Effects of an Exchange Field Distribution on the Low-Temperature Electrical Resistivity and Magnetization of Dilute *Pd*Fe Alloys

N. C. Koon and A. I. Schindler
Naval Research Laboratory, Washington, D. C. 20375
(Received 30 May 1973)

Detailed magnetization measurements have been performed on a sample of *Pd*–0.23-at.% Fe, which is the same one employed in a previous study of spin-disorder resistivity. The resistivity and magnetization were found to be correlated extremely well by a modified form of Yosida's theory of magnetoresistance. In particular, the Curie temperatures obtained by considering the resistivity and the low-field magnetization data were found to be identical. The temperature dependence of the zero-field resistivity and the extrapolated zero-field magnetization, however, differ markedly from predictions which employ a simple molecular-field description of the spin system. We therefore present a simple extension of molecular-field theory which takes into account the distribution of exchange fields expected in *Pd*Fe alloys of this concentration. With a single additional parameter to describe the width of the exchange-field distribution the theory can fit both the zero-field resistivity and magnetization data.

I. INTRODUCTION

Dilute *Pd*Fe alloys exhibit a number of striking magnetic properties. Because of the strongly exchange-enhanced nature of the host *d* bands the magnetic moment associated with each iron impurity is very large, approaching $(10–12)\mu_B$.[1] Neutron-diffraction measurements[2] have shown that only about one-third of this moment is localized on the impurity site, while the remainder is associated with a long-range polarization of the host matrix extending a distance on the order of 10 Å from each iron atom. Since this polarization provides a mechanism for long-range interaction between impurities, *Pd*Fe alloys remain ferromagnetic down to iron concentrations on the order of 0.1 at.% or less.[3] Because of the finite range of polarization together with the random location of the iron atoms, however, the effective exchange interaction "seen" by the iron impurities in low-concentration samples (less than about 4-at.% Fe) varies appreciably from site to site. Clear evidence for this phenomenon has been seen in both Mössbauer effect[4] and NMR[5] measurements. It is the purpose of the present work to discuss how this distribution of exchange fields can affect the spin-disorder resistivity and magnetization of these alloys.

The resistivity of dilute *Pd*Fe alloys has been studied extensively in the low-concentration region (below 1-at.% Fe) by Williams and Loram[6] and in the high-concentration region (1–12-at.% Fe) by Skalski *et al.*[7] One very interesting feature of these investigations was that in the low-temperature region ($T \ll T_c$) the resistivity was found to vary as $T^{3/2}$ for the low-concentration samples and as T^2 for the high-concentration samples. The low-temperature behavior of the 1-at.% sample was found to be intermediate between $T^{3/2}$ and T^2. The $T^{3/2}$ dependence is expected if conduction electrons scatter from a spatially disordered array of local moments and if the low-lying magnetic excitations have a magnonlike dispersion relation,[8–10] while a T^2 dependence is expected under similar conditions if the scattering moments are spatially periodic.[11–13]

Measurements of the resistivity in a magnetic field for $T \ll T_c$ on a sample of *Pd*–0.78-at.% Fe have been reported by Williams, Swallow, and Loram,[14] who obtained reasonably good agreement with spin-wave theory. Grassie, Swallow, Williams, and Loram[15] have measured the magnetoresistance of a 0.1-at.%-Fe sample for $T > T_c$. They fitted their data to a theory which ignored the presence of exchange interactions between spins and obtained values for the spin and g factor reasonably consistent with magnetization measurements.[1]

Recently we reported a study of the resistivity and magnetoresistance of two *Pd*Fe alloys containing 0.16- and 0.23-at.% Fe, respectively.[16] The data extended from temperatures below T_c to well above T_c in both cases and employed magnetic fields up to 60 kOe. A modified form of Yosida's theory of magnetoresistance[17] together with a simple molecular-field theory of the spin dynamics was used to analyze the data. One interesting feature of the results was that when the applied magnetic fields were large compared with the internal exchange fields, good agreement between theory and experiment could be obtained. At low and zero fields, however, there were significant differences between the calculated curves and the experimental data. We suggested that these differences were due primarily to the fact that the theory did not properly take into account the distribution of exchange fields. Based on a comparison of the calculated and experimental zero-field resistivity

data we also suggested that the zero-field magnetization of both alloys studied decreased *much* faster with temperature than predicted by simple molecular-field theory. This latter suggestion was in general agreement with the analysis of Mössbauer data on a *Pd*–0.4-at.% Fe sample by Kitchens and Trousdale,[4] although we knew of no magnetization measurements on alloys in this concentration range which were sufficiently detailed to check this point.

The present work was undertaken primarily to verify the above suggestions. To do this we first performed detailed magnetization measurements on one of the same alloys used in the previous resistivity study. The results, given in Sec. III, show that the zero-field magnetization does indeed decrease with temperature much faster than predicted by molecular-field theory. Furthermore, when the experimental magnetization is inserted into the theoretical expression for the resistivity in place of the values calculated from molecular-field theory, excellent agreement with the experimental resistivity is obtained. In particular, the Curie temperature as determined from resistivity is found to agree very well with an analysis of the low-field magnetization data. In Sec. IV we present a simple extension of molecular-field theory which takes into account the distribution of exchange fields. With one adjustable parameter describing the width of the exchange field distribution the model can fit both the zero-field resistivity and magnetization data.

II. EXPERIMENTAL

Preparation of the *Pd*Fe alloy used in this study has been described previously.[16] Wet chemical analysis gave the iron concentration as 0.23 at.%, and the Curie temperature as determined from resistivity measurements is 3.75 °K.

The magnetization measurements were made using a vibrating sample magnetometer mounted in the bore of a NbTi superconducting solenoid. The temperature was controlled and measured in all cases to better than 0.01 °K by a combination of resistance and gas thermometry. The magnetic field was measured with a resolution of 1 Oe and an estimated accuracy at low fields of 2 Oe.

III. MAGNETIZATION

Magnetization measurements were made as a function of magnetic field from approximately 50 to 1200 Oe and as a function of temperature from 1.40 to 5.18 °K. Corrections were made for the demagnetizing field of the sample. The results are presented in the form of an Arrott plot in Fig. 1. Although the constant temperature curves on this plot are not straight lines, they do exhibit some interesting features. Most significant, perhaps, is that, except for temperatures very near T_c, the low-field data can be extrapolated rather unambiguously to zero values of H/σ in order to obtain the zero-field magnetization. This is probably a reasonable procedure in view of the fact that Bagguley *et al.*[18] found from ferromagnetic resonance that anisotropy and magnetostriction effects in dilute *Pd*Fe alloys were extremely low.

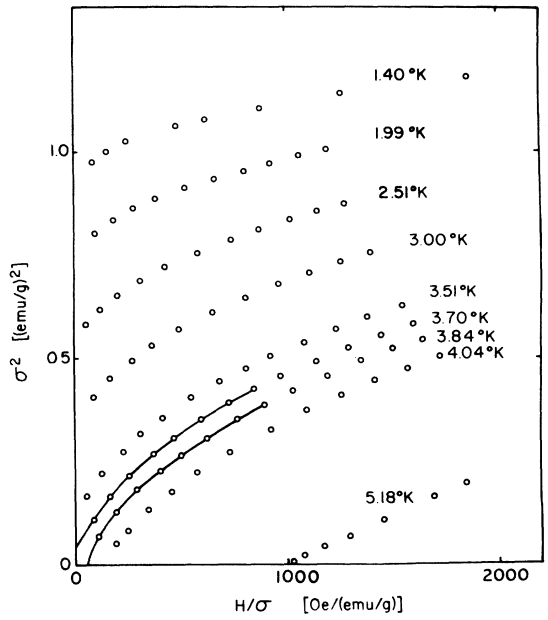

FIG. 1. Magnetization of *Pd*–0.23-at.% Fe presented in the form of an Arrott plot for temperatures between 1.40 and 5.18 °K and for fields between 50 and 1200 Oe. The solid lines through the data near T_c were calculated from Arrott's relation, which was fitted to the data by the method of least squares.

A second interesting point concerns the data near T_c. It is well known that high-field extrapolations of magnetization data on these alloys leads to Curie temperatures which are considerably higher than those obtained from resistivity or Mössbauer data.[19,20] It is clear from Fig. 1 that this is true in the present case also, since the Curie temperature as determined from resistivity measurements is 3.75 °K.[16] When the low-field results are considered, however, there does not necessarily appear to be any discrepancy, although it is difficult to tell for certain because of the curvature of the data. To analyze the data near T_c we use the approach of Arrott,[21] who pointed out on very general grounds that very near and above T_c the magnetization should obey the relation

$$H/\sigma = \chi_0^{-1} + a\sigma^2 + b\sigma^4 + \cdots , \qquad (1)$$

where χ_0 is the zero-field susceptibility. In a plot of σ^2 vs H/σ the value of χ_0^{-1} is given by the inter-

cept on the H/σ axis, which is uncertain in the present case because of the curvature of the data. We therefore fit the data near T_c to Eq. (1) by the method of least squares, retaining in each case a sufficient number of terms in the expansion to ensure that adding additional terms did not change χ_0^{-1} significantly. The values of σ^2 and H/σ calculated from this fit are shown in Fig. 1 as the solid lines through the data near T_c. If this procedure is correct then it is clear that at 3.70 °K the sample is ferromagnetic and at 3.84 °K it is paramagnetic. Within the limits of experimental error, therefore, resistivity and low-field magnetization appear to yield identical Curie temperatures.

In order to make a direct comparison between resistivity and magnetization data it was necessary to determine the relative magnetization $\sigma(T)/\sigma(0)$. The magnetization at temperatures greater than zero was obtained simply by smooth extrapolation of the low-field points to zero values of H/σ. The saturation magnetization at zero temperature was determined indirectly from high-field (40–60-kOe) measurements made at 1.3 °K. It was assumed that the magnetic moment associated with the iron atoms was completely saturated and that the change in magnetization was due to the susceptibility of the host. This assumption is supported by the fact that the high-field susceptibility was found to be 7.2×10^{-6}, which is close to that of pure Pd, and only slightly higher than obtained by Budnick *et al.*[22] from measurements on dilute *Pd*Fe alloys made at much higher fields. The saturation magnetization at zero temperature was then estimated by subtracting off the magnetization associated with the susceptibility of the host. The extrapolated zero-field moment per iron atom was $9.7\mu_B$, which should be regarded as somewhat uncertain because of possible errors in the concentration. It is interesting to note, however, that if one assumes a g factor of about 2, which is suggested by resonance data,[18] then the total spin per iron atom is 4.85, which is very close to the value of 5 deduced from high-field magnetoresistance data on the same sample.[16]

The theoretical expression used to relate the magnetization and the normalized spin-disorder resistivity was derived by Koon, Schindler, and Mills[16]:

$$\delta \equiv \frac{\rho_I(H,T)-\rho_I(0,0)}{\rho_I(0,T_c)-\rho_I(0,0)} \cong 1-\frac{2S}{2S+1}\left(\frac{\langle S^z\rangle}{S}\right)^2 - \frac{1}{2S+1}\frac{\sinh(\Delta)-\Delta}{\cosh(\Delta)-1}\frac{\langle S^z\rangle}{S}, \tag{2}$$

where

$$\Delta=\frac{3}{S+1}\frac{T_c}{T}\frac{\langle S^z\rangle}{S}+\frac{g\mu_B H}{k_B T_c}.$$

In this expression ρ_I is that contribution to the resistivity due to potential and exchange scattering from the iron impurities, S is the assumed spin of the scattering entity, and $\Delta=\omega/k_BT$, where ω is the Zeeman splitting. Molecular-field theory was used to calculate $\langle S^z\rangle/S$ and Δ. In Eq. (2) the second term, which is proportional to the square of the magnetization, is clearly dominant for large spins. Furthermore, the presence of this term does not depend upon the assumption of a molecular-field-theory description of the spin system.[16] One may therefore calculate this part of the expression for δ quite rigorously by inserting the experimental relative magnetization in place of $\langle S^z\rangle/S$. The last part of the expression does depend on the assumption of molecular-field theory, but since it is essentially a correction term it need not be accurately computed to fit the data. The idea of calculating a value of δ by inserting the experimental magnetization into Eq. (2) should therefore be rather generally valid.

The techniques used to extract the experimental values of δ have already been discussed.[16] The value of the spin S was assumed to be 5, which was found to fit the high-field magnetoresistance data. A comparison between the experimental δ, the δ

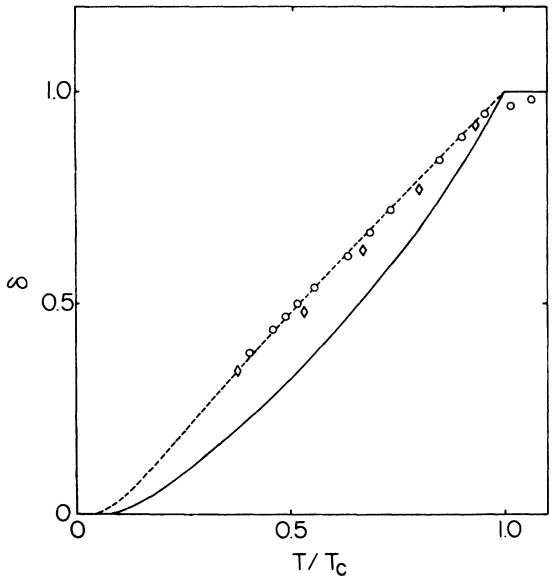

FIG. 2. Normalized spin-disorder resistivity of *Pd*–0.23-at.% Fe as a function of reduced temperature T/T_c. The diamonds are the resistivity calculated from the experimental magnetization. The solid line is a theoretical curve calculated using molecular-field theory assuming $S=5$. The dashed curve was calculated from the theory of Sec. IV assuming $S=5$ and $\epsilon=0.85$.

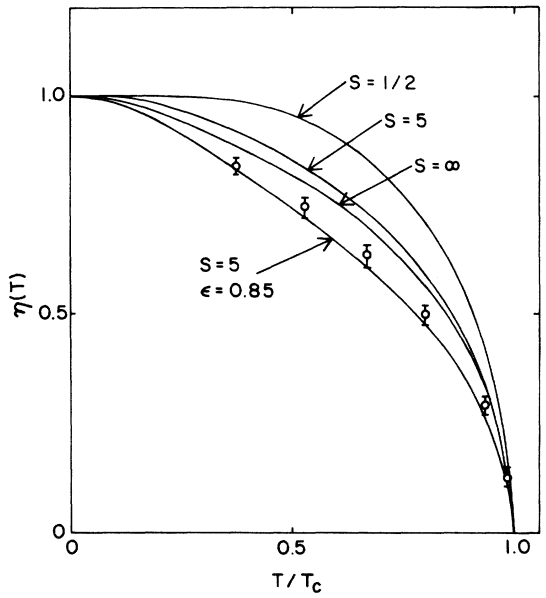

FIG. 3. Zero-field magnetization of *Pd*–0.23-at.% Fe as a function of reduced temperature T/T_c. The upper curves were calculated using molecular-field theory. The lowest curve was calculated from the theory of Sec. IV assuming $S=5$ and $\epsilon=0.85$. Circles are the experimental data.

calculated from molecular-field theory and the δ obtained from the experimental magnetization is given in Fig. 2, which shows very clearly that the resistivity calculated using the experimentally determined magnetization agrees far better with the experimental resistivity than the values calculated from molecular-field theory. The reason why is clear from Fig. 3, which shows that the experimental zero-field magnetization does fall well below that predicted by molecular-field theory for any value of spin S. Presumably the reason for this behavior is a broad distribution of exchange fields, as discussed previously.[16]

It is of interest to note that the full expression for the resistivity [Eq. (2)] fits the data better than the high-spin limiting form $\delta \approx 1-(\langle S^z\rangle/S)^2$. The reason is that the two terms in Eq. (2) have a markedly different temperature dependence, especially at low temperatures.

IV. MODEL OF EXCHANGE FIELD DISTRIBUTION

The subject of exchange field distributions in dilute magnetic alloys has been extensively treated by a number of authors.[4,23–25] Since the resistivity is such a crude probe of the actual exchange field distribution, however, we confine ourselves to a very simple model which has the advantage of being easily soluble for all values of the temperature and magnetic field. The model is based on the following set of approximations to the Heisenberg Hamiltonian for a spatially random set of spins:

$$\mathcal{H} = -\sum_{ij} J_{ij}\vec{S}_i \cdot \vec{S}_j - g\mu_B \vec{H}\cdot\sum_j \vec{S}_j$$
$$\rightarrow -\sum_{ij} J_{ij}\langle\vec{S}_i\rangle \cdot \vec{S}_j - g\mu_B \vec{H}\sum_j \vec{S}_j$$
$$\rightarrow -\sum_j (J_j\langle S^z\rangle_{av} + g\mu_B H)S_j^z \ ,$$

where

$$\langle S^z\rangle_{av} = \frac{1}{N}\sum_j \langle S_j^z\rangle$$

and

$$J_j = \sum_i J_{ij} \ .$$

If we assume that the exchange field at the various impurity sites has a zero-temperature probability distribution $P(J)$, then the following self-consistent integral equation is obtained for the average magnetization:

$$\eta_{av} \equiv \langle S^z\rangle_{av}/S$$
$$= \int dJ\, P(J) B_S[(J\langle S^z\rangle_{av} + g\mu_B H)/k_B T] \ , \qquad (3)$$

where B_S is the Brillouin function for spin S. Reasonable estimates for the general form of $P(J)$ have been derived for *Pd*Fe by Kitchens and Trousdale.[4] For simplicity, however, we assume the simple distribution shown in Fig. 4. With this distribution Eq. (3) can be immediately integrated to give

$$\eta_{av} = \frac{1}{S(\Delta_2-\Delta_1)} \ln\left(\frac{\sinh(S+\frac{1}{2})\Delta}{\sinh(\frac{1}{2}\Delta)}\right)\Bigg|_{\Delta_1}^{\Delta_2} \ ,$$

where

$$\Delta_2 = [J_0(1+\epsilon)\langle S^z\rangle_{av} + g\mu_B H]/k_B T \ ,$$
$$\Delta_1 = [J_0(1-\epsilon)\langle S^z\rangle_{av} + g\mu_B H]/k_B T \ .$$

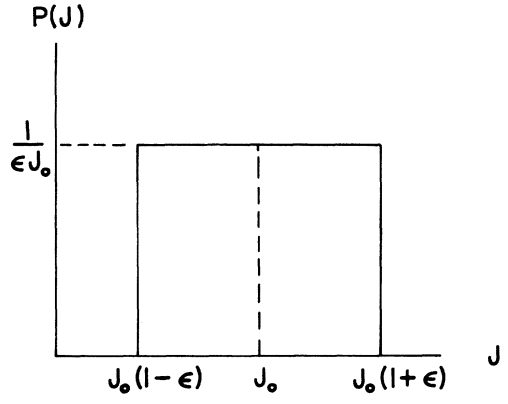

FIG. 4. The assumed probability distribution $P(J)$ for the exchange interaction at zero temperature for the model of Sec. IV.

This equation can be solved in the same way as the usual molecular-field-theory equation, to which it reduces in the limit as $\epsilon \to 0$.

To calculate the spin-disorder resistivity we simply replace $\langle S^z \rangle / S$, in Eq. (1) by $\langle S^z \rangle_{av}/S$. A more accurate expression for the resistivity can be written within the framework of the model, but it hardly seems warranted in view of the approximations already made. Since a spin value of approximately 5 has already been fixed by the high-field results,[16] the only adjustable parameter available to fit the zero-field data is ϵ, which describes the width of the exchange field distribution. The dashed curve through the resistivity data in Fig. 2 was calculated assuming $\epsilon = 0.85$, which indicates that the exchange field distribution is extremely broad. This is in good qualitative agreement with the exchange field distribution derived by Kitchens and Trousdale[4] on a more concentrated sample (0.4-at.% Fe) using the Mössbauer effect. At $T/T_c = 0.519$, for example, they found a very broad distribution with a width greater than the exchange energy at the peak of the distribution.

In Fig. 3 we have plotted the relative magnetization calculated using the same values of S and ϵ as were used to fit the resistivity. Agreement with experiment is within the estimated uncertainty of the extrapolation used to determine the zero-field magnetization. Within experimental accuracy, therefore, the model is capable of fitting both the zero-field resistivity and magnetization data. In Fig. 5 we show a comparison between the theoretical and experimental spin-disorder resistivity over the entire temperature and field range, with the same g factor assumed previously.[16] Agreement is very good except at low fields in the vicinity of T_c, where mean-field-type theories could be expected to do poorly in calculating the magnetization. When the experimental magnetization at 1 kOe is inserted into Eq. (2) the fit is much improved, as shown by the solid dots in the figure.

In comparing the theory outlined in this section to the zero-field resistivity data of Williams and Loram[6] (below 1-at.% Fe (and Skalski *et al.*[7] (1– 12-at.% Fe), it is apparent that the theory can fit the data reasonably well over this entire concentration range by an adjustment of ϵ and S, although it does not work quite so well in the low-temperature limit where the magnetic excitations are generally assumed to be spin waves. In general the higher-concentration samples appear to be consistent with small values of ϵ and the lower-concentration samples with large values, which is a reasonable result in view of the fact that the polarization range becomes large compared with the average separation between atoms in the higher-concentration samples. A more detailed discussion of the concentration-dependent data will be the subject of a separate publication.

The existence of a very broad exchange field distribution has some interesting implications concerning the nature of the dominant elementary excitations at very low temperatures. Even at temperatures such that $T \ll T_c$ it is possible, for example, to have a significant temperature dependence of the magnetization through local "molecular-field"-type excitations of thos impurity spins which are most weakly coupled to the rest ($J\langle S^z \rangle_{av} \sim k_B T \ll k_B T_c$). In fact, for the model of this section having a probability distribution $P(J)$ of arbitrary form it is possible to show that if $\lim_{J \to 0} P(J) > 0$, then both the low-temperature magnetization and resistivity contain terms linear in T which would dominate the $T^{3/2}$ terms expected from spin-wave theory in the limit as $T \to 0$.[9,10] Even for a very dilute ferromagnetic alloy one would normally expect, on very general grounds, to have well-defined spin waves for wavelengths much longer than the mean impurity spin separations. What the present result seems to suggest, however, is that under some circumstances the temperature dependence of the magnetization in the low-temperature limit may be dominated by localized excitations which can be described phenomenologically using a mean-field theory. It is not clear, however, that such excitations would broaden the long-wavelength spin-wave energies enough to render a spin-wave description inappropriate for very long wavelength excitations. There are, in fact, some experimental results on dilute *Pd*Fe alloys which might be explained in terms of "competing" spin-wave and molecular-field con-

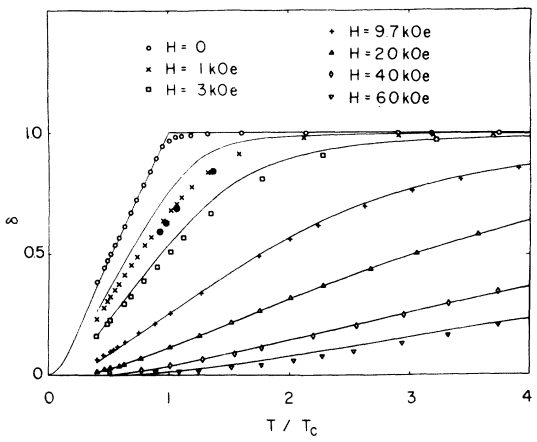

FIG. 5. Comparison of the experimental and calculated spin-disorder resistivity of *Pd*–0.23-at.% Fe as a function of temperature in magnetic fields up to 60 kOe. The solid curves were calculated from the theory of Sec. IV assuming $S = 5$, $g = 3.6$, and $\epsilon = 0.85$. The large solid dots were calculated from experimental magnetization data at 1 kOe.

tributions to the low-temperature magnetization. Among these are the observation that the acoustic spin-wave stiffness constant obtained by fitting low-temperature magnetization data appears to increase with increasing magnetic field.[26,27] This phenomenon is quite pronounced at very low concentrations and decreases with increasing concentration, as one might expect. Further evidence that spin-wave theory may not provide a complete description of the spin dynamics in the dilute limit comes from the specific-heat data of Veal and Rayne,[28] who found a well-defined spin-wave contribution for a sample containing 1.52-at.% Fe, but not for lower concentration samples.

V. SUMMARY AND CONCLUSIONS

It has been shown that the magnetization and spin-disorder resistivity of dilute *Pd*Fe alloys are correlated extremely well by a modified form of Yosida's theory of magnetoresistance.[16,17] When the effects of an exchange field distribution are included, the theory is able to fit both the zero-field magnetization and resistivity data. In addition, the theory can fit the magnetoresistance data except in low fields at temepratures near T_c. It is suggested that local molecular-field excitations of weakly coupled spins may be responsible for the marked magnetic field dependence of the acoustic spin-wave stiffness constant observed for the more dilute alloys.

ACKNOWLEDGMENTS

The authors would like to thank Professor D. L. Mills and Dr. M. Rubinstein for helpful discussions on various aspects of this problem.

[1]R. M. Bozorth, P. A. Wolff, D. D. Davis, V. B. Compton, and J. H. Wernick, Phys. Rev. **122,** 1157 (1961).
[2]G. G. Low and T. M. Holden, Proc. Phys. Soc. Lond. **89,** 119 (1966).
[3]J. Crangle and W. R. Scott, J. Appl. Phys. **36,** 921 (1965).
[4]T. A. Kitchens and W. L. Trousdale, Phys. Rev. **174,** 606 (1968).
[5]S. Skalski, J. I. Budnick, and J. Lechaton, J. Appl. Phys. **39,** 965 (1968).
[6]G. Williams and J. W. Loram, J. Phys. Chem. Solids **30,** 1827 (1970).
[7]S. Skalski, M. P. Kawatra, J. A. Mydosh, and J. I. Budnick, Phys. Rev. B **2,** 3613 (1970).
[8]Yu. Kagan, A. P. Zheinov, and H. Pashkaev, in *Localized Excitations in Solids*, edited by R. F. Wallis (Plenum, New York, 1968), p. 675.
[9]P. D. Long and R. I. Turner, J. Phys. C Suppl. Met. Phys. **2,** S127 (1970).
[10]D. L. Mills, A. Fert, and I. A. Campbell, Phys. Rev. B **4,** 196 (1971).
[11]T. Kasuya, Prog. Theor. Phys. **16,** 58 (1956).
[12]L. Colquitt and D. A. Goodings, in *Proceedings of the International Conference on Magnetism, Nottingham, England, 1964* (The Institute of Physics and The Physical Society, London, England, 1965), p. 29.
[13]D. L. Mills and P. Lederer, J. Chem. Phys. **27,** 1805 (1966).
[14]G. Williams, G. A. Swallow, and J. W. Loram, Phys. Rev. B **3,** 3863 (1971).
[15]A. D. C. Grassie, G. A. Swallow, G. Williams, and J. W. Loram, Phys. Rev. B **3,** 4154 (1971).
[16]N. C. Koon, A. I. Schindler, and D. L. Mills, Phys. Rev. B **6,** 4241 (1972).
[17]K. Yosida, Phys. Rev. **106,** 893 (1957).
[18]D. M. S. Bagguley, W. A. Crossely, and J. Leisgang, Proc. Phys. Soc. Lond. **90,** 1047 (1967).
[19]B. R. Coles, J. H. Waszink, and J. Loram, in Ref. 12, p. 165.
[20]P. P. Craig, R. C. Perisho, R. Segnan, and W. A. Steyert, Phys. Rev. **138,** A1460 (1965).
[21]A. Arrott, Phys. Rev. **107,** 1394 (1957).
[22]J. I. Budnick, J. Lechaton, J. H. Wernick, S. Foner, E. J. McNiff, Jr., D. J. Kim, and B. B. Schwartz, J. Appl. Phys. **39,** 960 (1968).
[23]G. J. Nieuwenhuys, B. M. Boerstoel, J. J. Zwart, H. D. Dokter, and G. J. van den Berg, Physica (Utr.) **62,** 278 (1972).
[24]T. Takahashi and M. Shimizu, J. Phys. Soc. Jap. **23,** 945 (1967).
[25]M. W. Klein, Phys. Rev. **136,** A1156 (1964).
[26]T. F. Smith, W. E. Gardner, and J. I. Budnick, Phys. Lett. A **27,** 326 (1968).
[27]T. F. Smith, W. E. Gardner, and H. Montgomery, J. Phys. C **3,** S370 (1970).
[28]B. W. Veal and J. A. Rayne, Phys. Rev. **135,** A442 (1964).