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Magnetic Ordering in Gold-Iron Alloys*

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In an attempt to characterize the magnetic ordering in *Au*Fe alloys, systematic studies were made of the temperature dependences of the thermoelectric power S and the low-field magnetic susceptibility χ for Fe concentrations C from 1 to 22 at.%. The concentration dependences of the magnitude and temperature of the maximum in $S(T)$ showed transitions clearly related to the magnetic ordering. Data analyses based on molecular field theories indicate the existence of small regions of short-range ferromagnetic order which undergo long-range interactions as the temperature is lowered. For $C \gtrsim 12$ at.%, long-range ferromagnetism is dominant. Lower-concentration alloys ($C \lesssim 12$ at.%) exhibit an antiferromagnetism with some properties similar to those of a magnetic spin-glass, but with well-defined ordering temperatures characterized by sharp cusps in $\chi(T)$, and with a negative Curie θ for $C = 1$ and 2 at.%. These properties indicate a more perfect antiferromagnetic order than that expected for a random alloy or a spin-glass, and this may be related to preferred local lattice arrangements in these alloys.

I. INTRODUCTION

The magnetic and transport properties of the system of alloys containing transition-metal solutes in the Au matrix have been of interest for about forty years.[1,2] Investigations of *Au*Fe alloys (and other similar alloy systems) sprang, in general, from two originally distinct problem areas which have converged considerably over the years. Studies, on the one hand, of the magnetic properties,[3] such as susceptibility, magnetization, etc., grew out of hope that by introducing magnetic impurities into nonmagnetic matrices one could come to understand the formation, interaction, and ordering of magnetic moments in metals and alloys, and in particular in these noble-metal–transition-series alloys. Interest in the transport properties, on the other hand, grew out of the discovery of the resistance minima, giant thermoelectric powers, and other anomalous transport phenomena found in dilute alloys.[4] With the realization that the anomalous transport properties were related to the formation of local magnetic moments in the dilute alloys[5,6] the two lines of investigation began to converge. It became clear that the s-d exchange interaction, which linked the localized moments to the conduction electrons, also provided an indirect exchange interaction between the local moments themselves, for example, the Ruderman–Kittel–Kasuya–Yosida (RKKY) interaction.[7] Thus the two problem areas became redefined: the problem of the formation and properties of single magnetic moments,[5,8] and the problem of the interactions or correlations between the moments leading to ordering. The *Au*Fe system is particularly interesting since it is one of the few alloy systems where not only single-impurity effects but also different types of long-range order can be observed in different concentration regimes. The single magnetic impurity problem deals, in general, with very dilute alloys. Our primary interest here is the understanding of the interactions between magnetic moments and the resultant magnetic ordering which occurs at somewhat higher concentrations. In an attempt to understand this magnetic behavior in the *Au*Fe alloy system we have undertaken a study of the thermoelectric power and the low-field magnetic susceptibility in alloys with concentrations from 1 to 22 at.% Fe. In the concentration ranges of interest to us, *Au*Fe alloys are solid solutions where Fe atoms substitutionally occupy sites in the fcc gold lattice.

In Sec. II we shall review the previous experimental work on *Au*Fe in this concentration range, and also some existing theoretical models. Section III will contain a brief description of our experimental techniques. In Secs. IV and V, we shall present our experimental results and analyses of the thermoelectric power and the magnetic susceptibility, respectively. The conclusions of our work are discussed in Sec. VI.

II. PREVIOUS WORK

A. Magnetic Properties

Early measurements of magnetization M and susceptibility χ in these alloys include the high-temperature work ($T > 300$ °K) of Shih,[1] the measurements of Pan *et al.*,[9] who found that ferromagnetism existed in alloys with concentrations C above about 10 at.% Fe, and the study of Kaufmann *et al.*,[3] who analyzed susceptibility data down to 14 °K and calculated the paramagnetic Curie temperature θ and the effective magnetic moment per Fe atom, P_{eff}. Kaufmann *et al.* found that, for $C < 6.4$ at.% Fe, θ and p_{eff} varied linearly with C, that θ was negative for $C < 3.5$ at.% and positive for C above, and that p_{eff} increased as C increased up to $C \simeq 13.7$ at.%, then decreased as C increased above. Their data, however, were sparse below 77 °K and, while their measurements indicated deviations from paramagnetic behavior, no conclusion could be drawn about the ordering. Similarly Schiel *et al.*[10] performed higher-temperature measurements of χ for the *Au*Fe system, but shed no light on the low-temperature ordering. In a study of the susceptibility and remanent magnetization of several similar alloy systems, Lutes and Schmit[11] found that, for *Au*Fe alloys with $C = 0.5$ and 1 at.%, χ showed broad maxima at low temperatures ($T < 10$ °K), and that the small temperature-dependent remanence went to zero at about the same temperature that the maximum in χ occurred. The results for *Au*Fe (and similar results for *Au*Mn, *Au*Cr,[11] and *Cu*Mn[12,13]) were interpreted as indicating a magnetic transition at the temperature of $\chi_{\max}$. For *Au*Fe alloys with $C = 0.5$ and 1 at.%, $\chi_{\max}$ was 4.0 and 7.4 °K, respectively, and θ was found to be -3 and 1 °K, respectively. In a more recent low-temperature study of M and χ for very dilute *Au*Fe, Tholence and Tournier[14] observed maxima in χ for alloys with $C = 0.1$, 0.2, and 0.5 at.%, similar to those found by Lutes and Schmit, while for $C < 0.1\%$ no maxima were observed. Following the work of Lutes and Schmit, Henry[15] studied the magnetization and remanence for a sample of *Au*Fe with $C = 5$ at.%, and Tournier and Ishikawa[16] performed a similar study for $C = 8$ at.%. This second work found a very high p_{eff} ($24\mu_B$) which was interpreted as an indication of superparamagnetism above the ordering temperature T_0, while below T_0 the inability to saturate M with very high fields suggested antiferromagnetic ordering. Crangle and Scott[17] performed systematic magnetization studies of eight *Au*Fe alloys with 5.1 at.% $\leqslant C \leqslant 29.5$ at.%. Using "Arrott plots"[18] of H/M vs M^2 for different temperatures, where M is the magnetization and H is the applied magnetic field, they found no ferromagnetic Curie temperatures for alloys with $C \leqslant 11.1$ at.% Fe, while for $C \geqslant 14.9$ at.% they found well-defined ordering temperatures. Crangle and Scott interpreted the results found by other authors for lower concentrations as superparamagnetism due, perhaps, to short-range clustering of the Fe atoms. de Mayo[19] has recently shown that increasingly large superparamagnetic clusters seem to appear as the Fe concentration approaches the critical concentration for ferromagnetism. He also notes, as do Borg, Lai, and Violet[20] in a Mössbauer study of a higher concentration, that the magnetic properties of these alloys are strongly affected by heat treatment and cold working. It is important to note that all of the magnetic studies mentioned thus far were performed in moderate to high fields ($H \sim 1000$ G), and that the low-field properties have not been investigated, although the true critical behavior of a magnetic transition is exhibited only in the limit of zero field. The ordering temperatures found from these magnetic properties are shown in Fig. 1.

Mössbauer studies of the hyperfine field at the Fe nucleus[21] provided one of the first definite indications that a low-temperature magnetic ordering was occurring in low-concentration *Au*Fe. Systematic studies of the Mössbauer spectra of these alloys by Borg, Booth, and Violet,[21] by Violet and Borg,[22] by Gonser *et al.*,[23] and by Borg,[24] have found magnetic transitions characterized by the onset of hyperfine splitting at well-defined temperatures for alloys with C down to 0.26 at.% Fe. By taking Mössbauer spectra in the presence of

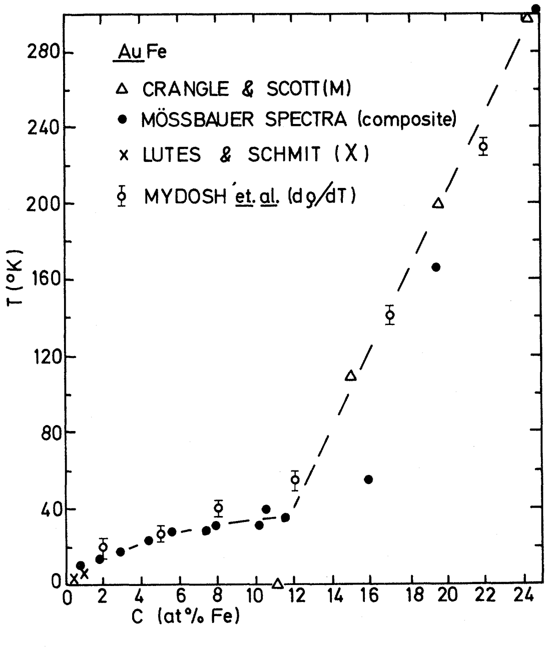


FIG. 1. Magnetic ordering temperature T_0 vs concentration C for *Au*Fe alloys. The triangles are from the magnetization data of Crangle and Scott (Ref. 16); closed circles are from the Mössbauer data of several authors (Refs. 21–23) (see text); the crosses represent the maxima in the susceptibility data of Lutes and Schmit (Ref. 11); and the open circles with flags represent the maxima in $d\rho/dT$ of Mydosh *et al.* (Ref. 42).

polarizing fields Craig and Steyert[25] and Gonser *et al.*[23] concluded that for lower concentrations the ordering was antiferromagnetic; that is, it corresponded to a complete distribution of orientations of the Fe spins in small external magnetic fields. The absence of any paramagnetic contributions to the Mössbauer spectra below T_0 implied that virtually all Fe atoms take part in the magnetic ordering. The hyperfine field at the *Au* nucleus has been examined by Borg and Pipkorn,[26] but these spectra were complex and poorly resolved, and while they have not led to any definite conclusions, they do suggest a small induced moment on the Au atom. More recent Mössbauer studies of *Au*Fe have been performed by Ridout[27] and by Window.[28] Window concludes that when an Fe atom has two or more neighbors, the Fe spins point in $\langle 111 \rangle$ crystallographic directions, thus providing preferred crystal axes for paramagnetic clusters in these alloys. All of these Mössbauer studies agreed essentially in their determination of the existence and value of a magnetic ordering temperature T_0 for these alloys, and showed that the concentration dependence of T_0 for $C < 12$ at.% was very different from the ferromagnetic alloys with $C > 12$ at.%. T_0 as determined from the Mössbauer data is plotted vs C in Fig. 1.

Several theoretical molecular field treatments of the thermodynamic and magnetic properties of alloys similar to *Au*Fe have been proposed. Owen *et al.*[12] applied classical molecular field analysis to the susceptibility data for *Cu*Mn. They assumed two short-range molecular field constants, ferro- and antiferromagnetic, and from T_0 and θ they calculated the magnitudes of the molecular field constants from which they could discuss the interactions in that alloy. Later models, taking a much more basic approach, assumed that the oscillatory RKKY interaction couples the local moments.[29-32] In the most complete of these studies Klein and Brout[31] and Klein[32] have obtained expressions for the internal field distribution and used these to calculate the temperature and field dependences of the specific heat, magnetization, and susceptibility of dilute-concentration magnetic impurities. Klein predicts oscillating short-range spin correlations which lead to broad field-independent maxima in $\chi(T)$, and also, contrary to experiment, that the magnitude of χ is, to first order, independent of C. Klein and Shen[33] have made a comparison of this mean random molecular field model with the experimental data of Lutes and Schmit.[11] Following this type of model, Liu[34] has introduced heuristic modifications to the field probability distribution of Marshall,[30] Klein and Brout,[31] and Klein,[32] and by parametrizing the internal field distribution, has found indications that this model may be extended to higher concentrations. In particular, by introducing an angular distribution of the internal field, Liu has shown that a helical antiferromagnetic angular distribution provides a concentration dependence for χ which is in qualitative agreement with experiment. Sato, Arrott, and Kikuchi[35] have examined various statistical approaches to the problem of nearest-neighbor interactions in dilute magnetic systems. In particular, they examine the critical concentrations required for cooperative magnetic phenomena, and discuss the complexity of interpreting magnetic data, especially for antiferromagnetic interactions. Although their study seems to show reasonable agreement with high-concentration ferromagnetic *Au*Fe alloys, it is not applicable to lower-concentration alloys where indirect *s-d* exchange interactions are important. For *Cu*Mn and related alloys Kouvel[36] has suggested a model which describes their magnetic properties as due to mutually interacting ferromagnetic and antiferromagnetic domains. In this model the susceptibility maxima do not correspond to cooperative magnetic transitions, but rather to the disappearance of strong magnetic anisotropy. Very recently Beck[37] has described the complex remanence and thermomagnetic properties of alloys of this type as due to the freezing of superparamagnetic clusters at low temperatures into random spin orientations—mictomagnetism (or, according to other authors, a magnetic spin-glass[38,39]). Beck suggests that exchange interactions between the clusters freeze the moments and cause the susceptibility to decrease at low temperatures, but there is no well-defined freezing temperature due to the range of interactions strengths. Finally, Bennemann *et al.*[40] have proposed a model to explain the large susceptibilities in dilute La–rare-earth alloys. In this model the spins which possess long-range quasiantiferromagnetic order (due to the oscillating RKKY interactions) may also possess short-range quasiferromagnetic spin coupling. They predict $\chi(T)$ with maxima which are strongly dependent upon concentration, field, and the amount of clustering in the alloy. At present, however, there does not seem to exist any quantitative theory applicable to *Au*Fe alloys, especially in the lower range of concentrations from about 1 to 8-at.% Fe.

B. Transport Properties

The anomalous transport phenomena associated with single magnetic impurities in dilute alloys[4,5,8] have clearly shown the importance of the *s-d* exchange interaction in determining the properties of these alloys. Furthermore, since the interactions between the magnetic moments in nondilute alloys also seem to be mediated by the conduction electrons via an RKKY or other indirect type of interaction, it is expected that the electron transport properties such as the resistivity ρ, magnetoresistance, and the thermoelectric power S will be quite sensitive to the magnetic state of the system. Although considerable experimental and theoretical effort has been expended to understand the transport phenomena related to the single-impurity problem, it is only recently that transport properties in the regions near magnetic transitions have generated great interest.[41] Thus far the only systematic work done to correlate magnetic ordering with transport phenomena in nondilute *Au*Fe alloys has been resistivity studies.[42,43] Mydosh *et al.*,[42] considering the temperature coefficient of the resistivity, have shown that a maximum in $d\rho/dT$ corresponds roughly to the ordering temperature T_0 determined by the Mössbauer measurements for 1 at.% $\leq C \leq$ 22 at.% (see Fig. 1). This agrees with the theory of Fisher and Langer,[44] who predict that $d\rho/dT$ in ferromagnets should exhibit a critical singularity at the magnetic ordering temperature, similar to the magnetic specific heat. In antiferromagnetic materials, Suezaki and Mori[45] predicted an anomaly: $d\rho/dT \propto (T - T_0)^{-(\alpha+\gamma-1)}$, where α and γ are the specific heat and susceptibility critical exponents. Sundahl *et al.*[43] have shown that the residual resistivity ρ_0 is greatest for alloys with $C \simeq 12$ at.%, where the type of long-range order changes.

The large thermoelectric powers found in very dilute concentrations of *Au*Fe and similar alloys have been extensively studied by MacDonald *et al.*,[46] Christenson,[47] and much earlier by Borelius *et al.*[48] All of these authors found large negative thermopowers S with low-temperature (negative) maxima whose magnitudes and temperatures were, for $C < 0.1$ at.%, only weakly dependent upon concentration. The magnitude of the peak reached a maximum below $C \simeq 0.1$ at.% and above this the magnitude decreased while the temperature of the peak increased much more rapidly. The results for $C < 0.1$ at.% have been interpreted by Kondo[49] as due to scattering from single magnetic impurities, but his theory does not explain the persistence of large S for higher concentrations and temperatures. Three essentially equivalent[50] molecular field calculations of the thermopower for this type of alloy have been made assuming magnetic ordering, by Kasuya,[51] by deVroomen and Potters,[52] and by Bailyn.[50] These studies predicted large thermopowers associated with ferromagnetic and mixed ordering, and no anomalous thermopower associated with antiferromagnetic ordering. Up to now these results have shown some rough qualitative agreement with experiment for low-concentration alloys, but the agreement is too approximate to shed any light on the magnetic ordering. Overhauser[53,54] has proposed a spin-density wave mechanism for antiferromagnetism in these alloys, and Van Zandt and Overhauser[55] have derived thermopowers from this model which are large and qualitatively somewhat similar to those observed experimentally. The predictions of this model are, however, difficult to compare quantitatively with experiment, and the model does not seem to predict the correct behavior for the resistivity. Thus far no attempt has been made to study the thermopower for higher C and correlate the results with the magnetic ordering.

C. Summary

The previous studies of the *Au*Fe alloy system have shown that ferromagnetic ordering exists for higher concentrations, $C \gtrsim 12$-at.% Fe. For lower concentrations, down to $C < 1$ at.%, Mössbauer measurements indicate that a magnetic ordering exists which exhibits some characteristics of antiferromagnetism, but which has not been unambiguously detected by macroscopic magnetic techniques, and whose interactions and properties are by no means understood. The ordering temperatures thus far determined for *Au*Fe are shown as a function of C in Fig. 1, including data from initial susceptibility, high-field magnetization, Mössbauer, and $d\rho/dT$ studies. This plot clearly shows a change in behavior at $C \simeq 12$ at.%. But there still remain large gaps in our experimental knowledge of the system. Despite the sensitivity of χ to the ordering as evidenced by the maxima in χ for 0.1 at.% $\leq C \leq$ 1 at.%, there have been no specific studies of χ in the regions of the ordering temperatures for $C > 1$ at.%, and no low-field susceptibility data. We have, therefore, performed a systematic study of the very-low-field (~ 5 G) magnetic susceptibility in the regions of T_0 of eight *Au*Fe alloys from $C = 1$ to 22 at.%. The success, moreover, of the study of $d\rho/dT$ by Mydosh *et al.*[42] suggested that measurements of the thermopower, the "most sensitive of electron transport properties,"[56] should be extended to higher concentrations in an attempt to understand the magnetic ordering and its effect upon the thermopower. We have, therefore, investigated the thermoelectric power of six *Au*Fe alloys from $C = 2$ to 22 at.% in the temperature range 4–300 °K. While the preliminary experimental results of these measurements have been previously reported in limited form,[57,58] this paper includes a fuller presentation of the data, with analyses and interpretations of our results, and an attempt at a more general phenomenological description of the *Au*Fe system, incorporating the experimental and theoretical studies of other authors.

III. DESCRIPTION OF EXPERIMENT

The *Au*Fe samples[59] for the thermopower measurements were in the form of wires 0.01 in. in diameter and for the susceptibility measurements the samples were spherically shaped with diameters of a few mm. In either form the samples were annealed at 850 °C, quenched to 20 °C, and then stored in liquid nitrogen until used. It was hoped that this heat treatment would present a uniform starting point for all the samples[60] and assure a random distribution of iron atoms in the gold matrix.

For the thermoelectric power, a Cu–*Au*Fe sample thermocouple was formed, and the voltage V of this thermocouple was measured as a function of temperature. Since the thermopower S_{Cu} of the Cu wires had previously been calibrated, $S(t)$ for the various *Au*Fe samples could be determined by computer differentiating $V(T)$ and subtracting the contribution S_{Cu}. This was carried out in the temperature region 4–300 °K and to an accuracy of S within 0.1 μV/ °K.

The low-field (≃ 5-G) low-frequency (155-Hz) susceptibility was measured by a mutual inductance bridge[61] for which a cryogenic arrangement permitted the sample to be moved in or out of the induction coil for temperatures 2–300 °K. The bridge was calibrated by using standard paramagnetic salts and was sensitive to changes in sample susceptibility of about 3×10^{-8} emu. The complete details of all of the above experimental techniques are given by Cannella.[62]

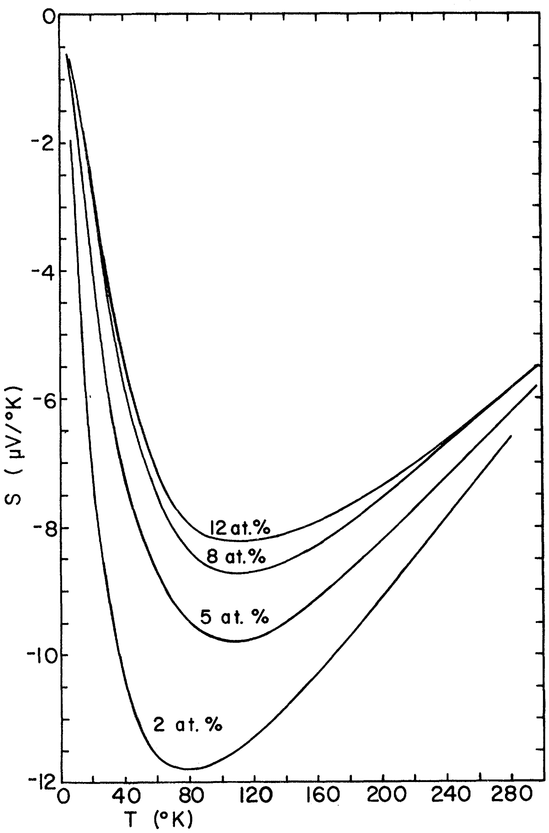


FIG. 2. Thermoelectric power $S(T)$ for *Au*Fe samples with $2 \leq C \leq 12$ at.%. The estimated errors and scatter are about the thickness of the lines. Below 80 °K the maximum interval between data points was 2 °K, and above 80 °K the maximum interval was 4 °K.

IV. EXPERIMENTAL RESULTS FOR THERMOELECTRIC POWER

A. Experimental Data

The measured values of the thermoelectric power $S(T)$ vs T are shown for *Au*Fe alloys with 2 at.% $\leq C \leq$ 12 at.% in Fig. 2 and for 12 at.% $\leq C \leq$ 22 at.% in Fig. 3. The thermoelectric power for all these samples is always negative below 300 °K, and, except at the lowest temperatures, large (~10 μV/ °K). $S(T)$ for all samples exhibits a negative peak (a maximum for $|S|$) between 80 and 110 °K. For all samples S becomes small at low temperatures (~4 °K), and appears approximately linear in T at high temperatures, ~300 °K. [Christenson,[47] however, shows for $C \simeq 1$ and 5 at.% that $S(T)$ becomes positive at about 640 °K, and is gently curved up to at least 960 °K.]

Despite the similarities in the $S(T)$ curves, we also find specific differences for different concentrations. For the samples with iron concentration of 17 and 22 at.%, Fig. 3, there is a distinct change in the slope of $S(T)$ in the region above the ordering temperatures determined from other measurements (see Fig. 1), while $S(T)$ for the lower concentrations does not show this change of slope. Although $S(T)$ for $C = 12$ at.% does not show the change in slope found at higher concentrations, it does show a repeatable fine structure at about 50 °K. For samples with $C < 12$-at.% Fe we do not see and evidence of a transition in $S(T)$ which indicates that the critical concentration is about 12 at.%, which agrees with the data in Fig. 1. We have examined the temperature derivative dS/dT near the ordering temperatures[63,64] for $C = 17$ and 22 at.% and find well-defined maxima in dS/dT for these concentrations. These maxima (indicated by arrows in Fig. 3) occur at temperatures which agree reasonably with T_0 shown in Fig. 1.

We have also examined the temperature dependence of $S(T)$ for all concentrations and made a least-squares computer fit to a polynomial of the form $S(T) = K + AT^n + BT^m$. Within limited low-temperature ranges we found excellent fits for all curves with a function of the form $S(T) = AT^{3/2} + BT^{5/2}$, where A and B are functions of the concentration. A is negative, B is positive and about

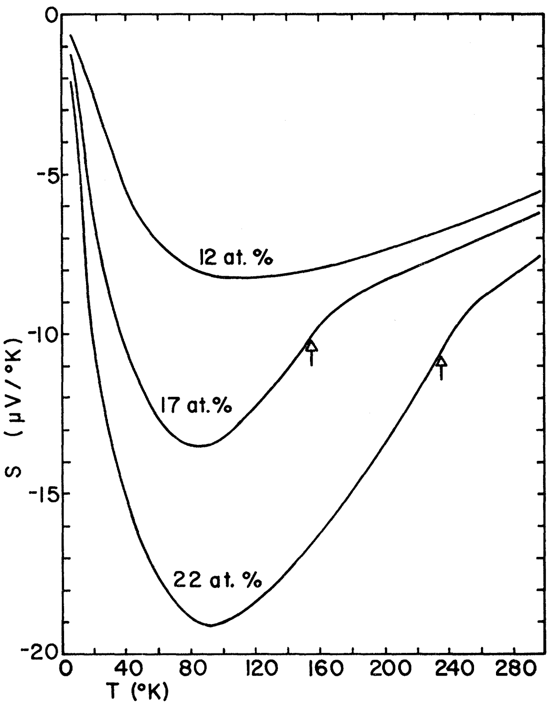


FIG. 3. Thermoelectric power $S(T)$, for *Au*Fe samples with $12 \leq C \leq 22$ at.%. The arrows indicate the position of the maximum in dS/dT. The scatter and errors are the same as in Fig. 2.

two orders of magnitude smaller than A. Table I shows the values for $A(C)$ and $B(C)$, the range of temperatures for which the fit to the polynomial is good, and the ordering temperatures from Fig. 1 for each concentration.

In studying the features of these $S(T)$ curves as a function of concentration we have examined the magnitude of the (negative) peak in the thermopower, $|S|_{\max}$, and the temperature at which this peak occurs $T_{|S|_{\max}}$, as a function of concentration. The data indicate a critical concentration at about 12 at.%, since $|S|_{\max}$ shows a sharp minimum at $C = 12$ at.% with a very marked change in behavior above and below, and $T_{|S|_{\max}}$ shows a maximum at $C = 12$ at.% with an apparent discontinuity in $T_{|S|_{\max}}$ above $C = 12$ at.%.

The significance of this behavior becomes clearer in the light of earlier thermopower studies of more dilute concentrations. For very dilute concentrations, *Au*Fe alloys show anomalously large thermopowers usually associated with scattering from single magnetic impurities as described by Kondo.[49] Ideally these large values of S occur at very low temperatures, are approximately independent of temperature and concentration, and are destroyed by interactions between the magnetic impurities. Figure 4 shows a plot of $|S|_{\max}$ vs concentration from $C = 0.0022$ to 22 at.%, using a semilogarithmic plot to allow the whole range of concentration, and incorporating the experimental values of MacDonald *et al.*,[46] Christenson,[47] Borelius *et al.*,[48] and Berman *et al.*[65] Figure 5 shows a similar semilogarithmic plot of $T_{|S|_{\max}}$ vs concentration. At low concentrations, below about 0.1 at.%, we see the relatively slow variation of $|S|_{\max}$ and $T_{|S|_{\max}}$ associated with the Kondo effect. But near $C = 0.1$ at.% we see distinct changes in the behavior of both $|S|_{\max}$ and $T_{|S|_{\max}}$. There is a maximum in $|S|_{\max}$ at about $C = 0.03$ at.%, and distinct changes in the concentration dependence between $C = 0.06$ and 0.3 at.%. Similarly, there is an apparent discontinuity in the concentration dependence of $T_{|S|_{\max}}$ between $C = 0.2$ and 0.3 at.%. These changes and discontinuities occur at about the same concentrations that the maxima begin to appear in the susceptibility data of Tholence and Tournier[14] (at about $C = 0.1$ at.%), and magnetic ordering temperatures begin to appear in the Mössbauer work of Borg[24] and others (see Sec. II A). The change in the concentration dependence of $|S|_{\max}$ and the discontinuity in $T_{|S|_{\max}}$ would seem to be associated, then, with the onset of magnetic ordering.

Examining our data for $|S|_{\max}$ and $T_{|S|_{\max}}$ for higher concentrations we see that between $C = 12$ and 17 at.% we again have distinct changes in the concentration dependences, but in this case $|S|_{\max}$ goes through a minimum and the discontinuity in $T_{|S|_{\max}}$ is negative. Again we know that the critical concentration for the onset of ferromagnetic ordering is near $C = 12$ at.% and it becomes clear that the changes in concentration dependences of $|S|_{\max}$ and $T_{|S|_{\max}}$ are due to magnetic ordering. It is difficult to analyze $|S|_{\max}$ further because of its slow and complicated concentration dependence. However, the log-log plot of $T_{|S|_{\max}}$ vs concentration in Fig. 6 shows that $T_{|S|_{\max}}$ is very closely proportional to $C^{1/3}$ for concentrations both below and above the discontinuity near $C = 0.1$ at.%. Surprisingly, the points for the ferromagnetic con-

TABLE I. Values for $A(C)$, $B(C)$, T_0, and the temperature range of the fit of $S(T) = A(C)\,T^{3/2} + B(C)\,T^{5/2}$ for various concentrations.

Conc. (at.% Fe)	$A(C)$ (μV/°K$^{5/2}$)	$B(C)$ (μV/°K$^{7/2}$)	Temp. range of fit	T_0 from Fig. 1 (°K)
2	−0.129	0.0020	up to 20 °K	14
5	−0.060	0.0008	up to 30 °K	22
8	−0.0407	0.00044	up to 45 °K	28
12	−0.0367	0.00038	up to 50 °K	50
17	−0.100	0.0015	up to 20 °K	140
22	−0.190	0.0037	up to 20 °K	230

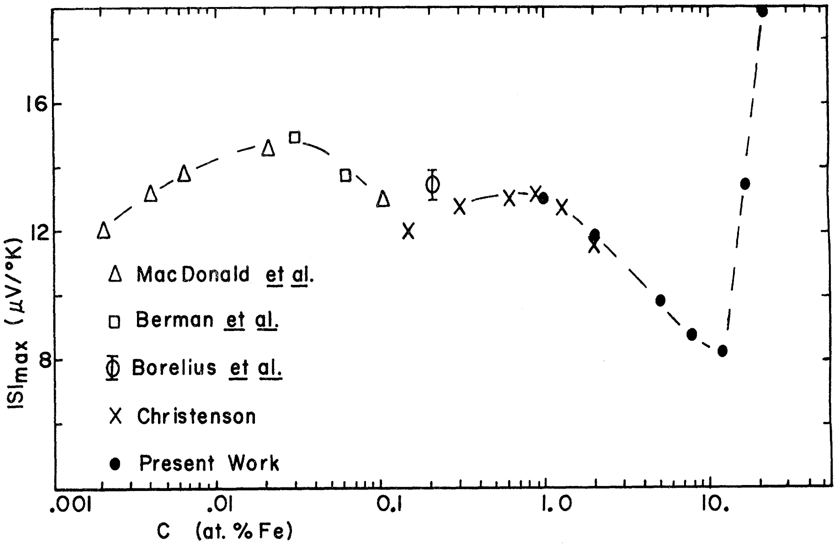


FIG. 4. Semilogarithmic plot of $|S|_{max}$ vs C for $0.0022 \leq C \leq 22$ at.% including the data of MacDonald *et al.* (Ref. 46), Christenson (Ref. 47), Berman *et al.* (Ref. 65), and Borelius *et al.* (Ref. 48).

centrations fall on the same curve as the points for $C \lesssim 0.1$ at.%.

Preliminary measurements of $S(T)$ were made over the complete temperature range for unquenched samples and in each case we observed a repeatable anomalous behavior between about 210 and 230 °K with a minimum usually occurring about 225 °K. Although this anomalous "kink" in the thermopower is effectively removed by annealing and quenching, there are, nevertheless, very small traces of the kink in the scatter of even the annealed and quenched curves. Since these kinks disappear with quenching it would seem that they may be associated with some sort of clustering or ordering of the Fe atoms, and since this behavior is not observed at a magnetic transition in a quenched sample, it is possible that it is due to some form of local crystal phase transition in the lattice. A similar anomaly was observed in the thermoelectric power of chromium by Meaden and Sze[66] and they attribute the effect to a phase transition with a latent heat.

B. Comparison of Thermoelectric Power with Theory of Kasuya

Figures 4–6 seem to indicate that at low concentrations the thermopower mechanism is similar to that described by Kondo[49] and by Suhl and Wong[49] but modified by interactions to provide a temperature and slight concentration dependence. The appearance of some type of magnetic ordering near $C = 0.1$ at.% inhibits this thermopower mechanism by causing Zeeman splitting of the spins in the internal field. This suddenly shifts the maxima in the thermopowers to temperatures well above the ordering temperatures, where the

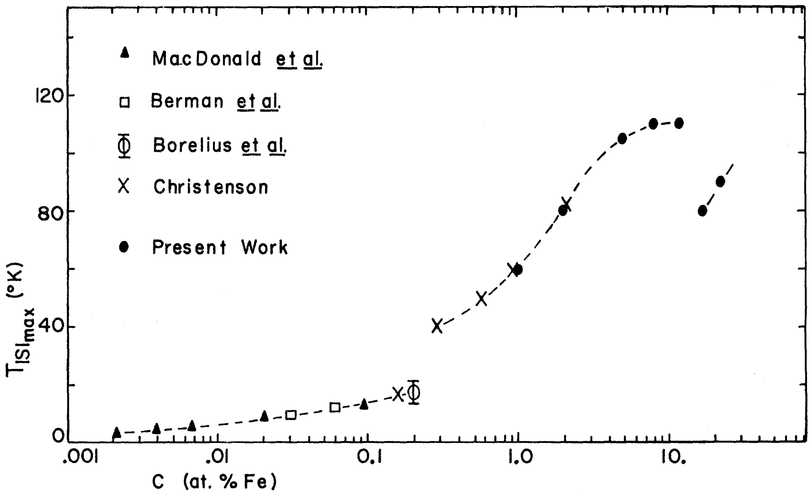


FIG. 5. Semilogarithmic plot of $T_{|S|_{max}}$ vs C for $0.0022 \leq C \leq 22$ at.% including the data of other authors as in Fig. 4.

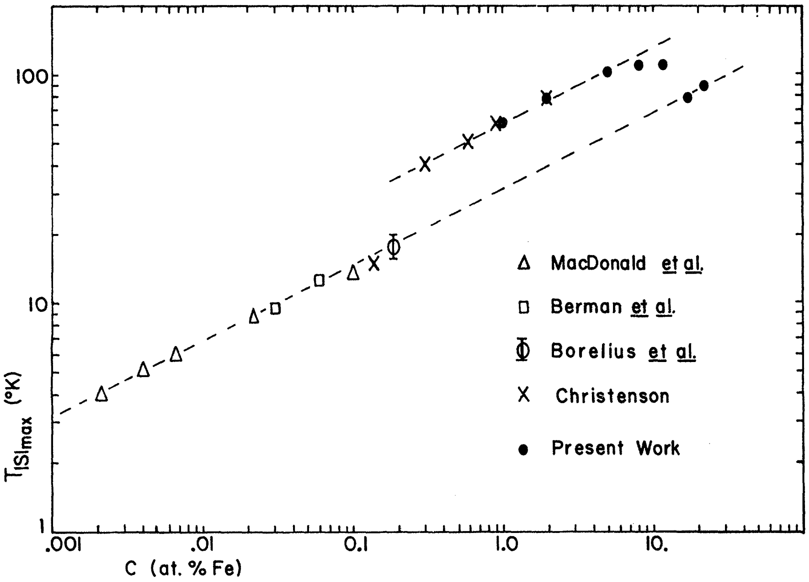


FIG. 6. Log-log plot of $T_{|S|_{\max}}$ vs C for $0.0022 \leq C \leq 22$ at.% including the data of other authors as in Figs. 4 and 5.

interactions between the paramagnetic spins are small and the Zeeman splitting is small comparable to $k_B T$. As the concentration increases it less likely that we can attribute the persistence of large thermopowers at high temperatures to a Kondo-type mechanism, especially for $C \gtrsim 5$ at.%, where superparamagnetic clusters seem to become important.[19] As C approaches the critical concentration for ferromagnetism, we expect that the molecular field theories for the thermopower should begin to be applicable.

Of the three essentially equivalent theories for the thermopower in this type of alloy mentioned in Sec. II B the work of Kasuya[51] seemed most tractable to calculations. Using a molecular field model and an s-d exchange interaction, Kasuya solved the Boltzmann transport equation to obtain the transport coefficients for both ferromagnetic metals and dilute alloys. In general, he finds a large "anomalous" thermopower for ferromagnetic systems, while there is none for antiferromagnetic systems. The ferromagnetism, however, need only extend over the mean free path of the conduction-electron spin, so that mixed order or clustering could also give large thermopowers. For dilute alloys he obtains an expression for the thermopower:

$$S = \frac{k}{\epsilon}\left(\pi^2 \frac{kT}{3\zeta} - \frac{F(C)\bar{J}_z(J^2 + J - \bar{J}_z^2 - \bar{J}_z)x^2}{1 - e^{-x}}\right) .$$

Here $F(C)$ is a function of concentration containing the exchange integral and the Coulomb interaction (both assumed independent of temperature); $\bar{J}_z$ is the mean value of the z component of the total angular momentum J on each magnetic atom; $x = H_0/kT$, where H_0 is the molecular field; k is Boltzmann's constant; ϵ is the electronic charge; ζ is the Fermi energy; and T is in °K. The first term in the expression is the normal diffusion thermopower S_n which is small compared to S_a, the "anomalous" second term (for Au, $S_n \simeq 5 \times 10^{-3} T$ μV/°K^2). The temperature dependence of S_a can be found by substituting Kasuya's value for $\bar{J}_z$:

$$\bar{J}_z = \left(J + \frac{2J+1}{e^{(2J+1)x} - 1} - \frac{1}{e^x - 1}\right),$$

giving

$$S_a = F(C)\left(J + \frac{2J+1}{e^{(2J+1)x} - 1} - \frac{1}{e^x - 1}\right)^2 \frac{2x^2}{e^x + e^{-x} - 2} \quad .$$

Assuming only s-d exchange interactions, we may write the molecular field $H_0 = H_m \bar{J}_z$, where H_m is the molecular field constant which may be approximated from a paramagnetic Curie temperature θ', $H_m = 3k\theta'/J(J+1)$.[51] In order to find $\bar{J}_z$ (and S_a) as a function of temperature, we performed a self-consistent iterative computer calculation of $\bar{J}_z$ at each temperature, with J and θ' as variable parameters. In view of the weak concentration dependence of the experimental S for nonferromagnetic alloys, and the approximate nature of Kasuya's calculations, we did not attempt to calculate the concentration-dependent factor $F(C)$. We have instead normalized the theoretical values of S_a with respect to $(S_a)_{\max}$ and compared the temperature dependence of the normalized S_a with the experimental $S(T)$ for various concentrations, normalized in the same way. In Fig. 7 normalized theoretical curves of S_a vs T for $J = 1.5$ and various values of θ' are compared with the normalized experimental $S(T)$ for $C = 8$ at.%. We have estimated the mean free path L_s of the conduction-electron spin from the magnetic contribution to the resistivity and find $L_s \lesssim 50$ Å (~10 lattice sites) for $C \gtrsim 5$ at.%. Superparamagnetic clusters of at least this size are indicated by the work of de Mayo[19] for these concentrations. Therefore, a contribution to the thermopower from the Kasuya model is reasonable, especially since this contribution should reflect a distribution of values for θ' owing to a distribution of cluster sizes and molecular field values. The data of Fig. 7 are consistent with such a contribution, but it is unlikely that this dominates the thermopower since experimentally $|S|_{\max}$ reaches a minimum at $C \simeq 12$ at.%, and the Kasuya thermopower would be expected to increase with concentration.

In comparing theoretical curves with the experimental data for $C = 17$ and 22 at.%, we find that S_a, computed using values of θ' close to the experimental value from the susceptibility, seemed to be somehow combined with or superimposed upon a curve similar to those found for $C \leqslant 12$ at.%. This is shown in Fig. 8, where we plot the normalized experimental $S(T)$ for $C = 17$ at.% (experimental $\theta = 140°$, see Table II) with the normalized theoretical S_a for $J = 1.5$, $\theta' = 140°$ and with the normalized experimental $S(T)$ for $C = 8$ at.%. Below the ferromagnetic Curie temperature in higher-concentration alloys the molecular field values should be very strongly peaked at the value describing the average ferromagnetic interaction in the bulk alloy; therefore use of the average bulk θ' in Kasuya's model would give the correct qualitative temperature dependence of the thermopower. Above the Curie temperature for the bulk system there would still remain local regions of ferromagnetism with much higher θ's due to locally high Fe densities, and these regions would generate a thermoelectric power similar to what we described for the lower concentrations. This could explain how large values of the thermopower persist above the bulk Curie temperatures in ferromagnetic alloys.

There are, however, serious limitations in our application of Kasuya's theory to the thermoelectric power of these alloys by assuming superparamagnetic regions of ferromagnetic ordering. We have used normalized curves to examine the temperature dependence of $S(T)$, and have ignored the concentration dependence of the magnitude of $S(T)$. Furthermore, it is not known whether the distribution of superparamagnetic clusters consistent with the concentration could actually produce the observed thermopowers. We feel, therefore, that we can only indicate the possibility of applying Kasuya's theory to the thermopower of *Au*Fe alloys, and that considerable work remains to be done before the application can be fully justified.

V. EXPERIMENTAL RESULTS FOR SUSCEPTIBILITY

A. Susceptibility Data for Lower Concentrations

The measured susceptibilities $\chi(T)$ of annealed and quenched ellipsoids of lower-concentration *Au*Fe alloys ($C \leqslant 8$-at.% Fe) are shown in Fig. 9. In contrast to the broad maxima observed by Lutes and Schmit,[11] and by Tholence and Tournier,[14] we find that $\chi(T)$ shows sharp cusplike peaks at temperatures which are defined and repeatable to within 0.25 °K. The temperatures of the peaks are in excellent agreement with the ordering temperature T_0 determined from the Mössbauer data (Fig. 1). The magnitudes of the peaks increase very strongly with increasing concentration; in fact, the increase is more rapid than a power law and approximates an exponential function of C. These sharp peaks in $\chi(T)$ are very suggestive of the susceptibility near the Néel temperature of a material ordering antiferromagnetically. Antiferromagnetism has already been suggested by several authors[25,53,67] as a possible explanation for the results of the Mössbauer and high-field magnetization

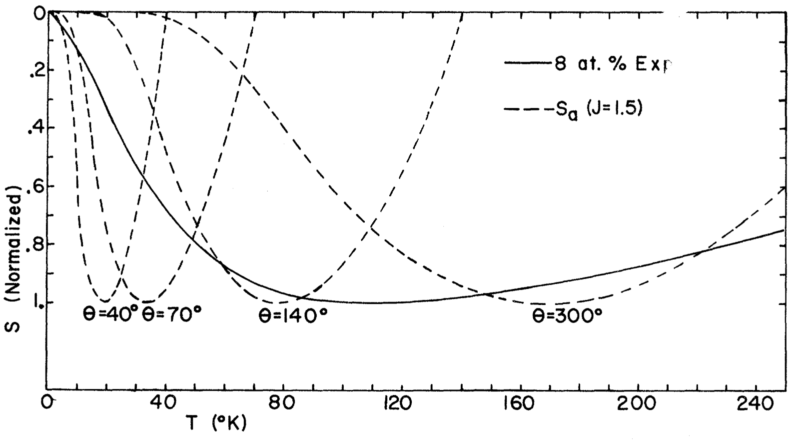


FIG. 7. Comparison of the normalized experimental curve of $S(T)$ for $C = 8$ at.% with normalized theoretical curves $S_a(T)$ for $J = 1.5$; $\theta' = 40$, 70, 150, and 300 °K.

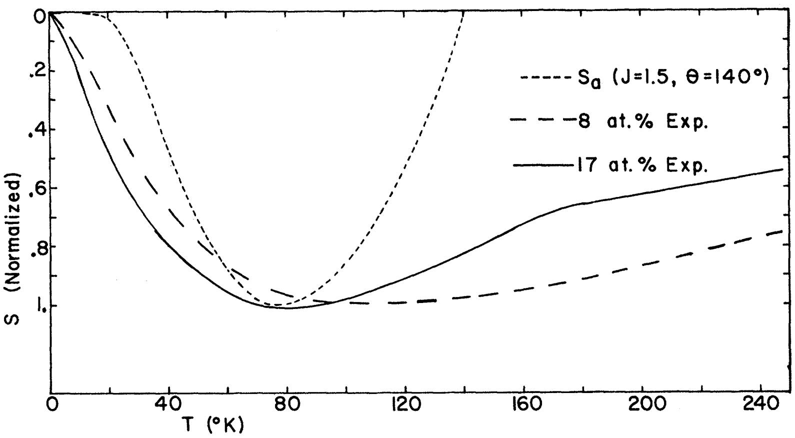


FIG. 8. Comparison of the experimental $S(T)$ curve for $C = 17$ at.% with the normalized theoretical curve S_a (T) for $J = 1.5$, $\theta' = 140$ °K and the normalized curve for $C = 8$ at.%.

studies. For antiferromagnetic materials Fisher[68] argues that the Néel temperature T_n should be associated with the maximum in $d(\chi T)/dT$ rather than the maximum in χ. For $1 \leq C \leq 13$ at.% the cusplike shape of our data shows that $[d(\chi T)/dT]_{\max}$ coincides with $\chi_{\max}$, and this will be used to determine the ordering temperature T_0.

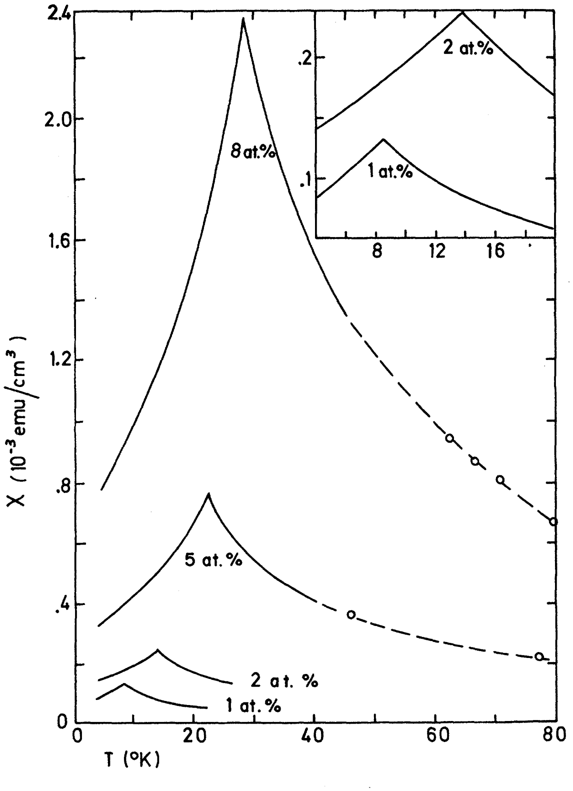
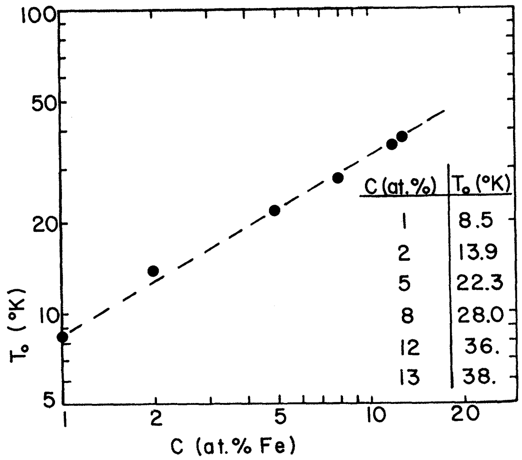


FIG. 9. Low-field susceptibility $\chi(T)$ for $1 \leq C \leq 8$ at.%. The data were taken every $\frac{1}{4}$ °K in the region of the peak, and every $\frac{1}{2}$ or 1 °K elsewhere. The scatter is of the order of the thickness of the lines. The open circles indicate isolated points taken at higher temperatures.

The concentration dependence of T_0 as determined by our $\chi_{\max}$ is tabulated and plotted on a log-log scale in Fig. 10. From the slope of this curve it is found that $T_0 = AC^m$, where $m = 0.58$, which may be compared with the value $m = 0.74$ of Gonser *et al.*[23] and the value $m = 0.45$ given by Kitchens and Craig.[67] Susceptibility data for these lower concentrations were also taken for wire samples oriented both parallel and perpendicular to the applied field. We found no noticeable shape dependence in $\chi(T)$ for $C \leq 8$ at.%, as is to be expected for samples with such low susceptibility.

We have also studied in some detail the effect of applied magnetic fields (up to 300 G) on the susceptibility of the lower-concentration alloys. We find that fields of only ~100 G will destroy the sharp susceptibility peaks and produce broader maxima similar to those observed by Lutes and Schmit,[11] and Tholence and Tournier.[14] In Figs. 11 and 12 we present, respectively, the suscepti-



C (at.%)	T₀ (°K)
1	8.5
2	13.9
5	22.3
8	28.0
12	36.
13	38.

FIG. 10. Table and log-log plot of the ordering temperature T_0 vs C for $1 \leq C \leq 13$ at.%, where T_0 is determined from $\chi_{\max}$.

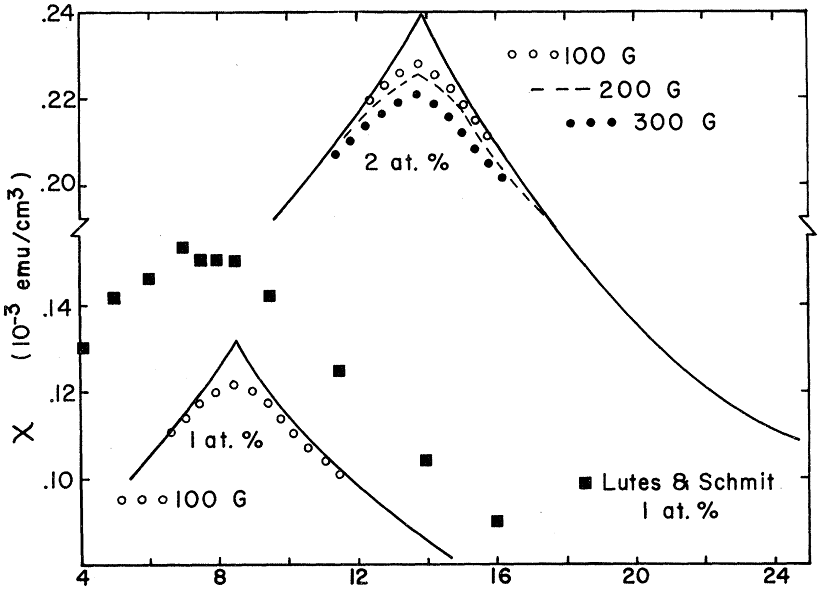


FIG. 11. Susceptibility vs T (°K) for samples with $C = 1$ and 2 at. %, showing the curves for zero field and for various applied fields, and including the data of Lutes and Schmit (Ref. 11) for $C = 1$ at. %.

bility data for samples with $C = 1$ and 2 at. %, $C = 5$ and 8 at. %, showing the curves for zero field and for various applied fields. For each concentration, as the applied field increased (up to 300 G), the maximum becomes smaller and broader. Figure 11 also includes the data of Lutes and Schmit[11] for $C = 1$ at. % taken in a field of 1000 G and, except for some discrepancy in the absolute value of the curves, the data of Lutes and Schmit seem consistent with our data, considering the difference in the applied fields.

In examining the concentration dependence of field effects, we found that for $C \leq 8$ at. % the decrease in $\chi_{\max}$ due to applied fields was relatively independent of concentration, while for a higher-concentration sample, $C = 13$ at. %, the decrease was much greater. For example, for 1 at. % $\leq C \leq 8$ at. % an applied field of 200 G reduced $\chi_{\max}$ by about 10%, but for $C = 13$ at. % the reduction was over 30%. For $C = 1$ and 2 at. % the applied fields do not appreciably shift the position of the peak, and even the $\chi_{\max}$ of Lutes and Schmit agrees well in temperature with our zero-field peak. For $C = 5$ and 8 at. %, $\chi_{\max}$ is shifted upwards by about 1 °K for fields between 100 and 300 G. For an antiferromagnet Fisher[68] indicates that, for small fields, $\chi(T)$ should show a sharp peak at T_n similar to the magnetic specific heat, and that T_n should shift downwards with increasing fields. It is, however, difficult to compare our complicated antiferromagnetic ordering directly with his theories.

B. Susceptibility Data for Higher Concentrations

The curves of $\chi(T)$ for annealed and quenched ellipsoidal samples with $C = 17$ and 22 at. % are given in Fig. 13. In contrast to the curves for the lower concentrations, $\chi(T)$ for $C = 17$ and 22 at.% is much more characteristic of ferromagnetic ordering. The curves show a rapid drop in $\chi(T)$ just above T_0 as determined by the maximum, while below T_0, $\chi(T)$ varies much more slowly with temperature. For these higher concentrations the magnitudes of χ are quite large, shape-dependent demagnetizing effects are very important, and the peak in the measured volume susceptibility χ_m has a magnitude $\simeq D^{-1}$, where D is the demagnetizing factor. In the temperature region below T_0, $\chi(T)$ is not perfectly flat as for

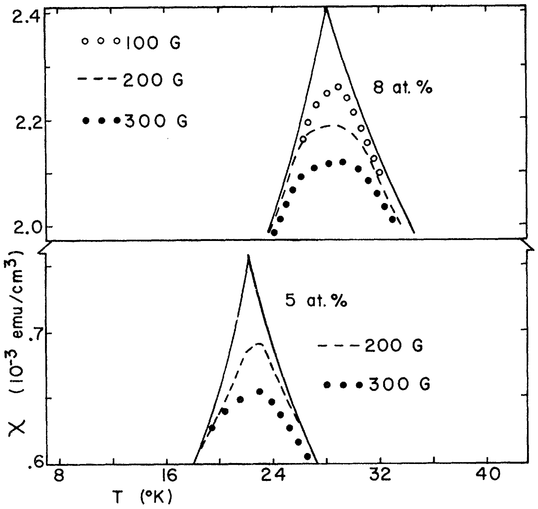


FIG. 12. Susceptibility data for samples with $C = 5$ and 8 at. %, showing the curves for zero field, and for various applied fields.

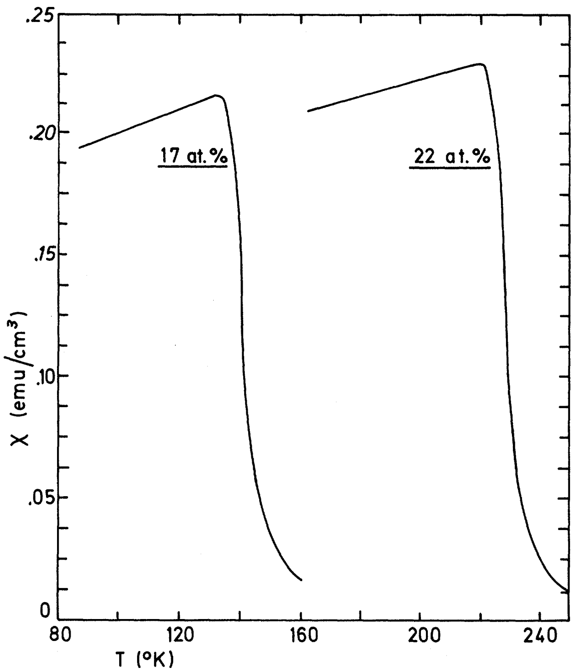


FIG. 13. $\chi(T)$ for annealed and quenched ellipsoidal samples with $C = 17$ and 22 at.%. Data were taken every $\frac{1}{2}$ °K in the region of the peak, and every 1°K elsewhere. The scatter is less than the thickness of the lines. The maximum error in the absolute value of the curves was less than 5% of the experimental values.

a good single-crystal spherical ideal ferromagnet,[69] but this is not surprising in polycrystalline multidomain samples of random ferromagnetic alloys, especially when the low applied fields (~ 5 G) cannot be expected to saturate the domain structure of the sample.

Susceptibility data for these concentrations were also taken for wire samples, both quenched and unquenched, oriented parallel to the applied field. The shape and position of χ_{max} varied with sample shape and thermal history, confirming that the ferromagnetic ordering is acutely sensitive to the details of the local crystal environment affected by the mechanical and thermal history, such as cold working, annealing, quenching, etc., as was found by other authors.[19,20] $\chi(T)$ of the unquenched 17-at.% wire sample showed a partially resolved second peak at ~ 175 °K, which was removed by annealing and quenching. The position of the second peak in the unquenched sample indicates preferential magnetic or crystal arrangement with a T_0 higher than the dominant (random) 17-at.% peak, which remains unchanged for both quenched and unquenched wires. For the 22-at.% sample, on the other hand, there was no resolved second peak, but the temperature of the maximum was shifted down in the unquenched sample. This seems to indicate a preferred magnetic or crystal structure with a T_0 around 200 °K, below T_0 for the random 22-at.% sample.

The curves of $\chi(T)$ for annealed and quenched ellipsoidal samples of the intermediate concentrations $C = 12$ and 13 at.% are shown in Fig. 14. These curves show a mixture of the properties of the lower- and higher-concentration regions. The shape of the curves is the cusplike peak found at lower concentrations, but the magnitudes are about a factor of ten larger than that for $C = 8$ at.%, and demagnetizing effects begin to be significant. For an annealed and quenched wire sample with $C = 12$ at.% (oriented parallel to the field) we find that the changes in the shape and magnitude of $\chi(T)$ are very large, and that there is a large shift in the position of χ_{max}. For the ellipsoidal samples, the maxima in χ correspond to temperatures fitting on the T_0-vs-C curve for the lower concentrations of Fig. 1, while the temperature of χ_{max} for the 12-at.% wire sample fits on the T_0-vs-C curve for the ferromagnetic concentrations in Fig. 1. This seems to indicate that, in the critical concentration region, not only is the ordering temperature T_0 sensitive to the sample shape and thermal history, but so also, perhaps, are the type, degree, and mixture of the various orderings.

C. Molecular Field Analysis of $\chi(T)$

According to classical molecular field theory,[70] in low fields where saturation effects are negligible,

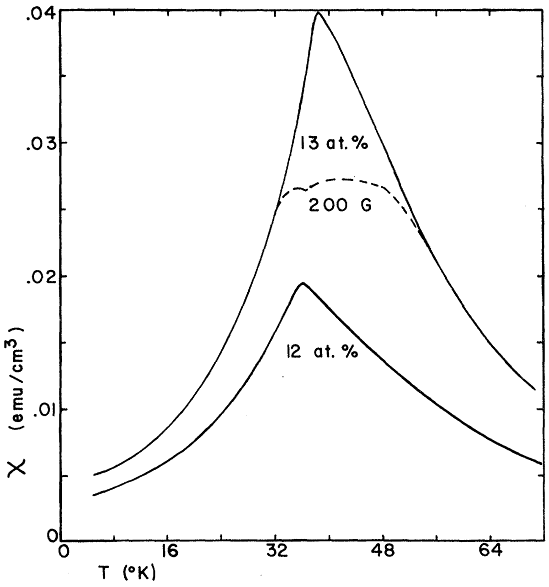


FIG. 14. $\chi(T)$ for annealed and quenched ellipsoidal samples with $C = 12$ and 13 at.% including data for $C = 13$ at.% in an applied field of 200 G. Data points were taken every $\frac{1}{2}$ or 1 °K. The scatter was of the order of the thickness of the lines and the maximum error in absolute value is less than 5% of the experimental value.

we may write the paramagnetic susceptibility of a material above its ordering temperature in the form $\chi = \mathcal{C}/T - \theta$, where $\mathcal{C}$ is the Curie constant, $\mathcal{C} = Dg^2\mu_B^2 J(J+1)/3k_B$, and θ is the paramagnetic Curie temperature characteristic of the molecular fields. Here D is the density of the magnetic atoms, J is their angular momentum, μ_B is the Bohr magneton, g is the Landé factor, and k_B is the Boltzmann constant. This form assumes that the magnetic atoms in the system are identical and interact singly with the applied and molecular fields. It should be noted that the θ used in analyzing the susceptibility is associated with long-range or bulk interactions and is not necessarily related to the short-range θ' used in discussing the thermopower. From the equation for χ, the temperature intercept of $1/\chi$ vs T gives the value of θ, and the slope $1/\chi$ yields the effective magnetic moment per Fe atom in Bohr magnetons, p_{eff}:

$$p_{\mathrm{eff}} = g[J(J+1)]^{1/2} = \left(\frac{3k}{D\mu_B^2\, d(1/\chi)/dT}\right)^{1/2} .$$

In our calculations we used χ in emu/g, and D is the number of Fe atoms per g.

We show a typical plot of $1/\chi$ vs T for $C = 1$ and 2 at.% in Fig. 15, and we have made similar plots for $C = 5$, 8, 12, 13, 17, and 22 at.%. From these plots we have found θ and p_{eff} using classical molecular field theory; Table II shows the values of T_0, θ, and p_{eff} for each concentration where T_0 is determined from $\chi_{\max}$. Figure 16 shows plots of p_{eff} and θ vs T. θ varies linearly with C for $C \leqslant 8$ at.%, and is negative for $C \lesssim 3.5$ at.% and positive for $C \gtrsim 3.5$ at.%. Kaufmann *et al.*[3] found that θ changed sign at the same concentration, even though their values for θ were much larger than ours. Lutes and Schmit[11] also found a negative θ (-3 °K) for $C = 0.5$ at.%. It is important to note that, even though θ changes sign at $C \simeq 3.5$ at.%, the values of θ are small compared with T_0 for all $C \leqslant 8$ at.%.

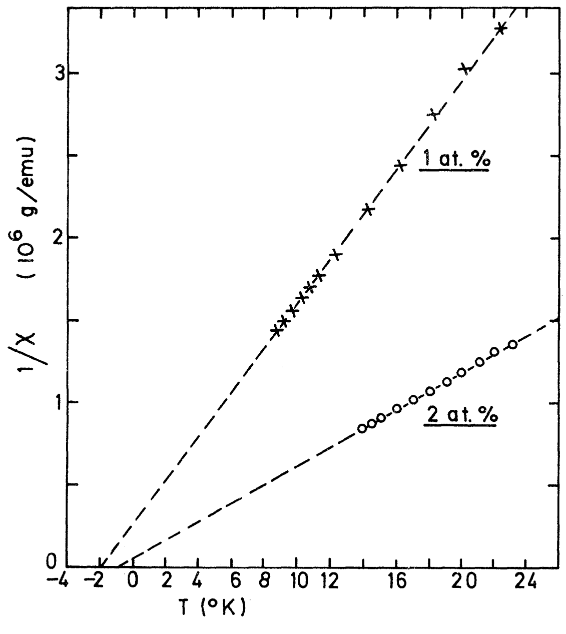


FIG. 15. $1/\chi$ vs T for $C = 1$ and 2 at. %.

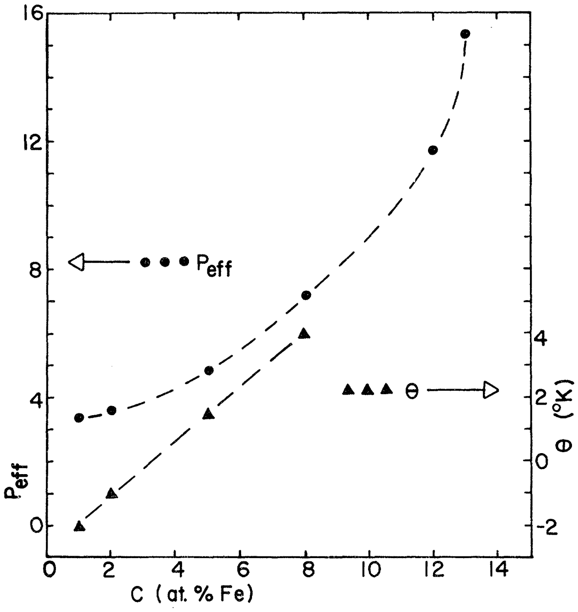


FIG. 16. Paramagnetic Curie temperature θ vs C and the effective magneton number p_{eff} vs C for *Au*Fe alloys.

The large values of p_{eff} confirm the existence of superparamagnetic clusters suggested by other authors and discussed earlier in our treatment of the thermoelectric power of these alloys. This

TABLE II. Ordering temperature T_0, paramagnetic Curie temperature θ, and p_{eff}, the effective number of Bohr magnetons per Fe atom, for the various *Au*Fe concentrations. T_0 is determined from $\chi_{\max}$. θ and p_{eff} are determined from $1/\chi$ vs T using classical molecular field theory.

Conc. (at.% Fe)	Ordering temp. T_0 (°K)	Paramagnetic θ (°K)	Magneton number p_{eff}
1	8.5	-2 ± 0.5	3.4
2	13.9	-1 ± 0.5	3.6
5	22.2	1.5 ± 0.5	4.8
8	27.9	4 ± 0.5	7.1
12	36.0	38 ± 1	11.4
13	38.0	40 ± 1	15.5
17	132.0	138 ± 2	13.5
22	218.0	230 ± 2	10.5

superparamagnetism makes the analysis of our susceptibility data more complex. If we assume for simplicity that all Fe atoms in a superparamagnetic cluster are perfectly aligned, then the magnetization M_n of a cluster containing n Fe atoms would be $M_n = M_n\ (T=0) = ng\mu_B J$, where J is the spin on each Fe atom. We assume, in effect, that we are well below the ordering temperature of the cluster. For an assembly of such noninteracting clusters with either a statistical or a cubic distribution of particle axis orientations, the susceptibility may be written $\chi \simeq \sum_n N_n M_n^2/3k_B T$, which is independent of the magnetic anisotropy.[71] Here N_n is the density of the clusters containing n Fe atoms. If n is small enough that quantum effects would be important we would expect to replace M_n^2 by $g^2 \mu_B^2 nJ(nJ+1)$. We now allow interactions between the clusters by again introducing an effective θ describing the molecular field due to these interactions:

$$\chi = \mathcal{C}/(T-\theta)\ ,$$

where

$$\mathcal{C} = \sum\nolimits_n N_n g^2 \mu_B^2 nJ(nJ+1)3k_B\ .$$

The question now arises as to the nature of the superparamagnetic clusters. The simplest assumption is that the cluster-forming ferromagnetic interactions exist only between Fe-Fe near neighbors. Then the superparamagnetic clusters are Fe-Fe near-neighbor chains. The arrangement of Fe atoms in the Au lattice may be either random, or nonrandom (preferring either Fe or Au near neighbors). Assuming only Fe-Fe near-neighbor interactions and random statistics we have made approximate calculations of N_n as a function of C, taking care that $\sum_n nN_n = D$ so that our values were self-consistent. From these values of $N_n(C)$ we have calculated statistical values of the Curie constant $\mathcal{C}_S(C)$ for $C \leq 8$ at.% using the values $J = 1.2$, $g = 2$, which are reasonable for Fe atoms in a cubic environment, and which are consistent with the low-concentration limit $p_{\text{eff}} \simeq 3.25$ found by Tholence and Tournier.[14] In Table III we compare for $C \leq 8$ at.% the experimental values of $\mathcal{C}_{\text{expt}}$ with $\mathcal{C}_S$ and with $\mathcal{C}_B$, the value calculated for single Fe atoms,

$$\mathcal{C}_B = Dg^2\mu_B^2 J(J+1)/3k_B\ .$$

We find that the values of $\mathcal{C}_S$ calculated using random statistics agree quite well with the experimental values for $C = 1$ and 2 at.%, but the growing discrepancy between $\mathcal{C}_{\text{expt}}$ and $\mathcal{C}_S$ for 5 and 8 at.% indicates that the mechanism which forms the superparamagnetic clusters is stronger than that provided by our simple assumptions. The conclusion is not necessarily that Fe atoms energetically prefer Fe nearest neighbors. There may well exist ferromagnetic interactions between Fe-Fe next-nearest neighbors, or some other local arrangement of Fe atoms which orders ferromagnetically.[72] Au_4Mn is an example of a ferromagnetic alloy in which each moment-bearing Mn atom has only Au first near neighbors.

TABLE III. Values of Curie constant for various concentrations. $\mathcal{C}_{\text{expt}}$ is determined experimentally from the slope of $1/\chi$ vs T, $\mathcal{C}_B$ is the value calculated for single Fe atoms, and $\mathcal{C}_S$ is the value calculated using random statistical clusters of Fe-Fe near neighbors.

Conc. (at.% Fe)	$\mathcal{C}_B$ (emu °K/g)	$\mathcal{C}_{\text{expt}}$ (emu °K/g)	$\mathcal{C}_S$ ($J = 1.2$) (emu °K/g)
1	6.7×10^{-5}	7.3×10^{-5}	7.2×10^{-5}
2	1.4×10^{-4}	1.7×10^{-4}	1.6×10^{-4}
5	3.5×10^{-4}	7.7×10^{-4}	5.3×10^{-4}
8	5.7×10^{-4}	2.7×10^{-3}	1.2×10^{-3}

In view of the complex nature of the ordering in these alloys, the application of a two-sublattice model of antiferromagnetism to the lower concentrations seems somewhat simplistic. We examine this model, nevertheless, in an attempt to gain some insight into the longer-range interactions between the magnetic atoms or superparamagnetic clusters, rather than because we believe it describes the ordering in these alloys. Modifying slightly the approach used by Owen *et al.*[12] for *Cu*Mn we assume two equivalent antiparallel sublattices or arrays, A and B, where each site in an array may be occupied by either a single magnetic atom or a superparamagnetic cluster. We then define ferromagnetic and antiferromagnetic molecular field constants μ and ν describing the effective interactions, and we write the magnetization M of each sublattice in the form

$$M_A = \mathcal{C}/2T(H + \mu M_A - \nu M_B),$$

$$M_B = \mathcal{C}/2T(H + \mu M_B - \nu M_A)\ .$$

Here $\mathcal{C}$ is the Curie constant as we have already defined, H is the applied magnetic field, and M_A and M_B are the respective sublattice magnetizations. We write the susceptibility $\chi = (M_A + M_B)/H = \mathcal{C}/(T-\theta)$, where $\theta = \frac{1}{2}\mathcal{C}(\mu - \nu)$. If we solve the magnetization equations for values of T for which M_A and M_B are nonzero when $H = 0$, we find the Néel temperature $T_N = \frac{1}{2}\mathcal{C}(\mu + \nu)$. In terms of θ and T_N we solve for μ and ν obtaining $\mu = (T_N + \theta)/\mathcal{C}$; $\nu = (T_N - \theta)/\mathcal{C}$. We have calculated μ, ν, and μ/ν from our experimentally determined values of θ and T_0 (assuming $T_N = T_0$) for $C = 1$–13 at.%, and the results are tabulated in Table IV. When θ is negative, ν is larger than μ, and ν is comparable to μ up to $C = 8$ at.%. It is difficult to interpret μ and ν in these lower-concentration alloys where indirect RKKY-type interactions seem to provide the coupling for the ordering. If we interpret μ

TABLE IV. Ferromagnetic and antiferromagnetic molecular field constants μ and ν, respectively, calculated for *Au*Fe alloys from experimental values of the Curie constant $\mathcal{C}$, and from θ and T_0, using a two-sublattice model of antiferromagnetism.

Conc. (at. % Fe)	$\mathcal{C}_{\text{expt}}$ (emu °K/g)	μ 10^4 (g/emu)	ν 10^4 (g/emu)	ν/μ
1	7.3×10^{-5}	8.9	14.4	1.62
2	1.7×10^{-4}	7.6	8.8	1.15
5	7.7×10^{-4}	3.1	2.7	0.87
8	2.7×10^{-3}	1.2	0.89	0.74
12	1.1×10^{-2}	0.67	...	...
13	2.1×10^{-2}	0.37	...	...

and ν broadly as average molecular field constants without attributing too much importance to the details of the model, then these results are consistent with an interpretation of antiferromagnetic ordering for $C \leq 8$ at.%.

The molecular field treatment of the susceptibilities for low-concentration alloys of this type by Klein[32] is not consistent with our results since this treatment predicts a small broad concentration-independent maximum in $\chi(T)$ occurring at a temperature directly proportional to C. Korn[73] has performed a study of the relatively low-field (~ 200 G) susceptibility of alloys of *Pb*Mn, *Cu*Mn, *Sn*Mn, and *La*Gd, using the thin-film samples which are deposited at very low temperatures (14 °K) to ensure a random distribution of the magnetic atoms. He finds that these samples exhibit an antiferromagnetic ordering (characterized by susceptibility maxima) similar to that observed by other investigators.[12] In contrast, however, to the positive values for θ found by other authors for these same alloys, Korn concludes that for truly random alloys, the paramagnetic θ is zero. He suggests that the positive θ's observed for other samples of these alloys are due to inhomogeneities in the paramagnetic spin distribution, resulting in local ferro- or ferrimagnetic coupling of the magnetic atoms.[73] Korn did not suggest the possibility of a negative θ, such as we found for lower concentrations, but it seems reasonable that a nonrandom spin distribution which favored a more perfect antiferromagnetic ordering than the random "quasi-antiferromagnetism" would result in a negative θ.

Bennemann, Garland, and Mueller[40] have constructed a molecular field treatment for the large field-dependent susceptibilities of La-rare-earth alloys, using an approach similar to that of Liu,[34] and incorporating the conclusions of Korn. Using an RKKY interaction Bennemann *et al.* show that short-range quasiferromagnetic spin coupling and long-range quasiantiferromagnetic spin order can explain much of the temperature, concentration, and field dependence of the susceptibility in these alloys. Of the existing theoretical treatments of the susceptibility this work does seem somewhat applicable to our *Au*Fe alloys. A comparison of our experimental $\chi(T)$ for $C = 12$ and 13 at.% with the predictions of the model of Bennemann *et al.* shows good agreement for the case of short-range ferrimagnetic and long-range antiferromagnetic order: $\theta > T_0$ and $\chi(T) \gg \chi_B(T)$, and $\chi(T_0)$ is strongly reduced ($\simeq 30\%$) by the application of small magnetic fields (200 G) because even weak applied fields will align spins which, as a result of inhomogeneities in the spin distribution, already feel weak molecular fields. Here $\chi_B(T)$ is the Curie susceptibility calculated for single noninteracting magnetic atoms. For alloys with $C \leq 8$ at.% our experimental $\chi(T)$ agrees with the general outlines of the predictions for predominant antiferromagnetic order: θ is less than T_0 and close to zero; $1/\chi$ varies linearly with T above T_0, and the reduction in $\chi(T_0)$ in small applied fields is small ($\simeq 10\%$) compared to that for $C = 13$ at.%. However, this reduction in $\chi(T_0)$ due to small applied fields, along with the fact that $\chi(T) \gtrsim \chi_B(T)$, implies that for $C \leq 8$ at.% there are inhomogeneities in the spin distribution; that is, there exist superparamagnetic clusters which affect the susceptibility as we have already seen. These superparamagnetic clusters explain the concentration dependence of θ and in their presence the model of Bennemann *et al.* seems correctly to predict that θ increases proportional to C, even though the long-range order remains antiferromagnetic. The sudden shift in the values of θ from $\theta \leq 4$ °K for $C \leq 8$ at.% to $\theta \geq 38$ °K for $C \geq 12$ at.% seems clearly to reflect the change in the type of magnetic behavior from a predominantly antiferromagnetic order to a highly mixed state. Nevertheless, this model does not predict the type of antiferromagnetic ordering implied by the negative values of θ for $C = 1$ and 2 at.%, particularly when we know that short-range ferromagnetic interactions raise the value of θ above that which would describe the antiferromagnetic interactions.

Somewhat similar to the model of Bennemann *et al.* is the suggestion that the type of antiferromagnetic ordering which occurs in the lower-concentration *Au*Fe alloys is related to that of a magnetic "spin-glass"[19,37] where the magnetic moments of superparamagnetic clusters are free to respond to external fields at high temperatures, but become "frozen in" at sufficiently low temperatures due to the exchange interactions between clusters. For example, the oscillating nature of the RKKY interaction could give a random antiferromagnetic orientation to the moments, and the susceptibility would decrease as the temperature is lowered and the moments become locked in random directions. The remanence, thermomagnetic properties, and field-dependent susceptibilities related to this model[37] have been observed in varying degrees in *Au*Fe for $1 \leq C \leq 12$ at.%. This model cannot, however, explain the sharpness of the magnetic transition evidenced by the sharp cusp in the susceptibility near T_0 in low fields. A spin-glass is expected to have a distribution of "freezing temperatures," due to different cluster environments and coupling strengths, and thus to have a broad rounded susceptibility maximum. Thus, although both the treatment of Bennemann *et al*. and the "spin-glass" model can explain many of the susceptibility characteristics and other magnetic properties of these *Au*Fe alloys, we do not yet have a model which can describe the antiferromagnetic ordering with sharp transitions and negative values of θ found for lower concentrations.

VI. CONCLUSIONS

In Sec. IV A we discussed the concentration dependence of the thermoelectric power of *Au*Fe alloys as reflected in the concentration dependences of the magnitudes $|S|_{\max}$ and the temperature $T_{|S|_{\max}}$ of the thermopower maximum (Figs. 4–6). On the basis of our study of the thermopowers of these *Au*Fe alloys, and incorporating the work of other authors,[46–48,65] we suggest the following description of the thermopower in *Au*Fe. For the lowest concentrations, 0.001 at.% $\lesssim C \lesssim$ 0.1 at.%, the magnitudes $|S|_{\max}$ of the large thermopowers are only weakly dependent upon concentration, and the temperature of the maximum thermopower $T_{|S|_{\max}}$ is proportional to $\sim C^{1/3}$. This can be explained by resonant scattering of the conduction electrons by magnetic impurities similar to that described by Kondo and others,[49] but modified to include the effects of impurity-impurity interactions.[74] The scattering from local moments should be temperature dependent if the local moments are coupled by temperature-dependent spin interactions, especially if the scattering is inelastic (spin-flip scattering). The apparent discontinuity in $T_{|S|_{\max}}$ found near $C \simeq 0.1$ at.% are a result of the growing importance of antiferromagnetic order which is seen both in the hyperfine splitting of Mössbauer spectral and in the appearance of maxima in the susceptibility. The Zeeman splitting of the impurity spins in the internal field destroys the thermopower mechanism[49] below the ordering temperature and discontinuously shifts the maxima in the thermopower to higher temperatures where the splittings are smaller than $k_B T$. The $C^{1/3}$ dependence of $T_{|S|_{\max}}$ continues for $C \gtrsim 0.1$ at.% until ferromagnetic interactions and superparamagnetic clusters become important ($C \gtrsim 5$ at.%). For $5 \lesssim C \lesssim 12$ at.% we expect contributions to the thermopower from the ferromagnetically ordered superparamagnetic clusters as predicted by the theories of Kasuya[51] and others.[50,52] This is consistent with the fact that in this concentration region the electrical resistivity[42,43] shows deviations from the expected linear high-temperature phonon scattering. These deviations occur at temperatures much greater than the antiferromagnetic ordering temperature, T_0, and indicate that the additional scattering processes which occur for $T \gg T_0$ are very likely related to scattering from short-range-correlated impurities or superparamagnetic clusters with ordering temperatures much greater than T_0. For $C \gtrsim 12$ at.% the onset of long-range ferromagnetic order produces the large thermopowers predicted by the mean-field theories of Kasuya[51] and others,[50,52] and this ferromagnetic ordering causes the large changes in $|S|_{\max}$ and $T_{|S|_{\max}}$ observed for $C \gtrsim 12$ at.%. Above the ferromagnetic Curie temperature the thermopower associated with the bulk molecular field disappears, but the contributions from superparamagnetic clusters which show local ferromagnetic order remain. These clusters produce, above the bulk Curie temperature, thermoelectric powers similar to those found for lower concentrations ($5 \lesssim C \lesssim 12$ at.%). These thermopowers persist to very high temperatures where contributions from the ordinary diffusion thermopower also become important and the thermopower becomes positive.[47]

Our study of the low-field susceptibility of the *Au*Fe alloy system has clearly shown that only at very low fields is it possible to observe the true critical behavior of the susceptibility χ for these alloys. For the lower concentrations, from $C \simeq 8$ at.% down at least to 1 at.%, χ exhibits at the magnetic ordering temperature T_0 a sharp cusplike peak which was previously unobserved because of the higher fields used in measurements. The Curie–Weiss behavior of χ down to T_0 and then the sharp drop and transition to a different behavior within 0.25 °K indicate the sharp onset of magnetic ordering. The large experimental values found for the Curie constant $\mathcal{C}$ (and p_{eff}) from the molecular field analysis of $\chi(T)$ clearly show that superparamagnetic clustering exists in these alloys, in agreement with other magnetic measurements,[19] and as is indicated by the transport properties. Futhermore, calculations of the Curie constant indicate that the superparamagnetic clustering is larger than can be explained by random statistics and Fe-Fe near-neighbor interactions. Despite this superparamagnetic clustering, negative values of the paramagnetic Curie temperature θ were found for $C = 1$ and 2 at.%, and small positive values were found for $C = 5$ and 8 at.%. This seems clearly to indicate antiferromagnetic ordering in these concentrations.

The description of a random antiferromagnetic alloy with some localized ferromagnetic regions[40] (discussed in Sec. V C) seems to describe adequately many of the properties of χ for the lower concentrations: the small values of θ, the concentration dependence of θ, the field dependence of $\chi(T_0)$. It does not, however, explain the negative values of θ for $C = 1$ and 2 at.%, nor does it seem that a random antiferromagnetism could produce such a sharp magnetic transition. Similar difficulties exist with the spin-glass model[37,38] discussed in Sec. V C. Although several aspects of each of these descriptions seem to apply to our alloys for $1 \leq C \leq 8$ at.%, the ordering which we find experimentally has sharp transitions and negative θ for low C, and thus seems to be a more perfect type of antiferromagnetism than those predicted by these models. For higher concentrations $C = 17$ and 22 at.%, the behavior of the susceptibility is clearly ferromagnetic, while for the intermediate concentrations $C = 12$ and 13 at.% the susceptibility agrees with that predicted for large amounts of local ferromagnetic clustering mixed with some longer-range antiferromagnetic interactions.

A hypothetical explanation for the ordering found in low-concentration alloys may be the local existence of a nonrandom crystal or magnetic structure in the crystal lattice which favors a more perfect antiferromagnetism. For example, if the superparamagnetic clusters were not Fe-Fe near neighbors but rather a local crystal arrangement where the Fe atoms were separated, similar perhaps to the known ferromagnetic Au_4Mn, then there would be a more uniform distribution of Fe atoms throughout the lattice, favoring sharper magnetic transitions. Furthermore, the puzzling existence of the anomaly in the thermopower found in unquenched samples for all concentrations at ~220 °K could easily be explained by some local crystal or magnetic phase transition. This type of hypothesis would also be fruitful in explaining the behavior of χ for $C = 17$ and 22 at.%. If we assume that there exists at higher concentrations a preferred local lattice arrangement, then we may interpret the double peak in χ for the unquenched 17-at.% (wire) sample as a lower peak due to the random phase, and a higher peak due to the preferred higher-concentration phase. The fact that for $C = 22$ at.%, χ for the unquenched (wire) sample peaks at a lower temperature than the same quenched sample seems to indicate that the preferred arrangement has a lower concentration than the bulk average. This might suggest a preferred crystal phase with a concentration of about 20 at.% (a hypothetical Au_4Fe). The point of this discussion is not to argue the existence of as yet unobserved crystal phases in these alloys, but merely to suggest that such local crystal structures could explain many of the puzzling properties of these alloys without affecting the agreement found with existing theories.

In an attempt to further understand the antiferromagnetic interactions found in the lower concentrations we are presently examining the low-field susceptibility of *Au*Fe samples with $0.05 \leq C \leq 0.5$ at.%, and extending our measurements to other dilute magnetic alloy systems. Our present results suggest that the low-concentration antiferromagnetic ordering might be further clarified by x-ray and neutron-diffraction studies, nuclear-magnetic-resonance studies, and specific-heat studies near the ordering temperatures.

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