Paramagnetic Excited State of FeSi

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(Received 14 March 1967)

The anomalous behavior of the temperature dependence of the susceptibility and specific heat of the intermetallic compound FeSi is reexamined from both an experimental and a theoretical point of view. It is shown that a consistent set of experimental data is obtained below a temperature of about 700°K. An interpretation of the thermodynamic properties is given, based on a model that requires the existence of correlated magnetic excited states only a few hundred degrees above the nonmagnetic ground state. Other, more conventional models are also explored, and the reasons for their rejection are discussed.

I. INTRODUCTION

FOR many years the magnetic properties of the intermetallic compound FeSi have intrigued a number of experimenters. Most unusual is the behavior of the susceptibility $\chi(T)$ which appears to exhibit a pronounced maximum in the neighborhood of 500°K. (There are both qualitative and quantitative differences in the measurements made by different workers—both as regards similar material in which hysteresis effects were observed and material of varying stoichiometry—and we will discuss this later on.) To some this has suggested the presence of strongly exchange-coupled isolated pairs of spins and to others it has suggested the behavior of a classical antiferromagnet as one passes through the ordering temperature T_n. The problem is made all the more interesting for two reasons: Firstly, FeSi is a metal or semimetal in the sense that its resistivity ($10^4\,\Omega$ cm) indicates a large carrier concentration which is comparable in magnitude to other transition-atom intermetallic compounds (e.g., V_3Si) and, secondly, the magnetic and transport properties of its isostructural counterparts MnSi and CoSi are as completely different from FeSi as they are from each other.

Recently we have reported in a brief paper[1] parallel studies of the temperature dependence of the Fe^{57} Mössbauer-effect quadrupole splitting, the Knight shift of the Si^{29} nuclear magnetic resonance, and a remeasurement of $\chi(T)$ below 300°K. From these measurements there was inferred the existence of a thermally populated excited state. In the present paper we will discuss two different models of the magnetism of FeSi and show that one of them quantitatively accounts for both the behavior of $\chi(T)$ and the magnetic specific heat. Some details concerning our earlier experiments are given as well as the results of more recent sample preparation and susceptibility studies at somewhat elevated temperatures.

II. CRYSTALLOGRAPHIC PROPERTIES AND SAMPLE PREPARATION

The monosilicides of the *3d* transition metals Mn, Fe, and Co possess the B–20 cubic structure shown in Fig. 1. The point symmetry of both sites is 3 and, being less than cubic, allows for the existence of nuclear electric quadrupole and anisotropic magnetic dipole interactions.

For our studies, samples were prepared by induction melting of high-purity iron (99.99%) and silicon (99.999%), with an excess of silicon in the melt. The nominal composition $Fe_{0.975}Si_{1.025}$ was chosen in order to avoid the formation of a ferromagnetic phase that is present in as-cast stoichiometric samples. The cast ingots were then multiply zone-refined in recrystallized aluminum-oxide boats in an argon atmosphere for the following reason. It was observed that all as-cast samples had a spurious rise in the susceptibility with decreasing temperature below 50°K that was not reflected in the microscopic nuclear measurements. The magnitude of this low-temperature contribution to $\chi(T)$ was observed to decrease with successive numbers of passes in the zone-refining process. We believe both the residual ferromagnetism and the low-temperature Curie-like behavior to $\chi(T)$ to result from local fluctuations in the relative concentrations of Fe and Si in the FeSi structure and to be atypical of the ideal perfect lattice.

Metallographic examination and powder x-ray diffraction studies showed that the final samples were single phase. The x-ray work was done at various tem-

[1] G. K. Wertheim, V. Jaccarino, J. H. Wernick, J. A. Seitchik, H. J. Williams, and R. C. Sherwood, Phys. Letters **18**, 88 (1965).

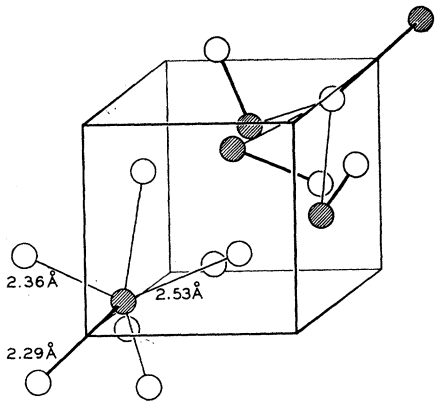

FIG. 1. The FeSi structure. The Fe atoms, shown shaded, have one Si neighbor in a ⟨111⟩ direction at 2.29 Å, three at 2.36 Å, and three at 2.53 Å. They have six equidistant Fe neighbors.

peratures between 78 and 1200°K. It revealed no crystallographic transformation, nor were there any changes in structure or lattice constant upon repeated cycling of the temperature in this region.

III. EXPERIMENTAL RESULTS ON MAGNETIC PROPERTIES

A. Susceptibility and Related Measurements

Besides the peak in $\chi(T)$ at about 500°K, troublesome hysteresis effects were found by the numerous investigators[2–6] of the magnetic properties of FeSi. These appeared to be related to both the existence of other magnetic Fe-Si phases (e.g., Fe_3Si) that would precipitate upon temperature cycling and the fact that the B-20 structure itself has an extensive homogeneity range. In fact, Shubina *et al.*[5] studied the high-temperature $\chi(T)$ as a function of relative iron-silicon composition ($Fe_{1-x}Si_{1+x}$) and found that the Curie constant and effective moment were strongly dependent on x. This work is important in that it emphasized the importance of composition as a parameter.

Recently we have examined the susceptibility of our newly prepared samples to temperatures as high as 1400°K. A general nonreproducibility of the data was found beyond about 700°K, the most marked effect being that of a discontinuity to the slope of $\chi(T)$-versus-T curve in this region (see Appendix). Since Fe_3Si has a Curie temperature of 763°K, we attribute our difficulties to precipitation of this phase. If, as a precautionary measure, a truly large excess of silicon was added to the melt the peak value of $\chi(T)$ noticeably decreased, a fact we attribute to the presence of the intermediate phase $FeSi_2$—the latter having a very small susceptibility.

[2] G. Föex, J. Phys. Radium **9**, 37 (1938).
[3] R. Benoit, J. Chim. Phys. **52**, 119 (1955).
[4] H. Watanabe, H. Yamamoto, and K. Ito, J. Phys. Soc. Japan **18**, 995 (1963).
[5] T. S. Shubina, F. A. Sidorenko, and P. V. Gel'd, Fiz. Metal. i Metalloved. **19**, 544 (1965).
[6] D. Shinoda and S. Asanabe, J. Phys. Soc. Japan **21**, 555 (1966).

Considering the ambiguities, past and present, connected with the high-temperature work, it was decided then to concentrate on measuring and interpreting the susceptibility of FeSi below 700°K. The general success of the model interpretation to be presented might be useful at some later time in extrapolation to aid in the understanding of the magnetic properties of mixed high-temperature phases of the FeSi system, but this is not our present purpose.

The new susceptibility data on FeSi below 700°K are shown in Fig. 2 as open circles. The low-temperature paramagnetism which we believe to be atypical of the ideal FeSi structure has already been subtracted in the manner previously discussed.[1] The peak value of approximately 10^{-5} emu/g is comparable with that of any reasonably dense insulating paramagnet (e.g., FeF_2) at this elevated temperature.

Since the susceptibility is large above 400°K and then rapidly decreases as the temperature is lowered, it is not surprising that some thought has been given to the onset of antiferromagnetic behavior below this temperature.

Three rather crucial experiments show this *not* to be the case: (1) Neutron diffraction studies by Watanabe *et al.*[4] show no evidence for the existence of a magnetic superlattice of any kind. (2) The proportionality of the Si^{29} Knight shift to the corrected $\chi(T)$ in the temperature region 100 to 400°K demonstrates that all of the magnetism in FeSi is *induced* by the field—any spontaneous moments must be smaller than $0.001\mu_B$. (3)

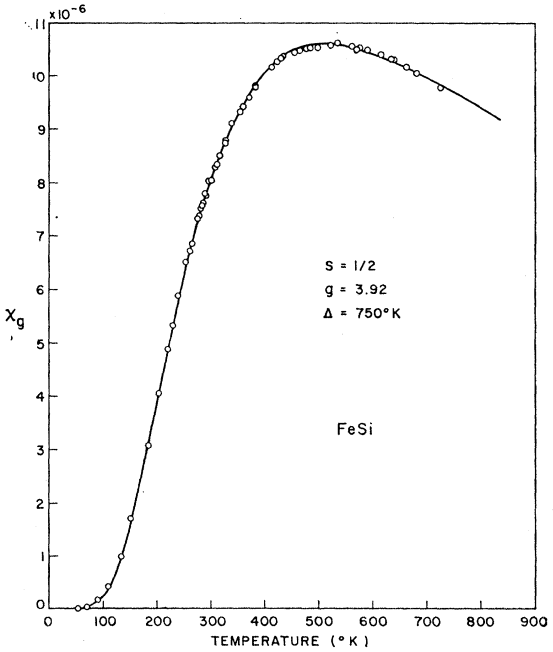

FIG. 2. Susceptibility of zone-refined FeSi after subtraction of the low-temperature paramagnetic contribution attributed to residual disorder. The curve is computed from the model discussed in the text using the parameters shown.

While the Fe^{57} Mössbauer effect showed a temperature-dependent nuclear quadrupole splitting, no evidence for a magnetic hyperfine interaction was present, as would result if a spontaneous moment developed in an antiferromagnetic material. Clearly, then, one has to seek elsewhere for the explanation of the anomalous $\chi(T)$-versus-T behavior below 700°K.

B. Heat Capacity

Extensive heat-capacity data exist on both FeSi and the isostructural CoSi.[7,8] The latter metal has a virtually temperature-independent diamagnetic susceptibility ($\chi \simeq -0.44\times10^{-6}$ emu/g), and one would therefore expect a negligible contribution to the magnetic specific heat to be present. Indeed a good fit to the observed heat capacity of CoSi is obtained from the usual $C_v=\gamma T+\beta T^3$ relation with the electronic specific heat $\gamma=2.8\times10^{-4}$ cal/mole (°K)^2 and $\beta=4.4\times10^{-6}$ cal/mole (°K)^4. Apart then from the magnetic anomaly, it is reasonable to assume that the heat capacities of CoSi and FeSi would be quite similar. By first correcting for the different value of γ in FeSi ($\gamma=1.5\times10^{-4}$) and taking the phonon contribution to C_v to be identical for the two lattices, we can abstract the additional magnetic contribution in FeSi by subtracting $(C_v-\gamma T)$ for CoSi from its counterpart in FeSi. This is shown as the shaded area in Fig. 3 where the values of the specific heat C_p for the two metals are plotted as a function of temperature. The fact that the two curves actually diverge at high temperatures we attribute to a slight difference in the coefficient of thermal expansion for the two metals and the fact that one measures C_p rather than C_v. The actual difference between C_p for the two metals multiplied by Δ/kT is plotted as the open circles in Fig. 4 versus the normalized temperature kT/Δ—the value of Δ/k is 750°K. The calculated curves arise from the model used to interpret both the $\chi(T)$ versus T and the magnetic heat-capacity data and will be discussed shortly.

IV. PHENOMENOLOGICAL INTERPRETATION OF THE THERMODYNAMIC PROPERTIES OF FeSi

A. Symmetry and Other Restrictions on Models Considered

A qualitative assessment of the magnetic properties of FeSi from a study of the $\chi(T)$-versus-T curve is that the ground state of the system is nonmagnetic and that with increasing temperature the system is thermally excited to a state (or states) which is (are) paramagnetic. To be more specific, we have to choose a model for the states of the system. Only three models suggest themselves: (a) coupled pairs of isolated spins, (b) metallic spin paramagnetism involving narrow bands and a small energy gap, and (c) metallic localized moments involving a nonmagnetic ground state. We will consider these in turn.

(1) *Coupled pairs of isolated spins.* Suppose the crystal topology of FeSi were such that Fe atoms could be grouped in pairs with the distance between pairs being large compared to the intrapair separation. Then, if a definite spin $\mathbf{S}$ is assumed to be associated with the configuration of $3d$ electrons on a given Fe atom and we assume negligible interaction between atoms of different pairs, there could exist an exchange interaction between pairs of the form $\mathcal{H}_x=-J\mathbf{S}_a\cdot\mathbf{S}_b$. If the exchange interaction were antiferromagnetic (i.e., $J<0$), the ground state of the pair system $\mathbf{S}=\mathbf{S}_a+\mathbf{S}_b$ would be that one for which $S=0$ and the first excited state $S=1$. The energy separation between ground and first excited state is $\Delta=|J|$. Because of absence of spin degeneracy in the ground state, the magnetization of the ensemble of pairs would be vanishingly small at low temperatures, and increase exponentially as $e^{-\Delta/kT}$ as the magnetic substates of the $S=1$ state are thermally populated. Indeed the behavior of $\chi(T)$ would closely resemble that which is seen in FeSi and is known to be the origin of the similar behavior of $\chi(T)$ in copper acetate.[9] In the latter substance the Cu^{2+} spins *can* be grouped in pairs.

However, the symmetry of the B–20 type structure (see Fig. 1) does not allow for such a simple grouping because the six nearest-neighbor Fe atoms of any given Fe atom fall into two groups of three which are equivalent under a threefold rotation. In principle a study of the paramagnetic diffuse scattering of neutrons as a function of temperature and the low-temperature nuclear spin relaxation of the Fe^{57} nuclei could also distinguish the coupled-pair configuration from the other models to be considered for the magnetism of FeSi.

(2) *Metallic spin paramagnetism.* As was mentioned earlier, FeSi exhibits a conductivity not unlike other typical transition-atom intermetallic compounds. It is reasonable then to question the use of any model which does not allow for the possible itinerant character of the magnetic electrons. Certainly one cannot rule out itineracy on the basis of small overlap—at least at first glance—since the Fe-Fe near-neighbor separations in FeSi (2.75 Å) are only 10% larger than the corresponding distances in bcc Fe (2.48 Å).

It is almost immediately obvious that, if one is to construct a band model for the paramagnetism of FeSi that is devoid of strong correlation effects, the magnitude and peculiar temperature dependence to the susceptibility requires a considerable size and structure to exist in the density of states near the Fermi level.

A model which can be seen qualitatively to reproduce

[7] R. P. Krentsis and P. V. Gel'd, Fiz. Metal. i Metalloved. **13**, 319 (1962); R. P. Krentsis, P. V. Gel'd, and G. I. Kalishevich, Izv. Vysshikh Uchebn. Zavedenii Chernaya Met. **6**, 161 (1963); P. V. Gel'd and R. P. Krentsis, Fiz. Metal. i Metalloved. **15**, 63 (1963).

[8] G. I. Kalishevich, P. V. Gel'd, and R. P. Krentsis, Teplofizika Vysokikh Temperatur **2**, 16 (1964) [English transl.: Soviet Phys. —High Temp. Phys. **2**, 11 (1964)].

[9] B. Bleaney and K. D. Bowers, Proc. Roy. Soc. (London) **A214**, 451 (1952).

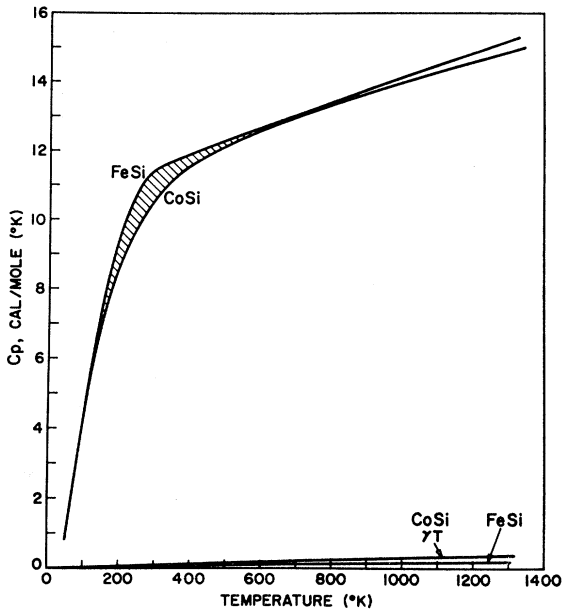

FIG. 3. Heat capacities of FeSi and CoSi from Krentsis, Gel'd, and Kalishevich, Ref. 7, Tables 1 and 4, and from Kalishevich, Gel'd, and Krentsis, Ref. 8, Tables 1 and 3. The shaded area denotes the heat-capacity anomaly. The difference at high temperature is due to a difference in the thermal expansion.

the behavior of $\chi(T)$ is the following: One assumes there to be *two* equal, rectangular (for simplicity) peaks in the density-of-states $N(E)$–versus–energy curve each of width w and separated by an amount 2Δ (see insert to Fig. 5). Both peaks are superimposed on a low, constant state-density conduction band and the Fermi level is chosen to lie midway between the two peaks. [The contribution to $\chi(T)$ from the conduction band is presumed to be negligible at all temperatures of interest.]

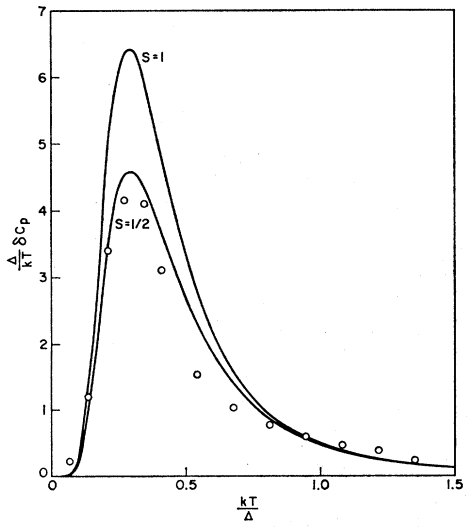

FIG. 4. Heat-capacity anomaly, plotted as $\delta Cp\ \Delta/kT$ against kT/Δ. The curves are theoretical for $S=\frac{1}{2}$ and 1. The circles are obtained from the data in Fig. 3, corrected for the difference in the electronic specific heat.

Thermal excitation of electrons across the gap yields the nearly exponential increase in $\chi(T)$ at low temperatures and the depletion of the narrow bands would tend to give a Curie-like behavior at high temperatures. The existence of a second peak, essentially similar to the lower one, above the Fermi level is necessary to prevent the latter moving rapidly upward in energy as electrons are moved into a region of low state density.

Calculations of the susceptibility for such a band model indicate that a satisfactory fit to the present data is found only for $2w \ll 2\Delta$. In Fig. 5 a calculated susceptibility curve is shown for the limiting case $w=0$.

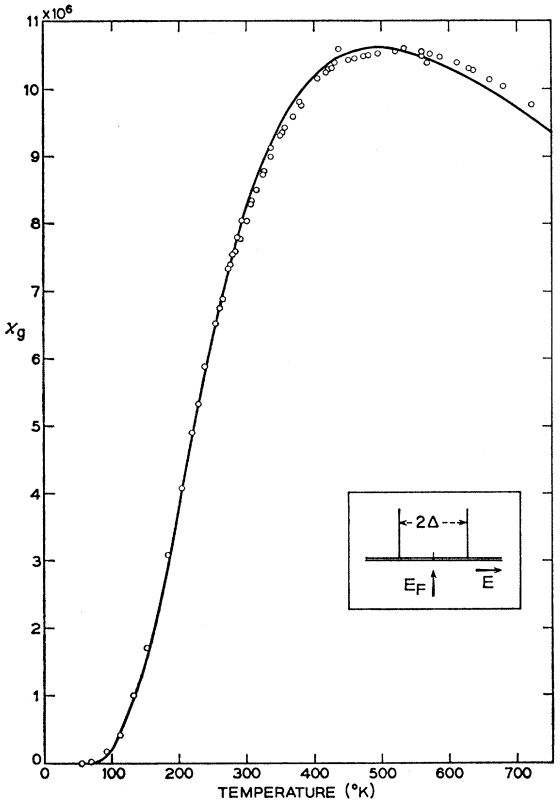

FIG. 5. Temperature dependence of the susceptibility for narrow-band model shown in the insert.

The fit is quite adequate at all save the highest temperatures. The separation of the two peaks from the Fermi level is 760°K and the two peaks each contain approximately 2.0 electrons per Fe atom. Exchange enhancement may be introduced, but not in such a way as to improve the over-all agreement with the data. A comparison of the results obtained for χ, C, and S for this model and the localized moment model to be discussed below is given at the end of the next section. Throughout we will ignore the difference between C_p and C_v in the magnetic contribution to the heat capacity.

The extreme narrow-band–small-energy-gap model, while accounting in a qualitative manner for the observed behavior of χ and C, seems inherently unsatis-

factory. There is no evidence in any band-structure calculations that have been made for such extremely narrow bands containing a substantial fraction of all the *itinerant* electrons in the metal in question. The necessary positioning of the Fermi level between the two giant peaks also seems somewhat artificial.

(3) *Localized moments.* Let us consider a system of isolated spins each of which has two distinct states: (1) a ground state with $S=0$, and (2), an excited state with spin S a distance Δ above the nonmagnetic state. It is readily shown that the molar susceptibility χ_m is

$$\chi_m=\frac{Ng^2\mu^2}{3kT}\frac{S(S+1)(2S+1)}{2S+1+\exp(\Delta/kT)}, \tag{1}$$

which for $T\ll\Delta/k$ reduces to

$$\chi_m=\frac{Ng^2\mu^2}{3kT}S(S+1)(2S+1)\exp\left(\frac{-\Delta}{kT}\right), \tag{2}$$

which is consistent with the simple activation energy previously assumed.[1] In the limit $T\gg\Delta/k$, (1) reduces to

$$\chi_m=\frac{Ng^2\mu^2}{3k}\frac{S(S+\frac{1}{2})}{T+\Theta}, \tag{3}$$

where

$$\Theta=\frac{\Delta}{(2S+2)k},$$

giving a Curie-Weiss–like decrease in $\chi(T)$ at high temperatures. If T_0 is the temperature at which the susceptibility achieves its maximum value, one can show that T_0, Δ, and S are parametrically related by the equation

$$2S+1=\left(\frac{\Delta}{kT_0}-1\right)\exp\frac{\Delta}{kT_0}. \tag{4}$$

A plot of Δ/kT_0 versus $2S+1$ is given in Fig. 6. Using the corrected experimental data below 700°K, fits for $S=\frac{1}{2}$, 1, $\frac{3}{2}$, etc. were obtained using Eq. (1) and adjusting Δ/kT_0 and g^2 so as to give the correct position and magnitude to the peak value of $\chi_m(T_0)$. An optimum fit is obtained with $S=\frac{1}{2}$, $g=3.92$, and $\Delta/k=750\pm5$°K; a somewhat poorer fit is obtained with $S=1$, $g=2.17$, and $\Delta/k=795\pm5$°K. The relative merit of these two fits may be affected by weakly temperature-independent paramagnetic or diamagnetic contributions which have not been taken into account. In spite of this, it would appear that the gap is reasonably well determined and the values of S restricted to $\frac{1}{2}$ or 1 since no other combinations of parameters give qualitative agreement with this model.

The calculated heat capacity C using the same model is

$$C=R\frac{(2S+1)\exp\Delta/kT}{(2S+1+\exp\Delta/kT)^2}\left(\frac{\Delta}{kT}\right)^2. \tag{5}$$

Since it is not easy to compare experimental measurements with the model in either the very low or the very high temperature limits, we will not consider the limiting forms of C. Instead we give the parametric equation which relates the temperature at which C is a maximum $T_{\max}$ and the quantities Δ and S, namely,

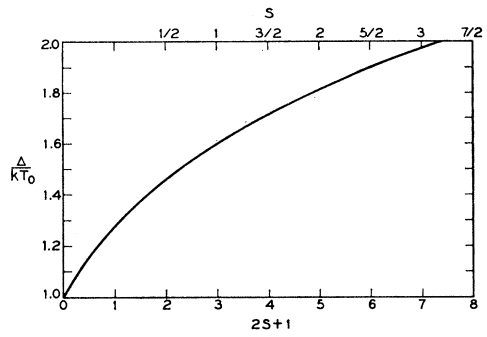

FIG. 6. The ratio of energy gap Δ to the position of the susceptibility maximum T_0 as a function of the spin S of the excited state.

$$2S+1=\frac{\Delta-2kT_{\max}}{\Delta+2kT_{\max}}\exp\frac{\Delta}{kT_{\max}}. \tag{6}$$

A comparison of Eqs. (4) and (6) shows that the $T_0>T_{\max}$ for any given value of S and Δ. Using the values of Δ previously determined by making a best fit for χ, we find that $T_{\max}(S=\frac{1}{2})=283$°K and $T_{\max}(S=1)=280$°K, both of which correspond well to the location of the anomaly in our plot of $\delta C_p\Delta/kT$ versus kT/Δ. The calculated curves for C versus T for $S=\frac{1}{2}$ and $S=1$ are given in the same figure. There are relatively large uncertainties in the experimental values because of the assumption of identical heat capacities for CoSi and FeSi, but it appears unlikely that they are sufficiently large so as to overlap the calculated $S=1$ curve. On this basis and the better fit between experiment and theory for $\chi(T)$ versus T for $S=\frac{1}{2}$ rather than $S=1$, we conclude that the former value is the only one consistent with our model.

Again on the basis of the simple model presented, the total entropy $\bar{S}$ is easily shown to be

$$\bar{S}=R\ln(2S+2), \tag{7}$$

which, of course, is an expression of the fact that the total degeneracy of the two-level system considered is $2S+1+1=2S+2$. If one numerically integrates C/T over all T to obtain $\bar{S}$, better agreement is found for the $S=\frac{1}{2}$ value, as must be clear simply by inspection of the two calculated C-versus-T curves.

It appears, then, that such an "ionic" model represents quite well the known thermodynamic properties of FeSi. For such a model to have validity it must be possible to assign at least two localized or correlated states to each Fe ion. The lower state in energy is nonmagnetic and the other has $S=\frac{1}{2}$. Transitions between these states must be possible on each individual ion.

It might initially be thought that the magnetic electrons are not band electrons, but that the d electrons in FeSi should be treated in the strictly localized way used for the $4f$ electrons in the rare-earth metals. That

is, one might suppose that there exists, on each Fe atom, a state with $S=1$ split by a predominantly axial crystal field into a singlet and a doublet. However, the susceptibility of such a state has a quite different temperature dependence[10] from that observed, since the singlet and doublet levels are not eigenstates of S_z. The states are mixed by a magnetic field and the degree of mixing depends on the relative orientation of the magnetic field to the axial crystalline field. We know of no simple crystal-field scheme for the d^6, d^7, or d^8 configurations, with or without spin-orbit coupling, which would reproduce the observed magnetic behavior of FeSi.

An alternative suggestion, more difficult to disprove, is that the states involved are of the type arising in the Anderson theory of local moments. These arise from the intereaction of a local d state with the conduction band, taking into account the effects of correlation due to the intra-atomic Coulomb repulsion in the double occupied d state. Normally, in this theory, one examines the Hartree-Fock ground state of the system to see whether or not a local moment exists. It is, perhaps, not unreasonable to assume that there may exist several localized solutions for the problem among which a magnetic one lies above the ground state. It is to be noted, however, that the localization of both ground and excited states must be such that there is negligible interaction between different ions, otherwise they will each spread into bands.

An interesting comparison can be made between the results of the narrow-band–small-energy-gap model—in the limit in which the band width vanishes—and the localized-moment model. We give in Table I expressions for χ_m, C, and the entropy $\bar{S}$ for the two models in terms of the parameters previously discussed, with $\beta=1/kT$. At temperatures small compared to the energy gap, the localized model with $S=\frac{1}{2}$, $g=2$, and a gap Δ gives the same susceptibility and specific heat as the band model with $2n=1$ and a peak separation of 2Δ. The correspondence, however, cannot be made between the two models over the entire temperature range.

As previously noted,[1] the Si^{29} NMR shift $(\Delta\nu/\nu)_{29}$ is proportional to the susceptibility—with temperature the implicit parameter. The magnitude and sign of the shift

$$\frac{\delta(\Delta\nu/\nu)_{29}}{\delta X}=7.0\left(\frac{\text{emu}}{\text{mole}}\right)^{-1}$$

indicates that there exists either a large overlap between Fe $3d$ and Si $3s$ and/or $3p$ wave functions, or an appreciable localized-moment–conduction-electron exchange interaction. Unfortunately, one cannot use the NMR observations to distinguish between either of the latter two models—they only serve to confirm that all of the induced macroscopic magnetization produces induced microscopic hyperfine interaction at the position of the Si^{29} nuclei.

The present analysis of the susceptibility shows that there is no direct relationship between it and the quadrupole splitting of the nuclear excited state of the Fe^{57}. The assignment of $S=\frac{1}{2}$ to the excited state means that it does not make a contribution to the electric field gradient. Moreover the number of electrons excited across the gap is measured by χT, whose temperature dependence differs very markedly from that of the quadrupole splitting. It is likely that the quadrupole splitting is more directly related to changes in conductivity which also occur in this range of temperature.[11]

TABLE I. Comparison of the susceptibility, heat capacity, and entropy for the narrow-band model in the limit of zero bandwidth and for the localized-moment model.

	Narrow-band model[a] (linewidth → 0)	Localized-moment model
$\chi\mu_B^{-1}$	$\dfrac{2nN\beta}{1+\cosh\beta\Delta}$	$N\dfrac{S(S+1)}{3}\dfrac{(2S+1)g^2\beta}{2S+1+e^{\beta\Delta}}$
C	$\dfrac{4nR(\Delta\beta)^2e^{\beta\Delta}}{(1+e^{\beta\Delta})^2}$	$(2S+1)R\dfrac{(\Delta\beta)^2e^{\beta\Delta}}{(2S+1+e^{\beta\Delta})^2}$
S	$2(2n)R\ln 2$	$R\ln(2S+2)$

[a] n is the number of states of one spin per iron atom in each peak and N is Avogadro's number.

ACKNOWLEDGMENTS

The authors are indebted to H. J. Williams, J. L. Davis, D. Dorsi, J. P. Maita, and A. R. Storm for assistance with various aspects of these measurements.

APPENDIX

The reason for limiting the analysis of the susceptibility data to the region below 700°K becomes apparent

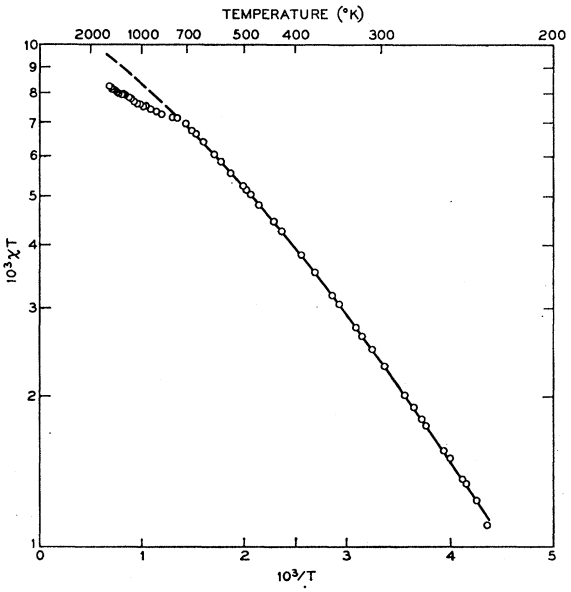

FIG. 7. Susceptibility measured with increasing temperature, plotted logarithmically as χT (in emu/g deg) against $10^3/T$.

[10] L. Berger and S. A. Friedberg, Phys. Rev. **136**, A158 (1964).
[11] R. Wolfe, J. H. Wernick, and S. E. Haszko, Phys. Letters **19**, 449 (1965).

when data extending to higher temperatures are examined. For this purpose it is advantageous to remove the T^{-1} dependence in order to simplify the variation of the measured quantity with temperature. Figure 7 shows a plot of $\ln\chi T$ versus $10^3/T$ for data taken at increasing temperature. (Subsequent data at decreasing temperature do not superpose on the data shown.) We take the break at $\sim 760°$K and the lack of reproducibility to be clear indications that the ideal FeSi structure begins to become disordered at the break in the slope of χT. X-ray data do not show a change in structure at this temperature.

PHYSICAL REVIEW VOLUME 160, NUMBER 3 15 AUGUST 1967

Pseudo-Atom Phase Shifts for Monovalent Metals and Alloys. I. Electrical Resistivities and Thermoelectric Powers of the Monovalent Liquid Metals*

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(Received 29 August 1966; revised manuscript received 19 December 1966)

Electrical resistivities and thermoelectric powers of the monovalent liquid metals are found using electron-ion scattering amplitudes calculated by partial-wave analysis rather than Born approximation. The results all correlate with experiment. An expression is derived for the thermoelectric power which emphasizes the importance of the gradient of the structure factor in the back-scattering direction and which could account for the fact that most monovalent (in contrast to polyvalent) metals have positive thermoelectric powers.

1. INTRODUCTION

IN another paper[1] (hereafter I), phase shifts of pseudo-atoms[2] of each of the monovalent metals have been evaluated as functions of Fermi level, using a pseudopotential technique.

The main purpose of these results will be to interpret alloy properties, and some success in this direction has already been obtained.[3] However, the pure-material Fermi level was of considerable interest to us, because only here have other calculations of the pseudopotentials[4–7] been made. It was desirable, therefore, to make comparisons and see how well each method predicted physical properties. For, only when it has been shown that the data of I are comparable with the best available hitherto, is it reasonable to employ them in more general situations. Two of the more directly accessible properties of a liquid metal, starting from the present kind of approach, are the electrical resistivity and the thermoelectric power,[8,9] and Sundström[10] and Animalu[6] have performed computations using screened Heine-Abarenkov pseudopotentials.[5]

The least satisfactory features of the above calculations are the results for Cs. The calculated resistivity is far below the experimental value and the thermoelectric power is of the wrong sign. This was attributed by Sundström, at least in part, to the use of Born approximation, the backscattering being thereby substantially underestimated. The present work represents a first procedure beyond Born approximation, the full standard form[11] for the scattering amplitude being used. Such an expression, moreover, requires, and is convenient for, a more complete calculation of thermoelectric powers than has been made hitherto. Specifically, we allow for

* Research sponsored by the U. S. Atomic Energy Commission under contract with Union Carbide Corporation.

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