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

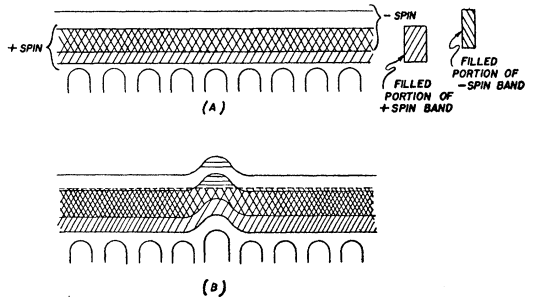

FIG. 1. Schematic representation of the perturbing effect of an alloying element on the energy bands in a metal.

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.

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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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