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Role of *s-d* Exchange Interactions in Dilute Alloys Exhibiting Both Low-Temperature Resistance Anomalies and Superconductivity*

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Measurements of the magnetic susceptibility of some dilute Zn-Mn alloys are reported in the temperature range where this alloy system is known to exhibit low-temperature resistance anomalies. All of the alloys studied obey a Curie law with the most concentrated alloy (0.43-at.% Mn) exhibiting deviations in the neighborhood of 6°K. The Curie constant indicates that manganese when dissolved in zinc has a spin value of $\frac{2}{3}$ which is temperature-independent between 5 and 273°K. Calculations of the exchange integral J from the magnetic properties of dilute Zn-Mn alloys have been made from the Néel temperature, the magnetoresistivity as a function of field strength and the suppression of the superconducting critical temperature based on theoretical equations which assume a scalar *s-d* interaction between the paramagnetic ions and conduction electrons. All of the derived values of J lie in the range of $(1.4\pm0.2)\times10^{-12}$ erg which would lead one to conclude that the magnetic interaction giving rise to these various effects is of the same nature. A graphical method for separating the resistance minimum from the total resistivity, in the presence of a resistance maximum produced by magnetic ordering in the Zn-Mn system, is presented.

INTRODUCTION

THEORY predicts[1,2] and some experiments substantiate[3–5] the fact that the critical temperature is suppressed in superconducting elements containing small concentrations of transition metal impurities. Recently, measurements have been reported[5] on the suppression of the superconducting transition temperature in a system that had been earlier reported to exhibit a low-temperature resistive anomaly.[6] It has been shown theoretically[7,8] and illustrated experimentally for the[9] Zn-Mn system that a sharply energy-dependent conduction-electron relaxation time in the neighborhood of the Fermi energy will produce a resistance rising with decreasing temperature to some finite value at absolute zero. It is observed in the Zn-Mn system that the resistive characteristic flattens off following the so-called resistance minimum.[9] A preliminary report[10] of the magnetic properties of this system show a weak antiferromagnetism and it is believed that although the resistivity is decreased by the decrease of spin scattering on ordering, the decrease is not sufficiently great to result in a resistive maximum. It is the purpose of the present paper to present more complete data on the spin value of manganese in zinc and to calculate and compare values for the *s-d* exchange integral J found from electron transport and magnetic properties. A comparison of the value of J found for the Zn-Mn system will be made with the values of J found for a system possessing only a resistive anomaly (Cu-Mn) and only a superconducting transition (Al-Mn).

MAGNETIC SUSCEPTIBILITY RESULTS AND DISCUSSION

Table I lists the results of the magnetic susceptibility measurements.

Nominal manganese concentration was obtained from a plot of "relative residual resistance" versus "weighed-out" concentration. Figure 1(a) shows the collected data from several series of alloys. In Fig. 1(b) the room temperature susceptibilities of some rolled strips and the cast pieces used in the present temperature runs are plotted against concentration obtained from relative residual resistances of rolled strips. The susceptibility measurements were regarded as being the most accurate and deviations of the points from the best straight line were attributed to concentration errors. Figure 1(b) was therefore used to obtain the sample concentration used in subsequent calculations.

In the temperature runs, relative susceptibility was measured and converted to susceptibility from the separately-measured room temperature values. Figure 2 shows the alloy susceptibility plotted against reciprocal temperature in the region between room temperature and liquid nitrogen. In Fig. 3 the inverse of the manganese component of susceptibility (ΔX^{-1}) is shown as a function of absolute temperature in the temperature range between liquid nitrogen and liquid helium. An insert shows the behavior of the most concentrated alloy in the vicinity of the Néel point. If one

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[10] E. W. Collings, F. T. Hedgcock, and W. B. Muir, Proceedings of the Eighth International Conference on Low-Temperature Physics, London, 1962 (unpublished).

Table I. Magnetic susceptibility samples with the derived concentrations, Curie constants, and calculated magneton numbers.

Sample	Nominal concentration from Fig. 1(a) weight (%)	Concentration from ΔX data [Fig. 1 (b)] weight (%)	$10^6 X$ at room temperature emu/gm	$10^5\times$ Curie constant Room temp. to nitrogen	$10^5\times$ Curie constant Nitrogen to helium	Effective magneton number; P_{eff} Room temp. to nitrogen	Effective magneton number; P_{eff} Nitrogen to helium
Pure Zn			−0.140				
VII	0.042	0.046	−0.077	1.5_5	1.6_2	3.8_5	3.9_4 3.8_5[a]
IV	0.18	0.20	+0.121	7.5_5	1.6_4	4.0_8	4.1_0
II	0.43	0.40	+0.381	18.0	15.2	4.4_5	4.1_0

[a] The effective magneton number for this sample is also determined from the zero susceptibility value as shown in Fig. 2.

considers that $(dX^{-1}/dT)_{T_N}=0$ defines the Néel temperature, a value for T_N of 6±1°K is obtained for sample II. From the linear portions of Figs. 2 and 3, Curie constants were calculated and using concentrations obtained from Fig. 1(b) these were converted into effective magneton numbers. The desired results are shown in Table I from which it can be seen that the spin state of the manganese ion in zinc corresponds to a value of $\frac{3}{2}$ which would give an effective magneton number of 3.9.[11]

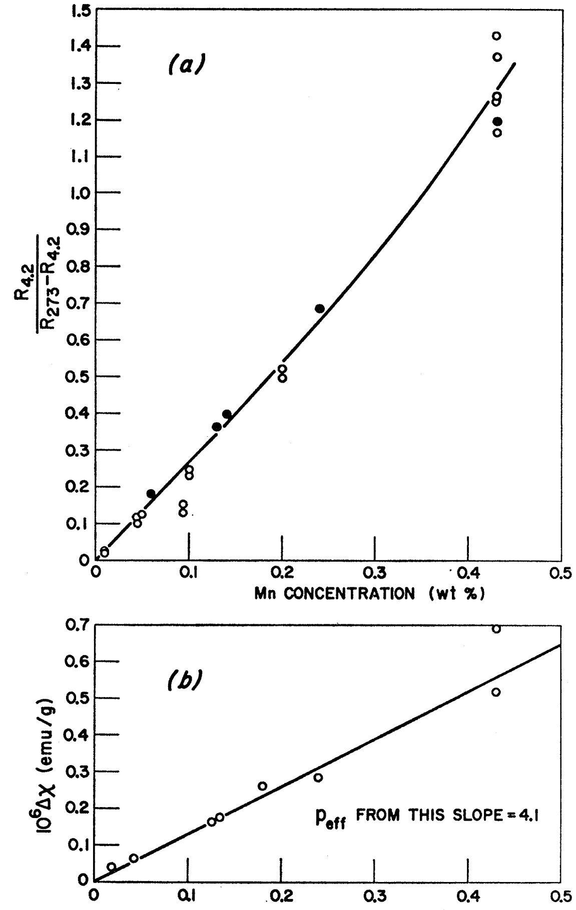

Fig. 1. (a) Resistance ratio as a function of weight percent manganese determined from spectroscopic analysis or quantity of manganese added to the melt. The solid circles represent data from the thesis of W. B. Muir, University of Ottawa. (b) The increase in susceptibility of pure zinc as a function of manganese concentration as determined from the resistance ratio of the alloys measured.

ANALYSIS OF THE MAGNETORESISTIVITY DATA FOR Zn-Mn SYSTEM

In an earlier publication[12] it was shown that the magnetoresistivity of dilute Cu-Fe alloys can be expressed as the sum of a normal magnetoresistive term ρ_n which is temperature-independent and obeys Kohlers' rule and an anomalous term ρ_s which is negative and decreases with decreasing temperature. The anomalous term ρ_s can be theoretically accounted for semiquantitatively for these alloys although the theory itself does not contain an explanation of the resistive minimum.[13,14] The magnetoresistive behavior for an alloy containing 0.11-at.% Mn is shown in Fig. 4 where it can be seen that the magnetoresistance is negative in sign and saturates at a field value of approximately 32 kOe. Shown in the insert of Fig. 4 is the magnetoresistance plotted as a function of H^2 where it can be seen that the magnetoresistance beyond the saturation value is a function of H^2. This we attribute to the normal magnetoresistive component, ρ_n. Using this device we can then separate ρ_n from ρ_{total} and obtain ρ_s as shown in Fig. 4.

Using Kasuya's expression for the term ρ_s and neglecting small terms, we can write:

$$\frac{\rho_{H\infty}}{\rho_{H_0}}=\frac{(b+C)_{H_0}}{(b+\langle j_z^2\rangle_{\text{av}})_{H_0}{}^2}\bigg/\frac{(b+C)_{H\infty}}{(b+\langle j_z^2\rangle_{\text{av}})_{H\infty}{}^2},\tag{1}$$

and

$$\rho_{H_0}=\frac{3\pi m^*c}{2h\zeta Ne^2}J^2\frac{(b+\langle j_z^2\rangle_{\text{av}})^2}{b+C},\tag{2}$$

where

$$C=\langle j_z^2\rangle_{\text{av}}-\langle j_z\rangle_{\text{av}}\frac{2xe^x}{(e^x-1)^2},$$

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[11] It should be pointed out that the earlier reported (Ref. 10) spin value of 2 for a concentrated Zn-Mn alloy resulted from a determination of the Curie constant too near the Néel temperature.

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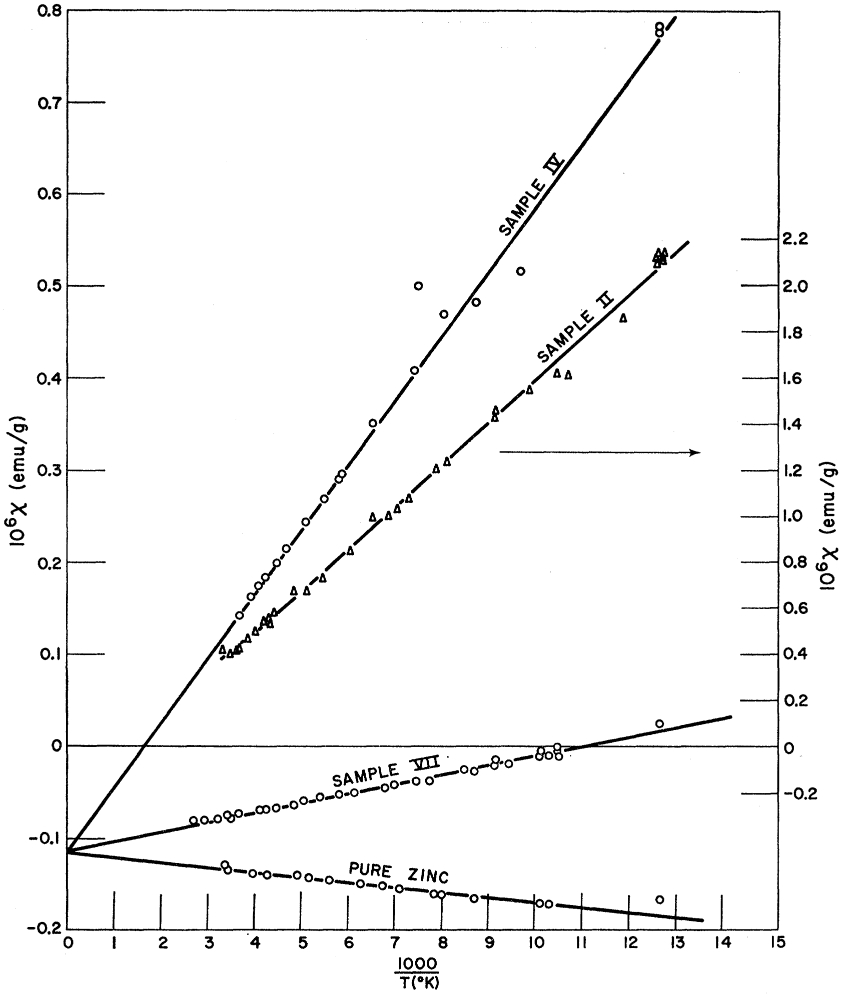

FIG. 2. Total susceptibility of the zinc manganese alloys and pure zinc as a function of reciprocal temperature between room temperature and the temperature of liquid nitrogen.

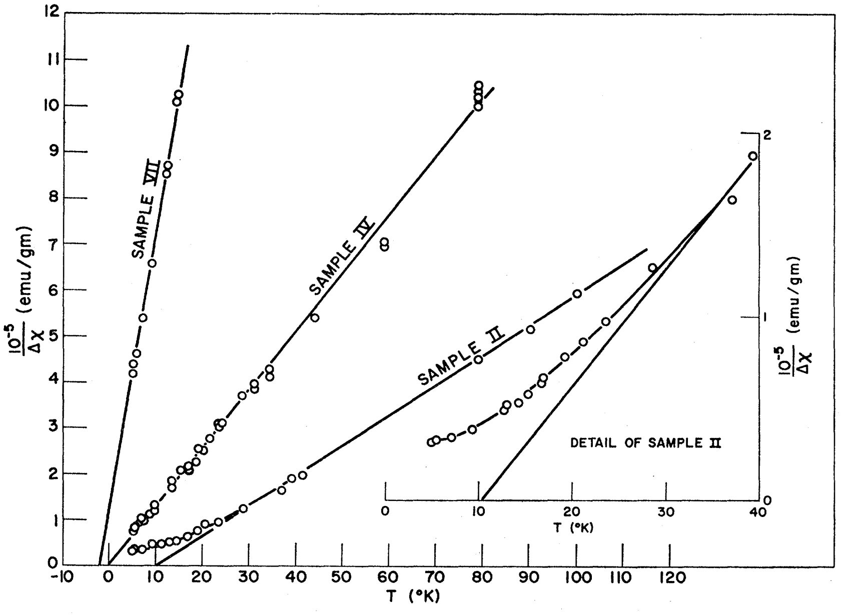

FIG. 3. The inverse of the susceptibility difference between the alloy and pure zinc as a function of temperature. The inset is an enlargement of the temperature interval below 40°K for sample II.

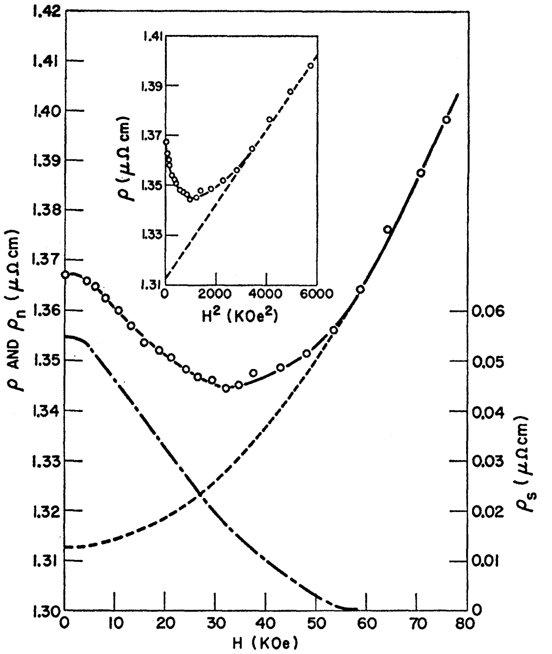

FIG. 4. Resistivity as a function of magnetic field strength for a Zn-Mn alloy containing 0.11 at.% Mn as determined from Fig. 1(a). The inset is the resistivity as a function of H^2 showing the normal magnetoresistivity component ρ_n as a dashed line. This normal component is also shown as a dashed line in the resistivity versus H plot and the dotted line is the difference $(\rho-\rho_n)$ and hence represents ρ_s.

and $b=(A/J)^2$; J is the s-d exchange integral; A is the Coulomb interaction constant; m^*, e is the effective mass and charge of the electron, respectively; ζ is the Fermi energy of the solvent; c is the concentration of paramagnetic ions per unit volume; N is the total number of atoms per unit volume; x is $g\mu_BH/kT$; $\langle j_z\rangle_{\rm av}$ is the average of the Z component of the paramagnetic ion angular moment vector j; $\langle j_z^2\rangle_{\rm av}$ is the average of the square of the Z component of the paramagnetic ion angular momentum. From Fig. 4 the saturation value of the magnetoresistance normalized to the zero-field resistivity value is

$$\rho_{H_{\rm sat}}/\rho_{H_0}\equiv\rho_{H_\infty}/\rho_{H_0}=0.960.$$

Then from Eq. (1) and using the value of $j=s=\frac{5}{2}$ from the susceptibility data a value of b can be found and, hence from Eq. (2), A and J calculated. The values of A and J are found to be 8.7×10^{-12} and 1.4×10^{-12} erg, respectively.

ESTIMATES OF J FROM THE NÉEL TEMPERATURE

Owen *et al.*[15] have given a molecular field derivation of the Curie point in terms of the s-d exchange integral J.[16] By writing the conduction electron and paramagnetic ion magnetization in terms of an s-d exchange interaction constant they find a nonzero magnetization when the temperature is equal to $S(S+1)J^2C/2k\zeta$. If we identify this temperature with the experimentally observed Néel point[17] we may then estimate a value of J. Using the most concentrated alloy which shows a Néel point of 6°K and using the Fermi energy of 1.64×10^{-11} erg for zinc yields a value of J equal to $(1.5\pm0.2)\times10^{-12}$ erg which is in good agreement with the value derived from the magnetoresistivity data.

SUPPRESSION OF THE CRITICAL TEMPERATURE IN DILUTE ALLOYS

The experimental situation at the present time indicates that if a transition metal impurity possesses a localized moment which corresponds closely to the free-ion value, then a suppression of the superconducting critical temperature will result. Baltenperger[1] has considered the influence of an s-d exchange interaction on the superconducting properties of a dilute paramagnetic alloy. The expression derived by him is

$$dT_c/dc=-2.49J^2s(s+1)\nu_0/kN, \qquad (3)$$

where ν_0 is the density of states at the Fermi level and the other symbols have the same meaning as before. The above expression is only valid if there is no spin ordering of the conduction electrons due to a cooperative magnetic interaction of the paramagnetic ions. Whether this condition is satisfied for the Zn-Mn system can be investigated by requiring that the field θ^n seen by the nonsuperconducting electrons is smaller than the thermal energy corresponding to the superconducting transition temperature. Baltensperger has, in fact, shown that

$$d\theta^n/dc=\nu_0H^2s(s+1)/6kN.$$

The inequality to be satisfied is then that

$$\partial\theta^n/\partial c<\partial T_c/dc.$$

Using a value of J found from the previous analysis and assuming ν_0 to be concentration-independent, yields a value of approximately 10°K/at.%. This value is certainly less than the value of 170°K/at.% reported for the Zn-Mn system in studies of the suppression of the critical temperature by Boato *et al.*[3] Having shown that this inequality is satisfied we can then use Eq. (3) derived by Baltensperger to calculate a value of the exchange integral J from the suppression of the critical temperature. This equation yields a value of 1.6×10^{-12} erg, which is in good agreement with the previously derived values.

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[16] This derivation neglects the nonuniform polarization of the conduction electrons and the resulting influence on the paramagnetic ion magnetization which undoubtedly forms a most significant aspect of any such calculation.

[17] Only for the simplest antiferromagnet will the Curie and Néel temperatures be equal. See C. Kittel *Introduction to Solid State Physics* (John Wiley & Sons, Inc., New York, 1953), p. 190.

RESISTANCE ANOMALY AND THE *s-d* EXCHANGE INTEGRAL

According to Yosida[13] and Kasuya[14] it should be possible to obtain a value for the *s-d* exchange integral in a dilute alloy exhibiting an antiferromagnetic ordering from the change in resistance above and below the Néel temperature

$$\Delta\rho \equiv \rho_N - \rho_0 = \frac{3\pi msc}{2e^2\hbar\zeta N} J^2. \tag{4}$$

This graphical method for evaluating $\Delta\rho$ is shown in Fig. 5(a) and in applying this method Yosida has assumed that the resistivity in the absence of a cooperative interaction would be temperature-independent. If the resistivity below the Néel temperature is the resultant of two opposing effects, viz., the resistance minimum mechanism and the cooperative interaction, the true $\Delta\rho$ would be $(\rho_1 - \rho_0)$ of Fig. 5(a). (For the Cu-Mn alloy referred to in Yosida's theoretical paper, application of this idea would lead to more than twice his value of $\Delta\rho$ and consequently a 50% increase in the calculated value of J to 3.0×10^{-12} erg resulting in better agreement with the theoretically free manganese ion value of 3.5×10^{-12} erg.) The true situation for this model, however, is not clear when the region over which the cooperative interaction sets in severely overlaps the region in which one would otherwise expect a resistance minimum resulting in the resistivity characteristic of Fig. 5(b). In estimating $\Delta\rho$ for a Zn-Mn alloy it is better to select an alloy sufficiently dilute that the antiferromagnetic transition is more clearly separated from the minimum. As indicated earlier we are proposing that in the Zn-Mn system the influence of the cooperative magnetic interaction exactly compensates the increase in resistance with lowering temperature characteristic of the resistivity minimum alone, resulting in a flattening-off of the resistivity curve below T_N [Fig. 5(b)]. In order to obtain $\Delta\rho$ we produce the resistivity curve as a circular arc having the same radius as the solid curve above T_N resulting in a value of ρ_1 from which $\Delta\rho = \rho_1 - \rho_0$ can be obtained. Applying this method to the Zn-Mn alloys of concentration 0.15-at.% Mn and 0.17-at.% Mn (Fig. 6) yields an average value for J of 1.5×10^{-12} erg.

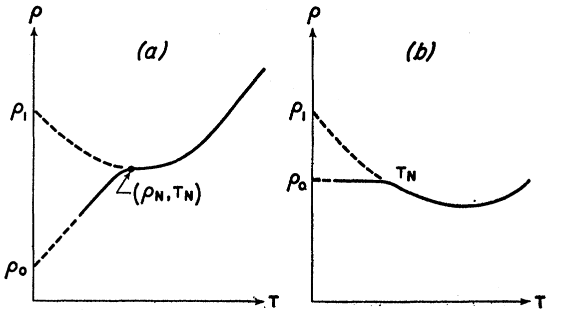

FIG. 5. (a) The resistivity as a function of temperature for a typical high concentration Cu-Mn alloy. (b) The resistivity as a function of temperature for a typical high concentration Zn-Mn alloy. The dashed lines represent the extrapolated curves.

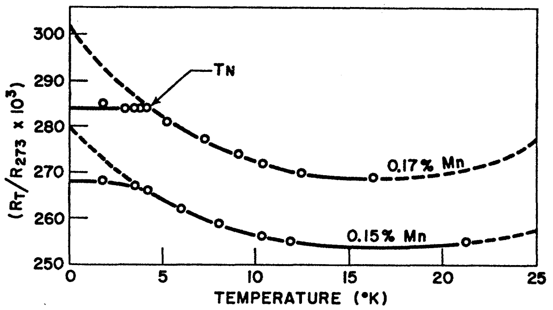

FIG. 6. The resistance ratio as a function of temperature of a 0.15 and 0.17-at.% Zn-Mn alloy. The resistivities of these two alloys is 6.7 and 6.9 μΩ-cm, respectively. T_N is the corresponding temperature indicated in Fig. 5.

There is good agreement between the value of J so calculated and that calculated from the magnetoresistance and the Néel temperature. This can be taken as evidence that the extrapolation procedure and its implications are valid, particularly since a direct application of the unmodified Yosida method would yield a $\Delta\rho$ of 0 for Zn-Mn alloys.

CONCLUSION

An estimate of J from the decrease in spin scattering on magnetic ordering in the Cu-Mn system has been estimated by Yosida to be 2.1×10^{-12} erg for a manganese ion of spin $\frac{5}{2}$. This value of J is higher but of the same order of magnitude as the value of 1.5×10^{-12} found for the zinc-manganese alloys reported in the present paper. An estimate for J from the suppression of the superconducting critical temperature for the Al-Mn system[3] yields a value of 0.23×10^{-12} erg for an estimated spin value for manganese of $\frac{1}{2}$. The fact that manganese possesses a very small moment, if any, when dissolved in aluminum[18] would indicate that the mechanism responsible for the suppression of T_c in the Al-Mn system is due to a cause other than that responsible for the observed effects in the Zn-Mn system.

Calculations of the exchange integral from the magnetic properties of dilute zinc alloys containing small concentrations of manganese have been made from the Néel temperature, the magnetoresistivity as a function of field strength and the suppression of the superconducting critical temperature. The theoretical equations used for these exchange integral determinations are all based on a conduction electron-paramagnetic ion exchange interaction of the form $2J$ S.s. The analysis of the experimental results based on this interaction all yield the same value for the exchange integral which

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[18] E. W. Collings and F. T. Hedgcock, Phys. Rev. **126**, 1654 (1962).

could lead one to conclude that the nature of the magnetic interaction that leads to these phenomena is of the same physical origin. Graphical analysis of the low-temperature resistance characteristics of dilute Zn-Mn alloys, assuming the sum of two terms; one due to magnetic ordering and one due to resonance scattering results in a value of J in agreement with that derived from other transport phenomena. This then suggests a method of separating the resistance minimum from total resistivity in the presence of a resistance maximum produced by magnetic ordering.

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Covalency in Crystal Field Theory: $KNiF_3$

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The theory of covalency in crystal field phenomena is examined, using, as example, the Ni-F_6 complex in $KNiF_3$. The Hund-Mulliken-Van Vleck molecular orbital-linear combination of atomic orbitals treatment is followed. The role of the antibonding *and* bonding electrons in the complex is discussed from a multielectron point of view. The exact self-consistent one-electron Hamiltonian is discussed in some detail. Emphasis is placed on elucidating the source and nature of the covalent effects appropriate to the various physical phenomena. We find that it is the covalent mixing of those *bonding* electrons having no antibonding partners which contribute to all experimental observables (including the crystal field splitting 10 Dq, transferred hyperfine interactions, neutron magnetic form factors, and superexchange interactions). This view of covalency differs markedly from the one followed by Sugano and Shulman, in that the covalency of the *antibonding* electrons, which are assigned the sole role in their approach, is totally irrelevant. Quantitative numerical estimates (using approximations to the exact Hamiltonian) are given for the two models of the covalent effects in $KNiF_3$, i.e., "unpaired" bonding and antibonding; they are shown to differ strongly. The relative roles of overlap and covalency are discussed; covalency is found to play an important but by no means dominant role. Numerical agreement between the present inexact cluster theory and experiment is found to be poor. The various sources of this disagreement are reviewed.

I. INTRODUCTION

CRYSTAL field theory[1,2] has had a long and varied history: when treated as a semiempirical theory, with the crystal field splitting 10 Dq considered as an adjustable parameter, it has been highly successful in fitting experimental data; when considered as a fundamental theory for the behavior of transition metal ions in crystalline fields, it has been strikingly unsuccessful in predicting, from first principles, the fundamental parameter 10 Dq. Following the pioneering computations of Van Vleck[3] and Polder,[4] a series of theoretical investigations[5-9] succeeded in pinpointing the basic shortcomings of the theory, and indicated the need for a multielectron many-center molecular approach.

The recent work of Sugano and Shulman[10] (henceforth denoted as S&S III), representing the most detailed computations undertaken to date, attempted to obtain a quantitative basis for the theory by including all the terms in the ionic model considered by their predecessors, as well as the effect of metal ion-ligand covalent mixing. A cluster model consisting of the metal ion and its nearest ligand neighbors in an external Madelung-like potential was invoked. Considering $KNiF_3$, they obtained a theoretical cubic field splitting parameter (10 Dq) for Ni which gave the first quantitative indication that covalency plays an important role in the crystal field interactions of salts as highly ionic as

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