

Possible Approach to the Low-Temperature Resistance Maximum in Dilute Alloys of Transition Metals in Noble Metals

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If a dilute alloy of a transition metal in a noble metal becomes ferromagnetic, the spin degeneracy of the ground state of the impurity atom is removed by the local field. Scattering of the conduction electrons by the impurity atoms can then take place by inelastic as well as elastic collisions. Assuming the scattering cross section for elastic scattering is larger for the lower lying nondegenerate states, one gets the following results: (1) There is a maximum in the temperature dependent resistivity. (2) The temperature at which the maximum occurs varies rapidly with concentration of the transition metal. (3) The magnetoresistance is negative up to some temperature higher than the temperature at which the maximum in resistivity occurs. The experimental observations of Gerritsen and Linde and of Gerritsen on the resistivity of these alloys are, for the most part, in qualitative agreement with these consequences. This model does not require the existence of localized electronic states with energy near the Fermi energy as does the model presented by Korringa and Gerritsen.

INTRODUCTION

THE anomalous behavior of the low-temperature resistance of manganese in copper, silver, or gold and of chromium in gold was reported several years ago by Gerritsen and Linde.¹ They found a maximum in the dependence of resistivity on temperature of sufficiently dilute alloys and, moreover, found that the temperature of the maximum varied rapidly with concentration of the transition metal. They^{1,2} also discovered that the magnetoresistance of most of these alloys was anomalous; the resistance decreased in a magnetic field at temperatures below T_1 . The temperature T_1 was somewhat higher than T_m , at which the maximum occurred.

Korringa and Gerritsen³ succeeded in fitting the resistance curves of these dilute alloys with a simple equation. This equation was derived by assuming an anomalous dependence on energy of the collision time, τ , for electrons near the Fermi level. This result suggested that a cooperative electron phenomenon was involved and, expressed in terms of a one-electron picture, their hypothesis was that extra localized states existed at the Fermi level. The consequences of their hypothesis were in qualitative agreement with the experimental observations. In some cases semiquantitative agreement was obtained and, at very least, their work provided a phenomenological framework.

Unfortunately, however, the existence of the extra electronic states has not yet been established theoretically. For this reason it is interesting to look for other explanations and phenomenologies of the peculiar behavior of these alloys. It is the purpose of this paper to indicate another possible direction for finding an explanation of the low-temperature resistance maximum.

Ferromagnetism of the Dilute Alloys

It is not difficult to find ways in which a resistance maximum can arise. For example, if the ground state of the impurity ion is split and the scattering cross sections of the resultant levels are different (with lower levels having higher cross sections), then a resistance maximum is possible. J. C. Fisher, of this Laboratory, pointed out that one possible way of removing the ground-state degeneracy is for the dilute alloy to become ferromagnetic. He also suggested that indirect exchange via the conduction electrons, recently emphasized by Zener,^{4,5} is one way in which ferromagnetism could arise in such alloys.

Unfortunately, no experiments have yet been made to relate anomalous magnetic properties with resistance maxima in the very dilute alloys where the latter effects are observed. Recently, however, ferromagnetism has been reported in some noble metal alloys containing above 10 atomic percent Mn.⁶ Paramagnetism in such alloys has been investigated earlier by several people,⁷⁻¹¹ but none of these investigations were at temperatures or concentrations where ferromagnetic behavior was observed. Experiments at this Laboratory by I. S. Jacobs and C. P. Bean indicate that a sample of about 2% Mn in Cu does exhibit a small remanent magnetization at 4.2°K and that this remanence disappears in the liquid hydrogen temperature region. This same sample has a large anomalous temperature-dependent resistivity at temperatures below that of liquid hydrogen, but there is no maximum in the resistivity (see Fig. 1). Further experiments to elucidate the relation between

⁴ C. Zener, *Phys. Rev.* **81**, 440 (1951); **83**, 299 (1951).

⁵ C. Zener and R. R. Heikes, *Revs. Modern Phys.* **25**, 191 (1953).

⁶ Otter, Flanders, and Klokholm, *Phys. Rev.* **99**, 599 (1955).

⁷ L. Neel, *J. phys. radium* **3**, 160 (1932).

⁸ S. Valentiner and G. Becker, *Z. Physik* **80**, 735 (1933).

⁹ G. Gustafson, *Ann. Physik* **25**, 345 (1936).

¹⁰ E. Kronqvist, *Arkiv. mat. astron. fysik* **34B**, No. 7 (1947).

¹¹ E. Kronqvist and A. Giansoldati, *Arkiv. fysik* **7**, No. 26, 343 (1954).

¹ A. N. Gerritsen and J. O. Linde, *Physica* **17**, 573, 584 (1951); **18**, 877 (1952).

² A. N. Gerritsen, *Physica* **19**, 61 (1953).

³ J. Korringa and A. N. Gerritsen, *Physica* **19**, 457 (1953).

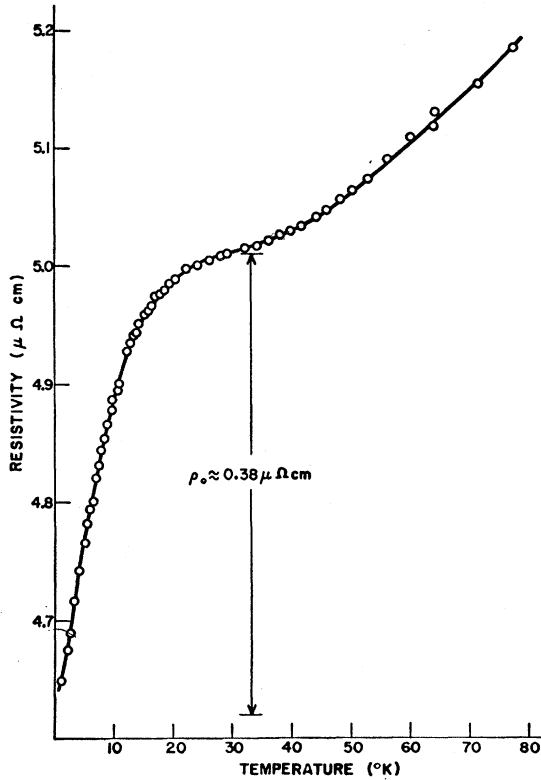


FIG. 1. Resistivity versus temperature of a 1.8 atomic percent manganese in copper alloy.

magnetic and resistance behavior of these alloys are underway.¹²

In spite of the present lack of experimental evidence, it will be assumed that even very dilute alloys of a paramagnetic ion in a noble metal may be ferromagnetic and that the Curie temperature varies linearly with concentration.¹³

For simplicity, consider the case where the impurity atoms have a d shell with net spin $\frac{1}{2}$ in units of \hbar . The case of spin $\geq \frac{1}{2}$ is outlined in the appendix. It will be assumed that orbital contributions to the moment are quenched. At temperatures below the Curie temperature the spin degeneracy is removed by the local field and the splitting of the states is given by

$$\Delta = g\mu_B H_l, \quad (1)$$

¹² Experiments directed to elucidating the magnetic behavior of such alloys have also been conducted at Berkeley, where similar ideas regarding the possible ferromagnetism of these alloys were arrived at independently by C. Kittel. I am indebted to Professor Kittel and to Dr. John Owen for informing me of this work prior to publication. *Note added in proof.*—J. Owen, M. Browne, W. D. Knight, and C. Kittel [Phys. Rev. (to be published)] suggest that susceptibility and spin resonance data on these alloys indicate an “antiferromagnetic” state to be present below a certain transition temperature, but with a ferromagnetic interaction also present. Resistance anomalies could arise from an antiferromagnetic transition in the same way as that described in this paper. Necessary modifications of the present model will become clear as we understand the precise nature of the magnetic ordering.

¹³ J. C. Fisher obtained this result in his calculation of the ferromagnetism of these alloys via the indirect exchange mechanism.

where, in the present case, $g=2$, μ_B is the Bohr magneton and H_l is the local field. The local field is given by

$$H_l = H + \lambda M, \quad (2)$$

where H is the externally applied field, M the magnetization, and λ a constant. Under these circumstances¹⁴ the magnetization versus temperature is given parametrically by

$$\begin{aligned} M &= \frac{1}{2} N c g \mu_B \tanh x = M_\infty \tanh x \\ T/T_c &= \tanh x / x + \mu_B H / k T_c x, \end{aligned} \quad (3)$$

where N is the number of atoms/cm³ and c is the atom fraction of these that are the magnetic impurity ions.

Resistance Anomalies

The problem is that of the scattering of conduction electrons by the impurity ions, each of which can occupy either of the two energy states. The scattering can then take place either elastically or inelastically. The elastic scattering may be temperature dependent because occupation of the two states varies with temperature. The inelastic scattering will be temperature-dependent not only because of varying occupation of the states by the ions, but also because the availability of states into which the electrons can be scattered will vary with temperature. Elliott¹⁵ has treated a problem bearing a strong relation to the one at hand. In view of this previous work, we shall not solve the transport problem rigorously, but shall proceed in a very simple manner. The validity of the approach can be checked by applying it to the specific problem considered by Elliott to see if his results are duplicated. It turns out that they are.

Consider first the elastic part of the scattering. For low concentrations of the impurity, the probability of scattering from each of the states will be proportional to the occupation of the states. Thus, if τ_e is the collision time for elastic collisions

$$1/\tau_e = c_1 A_1 + c_2 A_2, \quad (4)$$

where c_j is the atom fraction of ions in the j th state and A_j is an average scattering cross section for elastic collisions with ions in the j th state. If, in the presence of a current, the distribution of ions between the two states is an equilibrium one, then

$$c_1 + c_2 = c \quad \text{and} \quad c_2/c_1 = \exp(-\Delta/kT). \quad (5)$$

Employing the *ad hoc* assumption that

$$A_1 - A_2 = \begin{cases} 2\delta A; & T < T_c \\ 0; & T > T_c \end{cases}, \quad (6)$$

one gets

$$1/\tau_e \sim cA + c\delta A \tanh x, \quad (7)$$

where x is defined in (3) and $A = \frac{1}{2}(A_1 + A_2)$.

¹⁴ C. Kittel, *Introduction to Solid State Physics* (John Wiley and Sons, Inc., New York, 1953), Chap. 10.

¹⁵ R. J. Elliott, Phys. Rev. **94**, 564 (1954).

It is possible to get an estimation of the contribution to the resistance from inelastic scattering in the following way: The probability of scattering from each of the states will again be proportional to the occupation of the states and, in addition, to the probability that there is a vacant electronic state of the proper energy into which the electron can be scattered. Thus,

$$1/\tau_i = c_1 D [1 - f(\zeta - \Delta)] + c_2 D [1 - f(\zeta + \Delta)] \\ = 2Dc_1c_2/(c_1 + c_2), \quad (8)$$

where D is an average scattering cross section, $f(\epsilon)$ is the Fermi function, and ζ is the Fermi energy. The implication of Eq. (8) is that all scattered electrons are scattered from states having the energy ζ . In the present approximation this assumption need be relaxed only if one wishes to compute the thermoelectric effects. Equation (8) reduces to

$$1/\tau_i \sim \frac{1}{2} c D \operatorname{sech}^2 x, \quad (9)$$

so that the total resistivity is given by the expression

$$\rho = \rho_{00} + \rho_0 \operatorname{sech}^2 x + \rho_1 \tanh x, \quad (10)$$

with ρ_{00} , ρ_0 , and ρ_1 each being proportional to c . From Eq. (6), $\rho_1 > 0$ so that resistivity will have a maximum. The maximum occurs at x_m , where

$$\tanh x_m = \rho_1 / 2\rho_0. \quad (11)$$

Since ρ_1 and ρ_0 both vary linearly with c , x_m is independent of c . But, Eq. (3) then shows that T_m must increase linearly with T_c for $H=0$. Since we have taken T_c to vary linearly with concentration, so too does T_m .

To find the magnetoresistance, consider Eq. (10) and employ the relation $\operatorname{sech}^2 x = 1 - \tanh^2 x$. After rearranging terms and using (3), one gets

$$\Delta\rho \equiv \rho(H) - \rho(0) = (\rho_0/M_\infty^2) [M(H, T) - M(0, T)] \\ \times \{2[M(0, T_m) - M(0, T)] - [M(H, T) - M(0, T)]\}.$$

But clearly $M(H, T) > M(0, T)$ while $M(0, T)$ is greater or smaller than $M(0, T_m)$ depending on whether T is less than or greater than T_m . The magnetoresistance is, therefore, clearly negative for $T < T_1$ (with $T_1 > T_m$) and can become positive for $T > T_1$.

DISCUSSION

In view of the primitive state of development of the preceding theory, one should not expect it to reproduce the experimentally observed curves in detail. One hopes only for an indication of a direction in which to proceed. Thus, the two requirements placed on the preceding development will be (1) that it should yield qualitative reproduction of the experimental results, and (2) that it should require values of the parameters involved that do not violate one's physical sensibilities.

Qualitatively, the treatment reproduces the following experimentally observed facts: (1) a resistivity maximum, (2) rapid (linear) variation of the temperature of the maximum with concentration of the impurity, and

(3) a negative magnetoresistance for temperatures below some temperature T_1 , where T_1 is itself higher than the temperature of the maximum. On the other hand, the following experimental observations are not reproduced: (1) disappearance of the resistivity maximum at higher concentrations ($c \gtrsim 1$ atomic percent impurity), and (2) continued decrease in resistivity with increasing temperature for temperatures considerably higher than the temperature of the maximum. The latter point is illustrated by Gerritsen and Linde's 0.15 atomic percent Mn in Cu: for this alloy, the maximum occurs at about 5°K whereas the resistivity is still decreasing with increasing temperature as high as 20°K. Our present formulas cannot account for any further decrease in resistivity at temperatures higher than about twice the temperature of the maximum. One should recall, however, that uniform distribution of the impurity throughout the sample is seldom obtained in these alloys. In addition, even for an "ideal" alloy with the impurity having a macroscopically uniform distribution, the microscopic random distribution of impurity might result in fluctuations in the local fields within the sample. Such effects would tend to smear out the resistance anomalies.

Approximate values of the parameters can be obtained by comparison with available data on Mn in Cu. Figure 1 shows ρ versus T for the 1.8 atomic percent Mn in Cu sample mentioned earlier. The rise in resistivity with temperature above $T \approx 30^\circ\text{K}$ results from setting in of the normal temperature dependent resistivity so the magnitude of the anomalous part of the temperature dependent resistivity is $\approx 0.38 \mu\text{ohm cm}$, as shown in the figure. Assuming that in this sample at 30°K there is no contribution to the anomalous temperature dependent resistivity from elastic scattering processes, we may take $\rho_0/c \gtrsim 0.2 \mu\text{ohm cm per atom percent Mn}$. This is just the same order of magnitude as the amplitude of the resistance maxima observed by Gerritsen and Linde for Mn in Cu. In particular, for their 0.15% Mn in Cu sample $(\rho_{\text{max}} - \rho_{T=0})/c \approx 0.2 \mu\text{ohm cm per atom percent Mn}$. Thus the value of α in Eq. (10A) of the Appendix is $\alpha \lesssim 1$. Since $\rho_{00}/c \approx 2.9 \mu\text{ohm cm per atom percent Mn}$, this means that $\delta A \lesssim 0.02A$ for $S=4/2$ (the appropriate value indicated by high-temperature susceptibility data⁷⁻¹¹). Thus, the amplitude of the resistance maxima observed require differences in the elastic scattering cross section between the states of only a few percent of the total cross section.

As has been mentioned, the present model agrees with experiment in that it yields the correct negative sign for the magnetoresistance at sufficiently low temperatures. However, the experiments^{1,2} have indicated some instances where the decrease of resistance in a magnetic field resulted in a lower value than that obtained by extrapolation to $T=0$ in zero magnetic field. Such a result would be impossible on the basis of the simple picture developed in this paper. However, the reason is that we have not allowed for the possi-

bility that not all impurity moments are aligned at $T=0$. Korringa and Gerritsen³ assume implicitly that configurational disorder among the impurity spin moments persists even at $T=0$ and this would, of course, allow an external magnetic field to further order these moments and produce a decrease in resistance. It may be true, with either Korringa and Gerritsen's model or the present one, that the configurational disorder present as a result of the random distribution of impurity atoms in the lattice will allow a certain configurational disorder to remain among the spin moments even at $T=0$.¹⁶ Further experiments as well as theoretical development would appear to be necessary to clarify this point before any critical judgment could be made between the picture of Korringa and Gerritsen and the present one.

CONCLUSIONS

It has been shown that there is a possibility of explaining the low-temperature resistance maximum by a mechanism that does not invoke the assumption of specialized electronic states of the type envisaged by Korringa and Gerritsen. The present model assumes a cooperative interaction to take place between the magnetic impurity ions where Korringa and Gerritsen suggest that a cooperative interaction among the conduction electrons is responsible for the specialized electronic states required by their theory. It is hoped that the theoretical problems presented by the present model will be less severe than those presented by the Korringa and Gerritsen picture.

The nature of further experimental work suggested by the present model is also clear, i.e., it becomes crucial to examine the relation between magnetic and resistive properties of the dilute alloys. Preliminary experiments along this line indicate that anomalous magnetic behavior does accompany anomalous resistive behavior.

ACKNOWLEDGMENTS

I am indebted to J. C. Fisher, E. W. Hart, and C. P. Bean for valuable criticism and discussion. Mr. Richard Rea accomplished the resistance measurements reported in Fig. 1.

APPENDIX

Relevant Equations for $S \geq \frac{1}{2}$

If the impurity atoms have a d shell with net spin $S \geq \frac{1}{2}$ in units of \hbar , one can obtain the following results. Equation (3) of the text becomes

$$\begin{aligned} M_s &= M_\infty B_s(x), \\ T/T_c &= 3SB_s(x)/(S+1)x + Sg\mu_B H/kT_c x, \end{aligned} \quad (3A)$$

where $B_s(x)$ is the usual Brillouin function. Introducing

the *ad hoc* assumption, analogous to (6), that

$$A_m = \begin{cases} A - 2m\delta A; & T < T_c \\ 0 & ; T > T_c \end{cases}, \quad (6A)$$

where $-S \leq m \leq S$, the relaxation time for elastic scattering becomes

$$1/\tau_e \sim cA + 2cS\delta AB_s(x). \quad (7A)$$

For the inelastic scattering, one can easily show that for transitions between only adjacent levels

$$\frac{1}{\tau_i} \sim \sum_{m=-S}^{S-1} \frac{c_m c_{m+1}}{c_m + c_{m+1}} (D_m^+ + D_{m+1}^-),$$

where D_m^\pm = inelastic scattering cross section for scattering processes *from* the m th level (+ for transition of ion to a higher level, - for the opposite process). For a steady-state condition $D_m^+ = D_{m+1}^-$, and, as the simplest assumption, we take $D_m^+ = D$ for all m . One then gets

$$\frac{1}{\tau_i} = \frac{2S}{2S+1} Dc \left[1 - B_s(x) \tanh \frac{x}{2S} \right], \quad (9A)$$

so that, after rearranging (10) slightly,

$$(\rho - \rho_0)/\rho_0 = 1 - B_s(x) \tanh(x/2s) + \alpha B_s(x), \quad (10A)$$

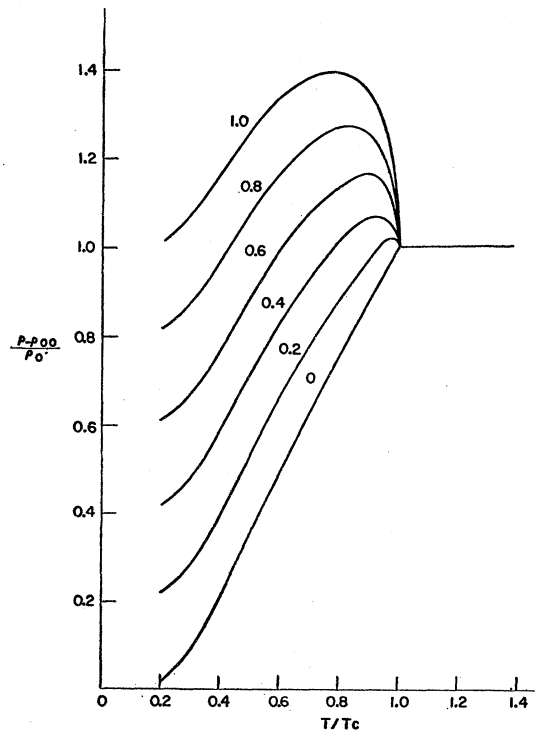


FIG. 2. Theoretical curves of resistivity versus temperature for $S=4/2$ and various values of α ; computed from Eq. (10A).

¹⁶ I am indebted to E. W. Hart for this observation.

where $\alpha = \rho_1/\rho_0$. Here $\rho_{00} \sim cA$, $\rho_0 \sim cD2S/(2S+1)$, $\rho_1 \sim c\delta A2S$. Figure 2 shows this function plotted for $S=4/2$ and for various values of α .

It should be remarked that where more than two levels are involved, certain special assumptions about the D_m 's can result in a resistance maximum arising from the inelastic scattering alone. For example, the

assumption $D_m^+ = D_{m+1}^- = D - 2(m + \frac{1}{2})\delta D$ yields such a result. This fact emphasizes that where ground-state degeneracy of the impurity ions is removed, there are several ways in which low-temperature resistance anomalies can arise. Until one understands better the states of the impurity ions, no useful purpose is served by developing all of the possibilities with equal vigor.

Intensities of the R_1 and R_2 Bands in KCl Crystals*†

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Measurements have been made of the intensities of the R_1 , R_2 , M , and N bands in KCl crystals as functions of F light irradiation time. Both x-rayed and additively colored crystals were used. The x-raying and F light irradiation were done at room temperature. The optical absorption measurements were made at liquid nitrogen temperature to improve the resolution of the bands. In both the x-rayed and additively colored samples the ratio of the R_2 and R_1 band intensities varied by less than a factor 1.5 when the individual intensities varied by a factor 6 or greater. No other pair of bands studied showed such a small variation in their intensity ratio.

Theoretical frequencies and oscillator strengths were obtained for the $1s\sigma-2p\sigma$ and $1s\sigma-2p\pi$ transitions of H_2^+ immersed in a dielectric medium and for the $1s-2p$ transition of the hydrogen atom immersed in a dielectric medium. Frequencies were also obtained for the $^1\Sigma_g^+-^1\Pi_u$ and $^1\Sigma_g^+-^1\Sigma_u^+$ transitions of H_2 immersed in a dielectric medium. For KCl the computed frequencies of the last three transitions named have approximately the same magnitude and fall in the same order as the observed F , R_1 , and R_2 bands, respectively. It appears possible that the observed R_1 and R_2 bands may arise from two transitions of the system of two electrons trapped at a pair of adjacent negative ion vacancies.

I. INTRODUCTION

MOLNAR¹ and Petroff² have found that in crystals of alkali halides such as NaCl and KCl, the F band bleaches when irradiated with F light at room temperature. As the F band intensity decreases, the R_1 , R_2 , M , and N bands grow. Both additively colored and heavily x-rayed crystals of NaCl and KCl exhibit this behavior. It has been stated by Molnar¹ that the R_1 and R_2 bands do not bleach when crystals exhibiting them are irradiated with R_1 and R_2 light, respectively, at room temperature. Oberly and Burstein³ have reported that additively colored KCl crystals exhibiting R bands become photoconductive when irradiated with R light at room temperature. Similar results have been

obtained by Oberly⁴ for x-rayed KBr crystals exhibiting R bands.

Casler, Pringsheim, and Yuster⁵ have found that R bands in crystals such as KCl and NaCl are destroyed by x-ray irradiation. These authors state that the R bands are somewhat unstable at room temperature in KCl which has been x-rayed at -195°C and irradiated at room temperature with F light. Prolonged irradiation of such crystals with F light at room temperature also causes the R bands to decrease in intensity.

Hesketh⁶ has obtained curves of growth for the R_1 , R_2 , and M bands formed in x-rayed KCl by irradiation with F light, presumably at room temperature. Corrections were made for the overlapping of the F and R_1 bands. Hesketh found that the M and R_1 band intensities increased rather rapidly to maximum values and then decreased. The R_2 band increased more slowly and reached an intensity maximum which was less than that for the R_1 band.

Seitz^{7,8} has suggested that the R_1 and R_2 bands arise

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† A preliminary account of this work was presented at the 1955 Thanksgiving Meeting of the American Physical Society. See Herman, Wallis, and Wallis, *Phys. Rev.* **100**, 1267 (A) (1955).

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