negative T^2 term is found at low temperatures. The magnitude of the additional observed T^2 term due to the presence of manganese in the Al-Mn alloys is consistent with the value of susceptibility calculated in the Hartree-Fock approximation of Friedel[2] and Andersen.[3,4] These theories lead to an exchange of the band paramagnetism.

The aluminum sample was made from Cominco 99.9999+% pure aluminum and the Al 0.045 at.% Mn alloy was made by the Aluminum Company of Canada.[5] The two other alloys were made from the 0.045 at.% Al-Mn alloy and 99.99% pure manganese. The alloys were melted at 850 °C and quenched in ice water from 600 °C after a 60-h homogenizing anneal. The pure aluminum specimen was given a strain-relieving anneal for 24 h at 450 °C. Shown in Table I are the concentrations determined for the various samples.

To check the ferromagnetic impurity content in each sample, the magnetization was measured as a function of magnetic field in the temperature range from 300 to 2 °K. All samples showed the susceptibility to be independent of magnetic field within the experimental error ± 0.5% up to an average magnetic field strength of 15kG.

The room-temperature susceptibility was measured on a Cahn servobalance and the susceptibility determined relative to oxygen gas, where the susceptibility of oxygen was taken as 106.2×10^{-6} emu/gm at 20 °C. The maximum error in the room-temperature susceptibility relative to oxygen gas is ±0.8%. The low-temperature magnetic susceptibility was measured on a high-gain servobalance previously described by Hedgcock and Muir.[7] The maximum error in the relative susceptibility at low temperatures is approximately ±0.5% over the whole low-temperature range of measurement. The probable error in the determination of the susceptibility at any particular temperature is approximately ±0.3%.

Shown in Fig. 1 are the susceptibility data for pure aluminum fitted to a T^2 law. Summarized in Table II are the experimental values of the volume susceptibility at room temperature, the coefficients of the T^2 term, and the value for K extrapolated to $T = 0$. These values are in good agreement with previous measurements on pure aluminum and can be explained theoretically[12] if it is assumed that the Fermi surface[13] can be divided into a spherical part with a degeneracy temperature of 1.35×10^5 °K and a nonspherical part with a degeneracy temperature of 387 °K,[14] where each degeneracy temperature is measured from the bottom of the individual band. The theoretical coefficients derived lead to the equation

$$K_{\mathrm{Al}}(T) = 19.3\times 10^{-7} - 4.0\times 10^{-12}\,T^2 \text{ emu/cc} \tag{1}$$

which is in good agreement with the experimental results summarized in Table II. The increase in the susceptibility of pure aluminum at temperatures below 30 °K previously reported by Wheeler[15] and by Aoki[6] is also observed in the aluminum alloys. We believe this effect is an intrinsic property of aluminum[16] and is under further investigation.

TABLE I. Manganese concentrations for the various Al-Mn alloys studied.[a]

	Alloy 1	Alloy 2	Alloy 3
Nominal concentration	···	0.20_6 at.%	0.34_3 at.%
Spectroscopic analysis	0.0452 at.%	···	···
Residual resistance ratio	0.0449 at.%	0.21_0 at.%	0.35_1 at.%
Electron microprobe	···	0.21 at.%	0.34 at.%

[a] The resistance ratio per at.% manganese was determined from the work of Aoki and Ohtsuka (Ref. 6) and has the value of 3.2/at.% Mn.

Figure 1 includes the susceptibility of the Al-Mn alloys shown as a function of T^2, and included as an insert in the figure is the concentration dependence of the coefficient of the T^2 term. It can be seen to vary linearly with concentration as would be expected for a noninteracting spin system. The experimental results for the Al-Mn alloys can be characterized by the equation

$$\begin{aligned}\Delta K_{\mathrm{Mn}}(T)/c &= (13.8\pm 0.8)\times 10^{-7}\\ &\quad - [(13.8\pm 3.0)\times 10^{-13}]T^2 \text{ emu/cc at.\% Mn.}\end{aligned} \tag{2}$$

Lederer and Mills[4] have discussed the case of an exchange-enhanced band paramagnetism due to the mixing of a d level in the conduction band of a nonmagnetic solvent. The resulting increase in the band paramagnetism per atomic percent paramagnetic ion is given by

$$\Delta K_{\mathrm{Mn}}(T)/c = 2N\mu_B^2\, N_d[E_F(T)]\eta(T) \text{ emu/cc at.\% Mn,} \tag{3}$$

where

$$\eta(T) = \{1 - [(U+4J)/(2l+1)]N_d[E_F(T)]\}^{-1},$$

$$N_d[E_F(T)] = N_d[E_F(0)][1 - \tfrac{1}{3}\pi^2(kT/\Delta)^2] \quad ,$$

$$\begin{aligned}N_d[E_F(0)] &= [(2l+1)/\pi]\Delta/[(E_d-E_F)^2+\Delta^2]\\ &\simeq [(2l+1)/\pi](1/\Delta) \quad \text{for } E_d - E_F \ll \Delta \quad ,\end{aligned}$$

and c is the concentration of the transition metal impurities; N is the number of atoms per cc; η is the enhancement factor of the d states; $N_d(E_F)$ is the density of d states at Fermi energy E_F; U and J are the intra-atomic d-d Coulomb and exchange energies, respectively; $2l+1$ is the degeneracy factor; E_d is the position of the atomic d level relative to the bottom of the conduction band; and Δ is the width of virtual bound d states. For a transition-metal ion such as manganese, Eq. (3) reduces to

$$\frac{\Delta K_{\mathrm{Mn}}(T)}{c} = \frac{10N\mu_B^2}{\pi}\,\frac{1}{\Delta}\,\eta(0)\left[1 - \frac{\pi^2}{3}\eta(0)\left(\frac{kT}{\Delta}\right)^2\right]. \tag{4}$$

It should be mentioned that the temperature dependence in the susceptibility in Eq. (4) is due to the

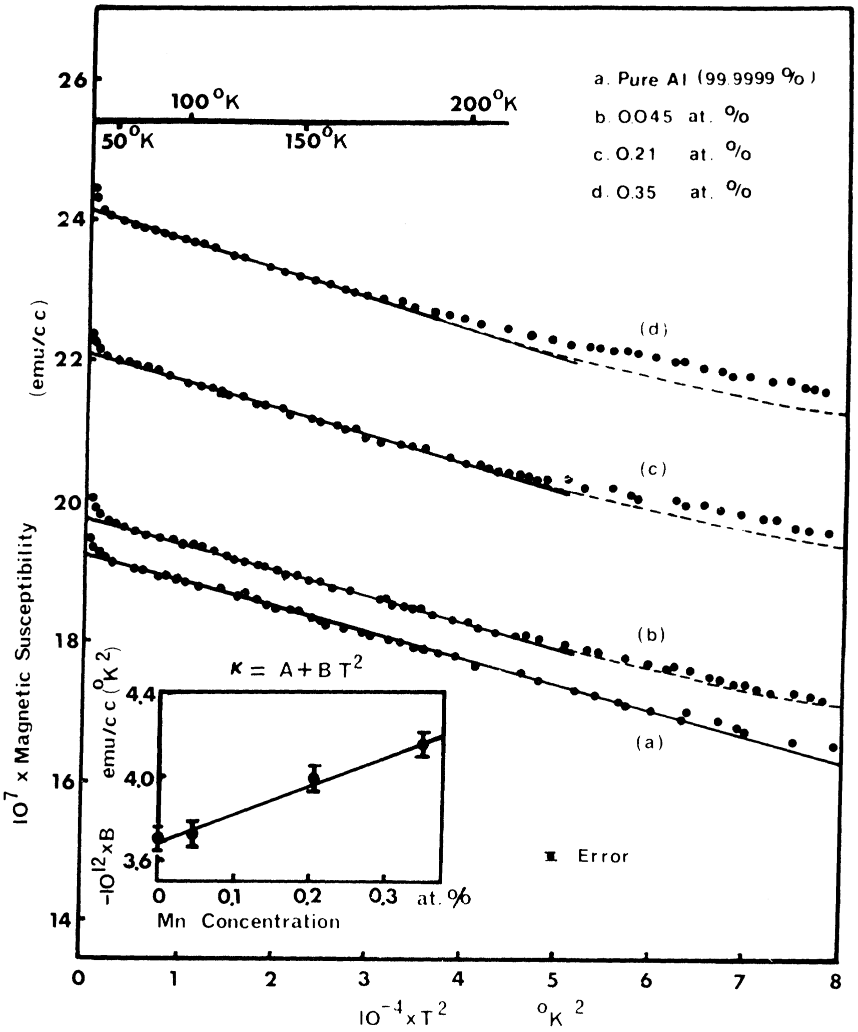

FIG. 1. Magnetic susceptibility per unit volume, K versus T^2. Note that in Eq. (3), ΔK_{Mn} will depend on $N_d\,[E_F]$ in two ways, i.e., through $N_d\,[E_F]$ directly and through the enhancement factor η. A correction due to thermal expansion has been made on ΔK_{Mn} by assuming that for each alloy

$$N_d[E_F]=N_d^0\,[E_F]\;[1+\tfrac{2}{3}\,\alpha_v\,T]$$

(Ref. 8). α_v is the volume thermal expansion coefficient of pure aluminum (c.f. Flynn, Ref. 9). Dashed lines are the high-temperature experimental data corrected for the volume dependence of ΔK_{Mn} which amounts to multiplying the experimental results by a factor of $\tfrac{2}{3}\,\alpha_v\eta T$. Volume correction below 150 °K is within experimental error and has been neglected. Coefficient of T^2 term estimated below 150 °K of Al-Mn system versus Mn concentration is shown in the inset of the figure.

temperature dependence of the density of d states only. The major difference between Eq. (4) and that derived by Rivier and Zuckermann[17] is the coefficients of the T^2 term, the two coefficients differing by a factor $\eta(0)$. The experimental error in the determination of the T^2 coefficient for the alloys is sufficiently small to permit an evaluation of the power of $\eta(0)$ required to fit the data. The

TABLE II. Room temperature and 0 °K volume susceptibility and the T^2 coefficient for pure aluminum.

	$10^7\times K$(RT) emu/cc	$10^7\times K(T\rightarrow 0)$ emu/cc [a]	$10^{12}\times$(coefficient of T^2)(emu/cc) (°K²)
Lingelbach and Vogt[b]	16.2±0.3	19.1±0.3	3.7±0.3
Taylor[c]	16.7±0.3	19.3±0.3	3.4±0.3
Wheeler[d]	16.3±0.3	18.9±0.3	3.4±0.3
Present work	16.3±0.1	19.2±0.1	3.7±0.1

[a] The value of $K(T\rightarrow 0)$ was determined by extrapolating K_{alloy} versus T^2 to $T=0$.

[b] Reference 10.

[c] Reference 11.

[d] Reference 15.

value of $\Delta K_{\mathrm{Mn}}(0)/c$ yields a value of $\eta(0)/\Delta$ of 0.83×10^{-13} ergs^{-1}, which is in good agreement with the value 0.75×10^{-13} ergs^{-1} derived by Caplin and Rizzuto.[18] Using values for Δ of 0.17 eV as derived from specific heat[6] or a value of 0.26 eV derived from thermoelectric power[19] produces values for $\eta(0)$ that fix the power of $\eta(0)$ in the T^2 coefficient to a value less than or equal to 2 (within the experimental error of ± 0.05 eV for Δ) but in no case equal to 3. The present measurements on the static magnetic susceptibility of Al-Mn show that an exchange enhancement of the Pauli paramagnetism within the framework of a Hartree-Fock approximation is adequate, i.e., the dynamics of localized spin fluctuations do not effect the static susceptibility. It is, therefore, possible to use the susceptibility results alone to solve for $\eta(0)$ and Δ from Eq. (4). The following values are found: $\Delta = 0.33 \pm 0.05$ eV and $\eta = 4.4 \pm 1$. The parameter $(U+4J)/\pi\Delta$ is the criterion for magnetism and on the Hartree-Fock theory should be less than unity.[3] Using the value of η derived above, we estimate the value of $(U+4J)/\pi\Delta$ to be $0.7_7 \pm 0.1$, which is consistent with the assumptions used in deriving Eq. (4). The Hartree-Fock theory, however, is not adequate to explain the temperature dependence observed in the NMR studies made on Al-Mn by Launois and Alloul.[20] An explanation for this may lie in the fact that the NMR measurements depend on the dynamic susceptibility and, hence, are sensitive to localized spin fluctuations.

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