The Saturation Magnetic Moment of Alloys on the Collective Electron Theory*

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BOZORTH[1] has called attention to the fact that for certain alloy systems, the Pauling curve for the saturation magnetic moment of the ferromagnetic metals and alloys of the first transition series does not apply. Specifically for the alloys Ni-Mn, Ni-Cr, Ni-V, Co-Mn, and Co-Cr, the addition of small amounts of the nonferromagnetic constituent causes the average moment of the alloy to decrease by anomalously large values instead of the increase predicted by the Pauling curve. A qualitative explanation of this anomaly on the basis of the Heitler-London-Heisenberg approach to the exchange interaction using the Néel criterion[2] has previously been proposed by the author for the case of Ni-Mn[3] and is readily extended to the other four alloys. Néel's condition for ferromagnetism is determined by the difference between the interatomic spacing of the interacting neighbors and the sum of the radii of the magnetic shells. If one uses the radii calculated by Slater,[4] then on the Néel theory, the interaction in the case of all five of the alloy combinations cited is negative, i.e., antiferromagnetic. One might suppose, therefore, on this localized electron picture that the atomic moment of the solute atom is oppositely directed to that of the ferromagnetic matrix. Reasonable agreement in magnitude can then be obtained if one uses an atomic moment consistent with Hund's rule of maximum multiplicity within the atom, allowing for the same number of noncontributing conduction electrons as in the ferromagnetic elements. Zener[5] and his collaborators have given a somewhat analogous interpretation, in which the interaction is again assumed to be an antiferromagnetic one but originating in the probable role of the conduction electrons as originally set forth in Zener's theory.[5] Both these theories have in common that they use a strictly localized electron (Heitler-London-Heisenberg) approximation. The purpose of this note is to propose an alternative explanation in terms of the collective electron model and to suggest an experiment which may permit one to decide between these two approaches to ferromagnetism—at least as applied to the saturation moment of such alloys.

Consideration of the effect of a perturbation in the periodic potential due to a foreign atom on the energy bands of the matrix has led Slater, James,[6] Jones,[7] and others to the conclusion that the band is itself perturbed in such a way that localized in the region near the impurity are allowed levels with energy values, which in the nonperturbed case would normally lie in the forbidden range. For the case of an impurity atom of lower atomic number these states are above the band, and there results a region of depleted charge in the neighborhood of the impurity atom. The argument is readily carried over to the case of a *d*-band in transition elements, with the *d*-electrons considered as itinerant. Thus the *d*-band in cobalt is altered by the presence of a Cr atom in the manner shown schematically in Fig. 1, which corresponds to Slater's picture of an Al impurity in Ge except that the spectrum of discrete states is shown as a continuum. Stated otherwise, the probability of finding an electron of low energy (near the bottom of the band) in the neighborhood of the impurity is small due to the higher potential of the impurity atom with a consequent depletion of charge in that region. Thus the density of states at the bottom of the band is decreased. The redistribution of the electrons among the available states means that in order to minimize the Fermi energy some previously empty states of negative spin (opposite to the macroscopic moment) be occupied. The extent of the decrease in moment is determined by the magnitude of the perturbing potential and should be greater as the atomic number of the impurity is decreased, in agreement with observation.

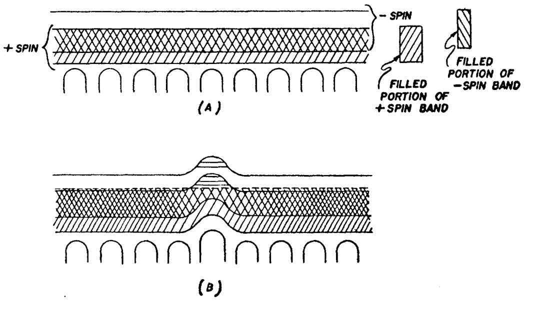

FIG. 1. Schematic representation of the perturbing effect of an alloying element on the energy bands in a metal.

This now suggests an experiment, the result of which will enable one to distinguish between the two approaches previously outlined. If one were to study the susceptibility as a function of temperature of alloys containing enough dissolved nonferromagnetic constituent to reduce the saturation moment to zero, then according to the atomic viewpoint these should be antiferromagnetic, whereas on the collective electron theory one is more likely to find either diamagnetism or a modified Pauli paramagnetism similar, perhaps, to that in copper-nickel alloys with copper concentrations greater than 60 percent in which anomalous susceptibilities have been observed and have been given an analogous interpretation by the author.[8] Such an experiment is currently in progress in this laboratory. The author is indebted to Professor R. Smoluchowski and Dr. N. Rostoker for helpful criticism.

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* Supported by the ONR.

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The Electronic Specific Heat in Chromium and Magnesium*

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THE specific heats of several metals, including some in the first transition series, have been measured as a function of temperature between 1 and 4°K. The measurements permit an accurate calculation of the electronic contribution to the specific heat and evaluation of the density of energy states at the top of the Fermi distribution. The cryogenic technique and details of the measurement will be reported elsewhere.[1] The purpose of this note is to call attention to some of the results and their relations to certain fundamental properties of these metals.

The specific heat of metals can generally be represented by a relation of the form $C_v=\gamma T+\beta T^3$. The linear term in temperature represents the electronic contribution, and the coefficient γ gives a direct measure of the density of states at the Fermi surface; the second term is the well-known Debye term that is present in insulators as well as in metals. The two may readily be separated at very low temperatures. This is conveniently done by plotting C_v/T against T^2. The intercept then gives γ directly and the slope gives the Debye characteristic temperature. Our results for Mg and Cr plotted in this manner are given in Fig. 1. The values of γ thus obtained, as well as those for Ti and Zr measured in this laboratory, are compared with measurements on other metals in Table I. The data for V are determined from the critical field data obtained on superconducting vanadium.[2]

The very high values of γ for the transition elements are associated with contributions to the specific heat from the highly dense

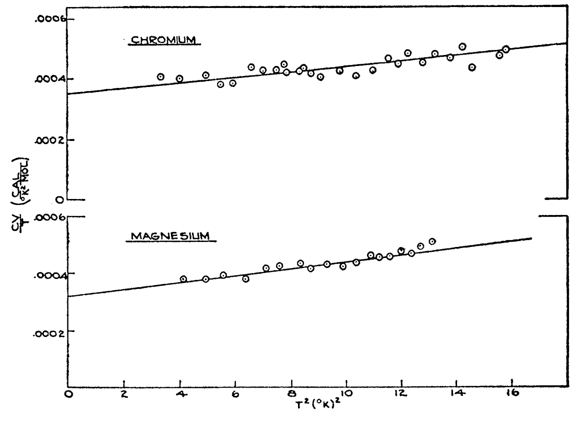

FIG. 1. C_v/T as a function of T^2, for Cr and Mg.

incomplete 3*d*-band. The value in Cr thus appears anomalously low. This is particularly surprising in view of the remarkable similarity between Cr and V, both of which have identical crystals structures with nearly identical spacing and are neighbors in the periodic table. A possible interpretation may be given this phenomenon in terms of the *d*-band shape calculated by Slater and Krutter[3] and by Fletcher and Wohlfarth[4] for the case of Cu, which shows a minimum in the density curve when the band is about half-full. It is not likely that this shape would change significantly as the number of *d*-electrons is decreased. Also, the change in crystal structure is probably not significant, as shown by Manning[5] who finds only minor differences between the Slater-Krutter curve of density of states *vs* energy for Cu and his own for body-centered Fe. In Cr, the Fermi level may be close to this minimum. Another possibility involves the suggestion recently put forward by Zener,[6] that Cr is probably antiferromagnetic and that in a case where the *d*-band is half-full (as in Cr) transitions involving electronic 3*d*-states would require an energy greater than the exchange energy since an electron would have to reverse its spin during the transition. In an antiferromagnet, the band is split in two,[7] and in this case the lower band is full and the upper one empty. This supposition is apparently confirmed by the high temperature specific heat measurements of Armstrong and Grayson-Smith,[8] who observe a rapid increase in C_v above the Dulong-Petit value at temperatures well below the degeneracy temperature, which can be understood if at those temperatures kT is approaching the magnitude of the exchange energy where this anomalous rise begins. On the other hand, the inability of Shull[9] to find evidence for marked antiferromagnetism in Cr, or for a significant magnetic scattering for the chromium atom, tends to support the former interpretation.

The case of magnesium is also of particular interest. From Fig. 1 it is evident that the electronic contribution is very well represented by a linear temperature term. In this material, several investigators have observed a minimum in the curve of resistance *vs* temperature at temperatures between 5° and 15°K. One of the possible interpretations given for this phenomenon has been that there is a small but finite energy gap between the 3*s*- and 3*p*-bands which causes the material to behave as a semiconductor at very low temperatures. In that case, the electronic terms in the specific heat would come from the tail end of the Fermi distribution which is essentially a classical distribution and should therefore depend exponentially on temperature. Our results preclude this interpretation. This is confirmed by estimates of the effective mass of the conduction electrons based on our measured density of states and the magnetic susceptibility data of McGuire,[10] which gives a result considerably greater than the free electron mass. Such an estimate is reasonable when the susceptibility is isotropic and independent of field as found by McGuire at 2.2°K. If the conduction electrons had been in pure *p*-states (at the bottom of the *p*-band), their effective mass would probably be smaller than the free electron mass. The authors are indebted to Professor J. C. Slater for pointing out Shull's results on chromium as well as for discussions of the band theory interpretation. We are also indebted to Dr. Clarence Zener for discussions of his theory of the properties of transition elements.

TABLE I. Values of γ, the coefficient of the term linear in T in the specific heat; and $n(\epsilon)$, the density of states at the Fermi surface.

Metal	$\gamma\times10^4$	$n(\epsilon)$ levels/atom/ev
Copper	1.80	0.16
Magnesium	3.25	0.29
Titanium	8.3	0.74
Vanadium	14	
Zirconium	6.92	0.62
Chromium	3.74	0.33

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A Relativistic Modification of Bose and Fermi Statistics

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ONE of the most striking results in our previous investigations[1] on the quantum statistics of fields was that the thermodynamics of the relativistic Schrödinger-Gordon field does not yield the thermodynamics of the nonrelativistic field if c (the velocity of light) approaches infinity. One can show that this is the result of the fact that the rest energy of the particles is included in the Hamiltonian of the relativistic field, whereas in the nonrelativistic case it is not. This is most easily seen if the average energy per particle is calculated. A straightforward computation by means of the results of our earlier publication yields for $kT \ll mc^2$

$$E/N \simeq mc^2 + \tfrac{3}{2}kT. \qquad (1)$$

It seems therefore desirable to develop a subtraction formalism which effects that the thermodynamic functions of the relativistic field refer only to that part of the energy whose classical analog is the kinetic energy of the particles. In order to do this one has to replace the Schrödinger-Gordon equation by a wave equation such that the Hamiltonian of the quantized field may be written as

$$H = \Sigma_K N_K \hbar c[(\mu^2+K^2)^{\frac{1}{2}} - \mu]; \quad \mu = mc/\hbar. \qquad (2)$$

The calculation of the thermodynamic functions will be exactly as in our earlier paper,[1] except that everywhere $(\mu^2+K^2)^{\frac{1}{2}}$ has to be replaced by $\{(\mu^2+K^2)^{\frac{1}{2}} - \mu\}$. For the internal energy E, for instance, this yields the result

$$\frac{E}{V} = \frac{3}{2}\frac{(2\pi m)^{3/2}}{h^3}(kT)^{5/2}\Sigma\frac{1}{n^{5/2}}\left\{1 + \frac{75}{16n}\frac{kT}{mc^2} + \cdots\right\}. \qquad (3)$$

This expression, indeed, yields the nonrelativistic formula if c approaches infinity. It might be regarded as a relativistic generalization of Bose statistics; the correct relativistic energy resulting