Many-body small-cluster theory of bcc Fe, Co, and the Fe-Co alloy

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An exact solution for a two-site crystal model, the smallest body-centered-cubic crystal, is presented for cobalt, iron, and the virtual-crystal iron-cobalt alloy. The model consists of five d-like orbitals per site per spin, with interatomic hopping terms and an on-site Coulomb interaction of the fullest generality allowed by atomic symmetry. The ground-state spin polarization per atom is found to begin at 2 for cobalt, rise to 2.5 for the iron-cobalt alloy, and drop back down to 2 for iron. This behavior, which mimics the peak in the Slater-Pauling magnetization curve for this system, is dominated by one-electron properties rather than the Coulomb interaction. The many-body energy-level spectra and intracluster charge and spin fluctuations are also computed.

I. INTRODUCTION

The Slater-Pauling curve[1] is a plot of magnetization versus the electron-to-atom ratio for a variety of disordered transition-metal alloys. The Fe-Co alloy system is the strongest and sharpest maximum on the plot; the maximum occurs at approximately 30 at. % Co. Pauling[2] explained this by the suggestion that the number of unbalanced d holes cannot exceed approximately 2.4 because the other 2.6 d electrons of each spin belong to a lower band which cannot lose electrons until the upper one is completely emptied. Williams *et al.*[3] have argued that the only relevant features are magnetic saturation on the Co side of the maximum and ferromagnetic weakness on the Fe side. A self-consistent tight-binding treatment[4] of the disordered Fe-Co alloy indeed showed that the magnetization of Co-rich alloys depended essentially on the number of available d holes, while the magnetization of Fe-rich alloys is influenced by a relatively weak electron-electron interaction. These ideas, along with surface narrowing of the d band, were used to calculate[5] surface properties of Fe and the ordered Fe-Co alloy. An analysis of Fe, Co, and the disorder Fe-Co alloy using the many-body small-cluster method is presented in this paper. Because this maximum is determined by a competition between band-structure effects (the numbers and energies of the available d states) and many-body interactions (Coulomb repulsion and exchange correlation), the small-cluster method is uniquely qualified to shed further light on this issue.

The many-body small-cluster method has been successfully used to study many-body effects in various systems in which many-body and single-particle effects are of similar magnitudes. In this approach, a model Hamiltonian which explicitly includes band-structure effects and many-body interactions is solved exactly, eliminating the need to assume the one-particle picture as basic while treating many-body interactions as a perturbation. The problem is made tractable by modeling the solid as a limited-size crystal with periodic boundary conditions. For example, an fcc crystal can be modeled as a four-center tetrahedral cluster; this is equivalent to the infinite crystal sampled only at Γ and the three X points of the Brillouin zone. A bcc crystal may be modeled as a two-atom cluster; this is equivalent to the infinite crystal sampled only at the Γ and H points of the Brillouin zone. Clearly, one would not expect this method to yield accurate long-range correlations and sharp phase transitions, but uniform properties and short-range correlations should be well represented.

The Hubbard Hamiltonian has been solved[6] in a tetrahedral cluster, and similar Hamiltonians have been used to study intermediate-valence[7,8] systems as well as binary and ternary alloys.[9] Magnetic properties of the $3d$ transition metals have also been examined. The valence-band photoemission satellite of fcc Ni was explained by a many-body small-cluster calculation[10] using a basis of five $3d$-like orbitals per spin, and photoemission, inverse-photoemission, and many-body fluctuations of bcc Fe have been computed.[11] (The Hamiltonian for these $3d$ transition metals is discussed in detail in the next section.) An important conclusion of this work is that the effect of realistic many-body interactions is to make the system extremely sensitive to the energies and degeneracies of the one-electron levels. This is an important feature of the physics of the Slater-Pauling curve.

II. THE MODEL HAMILTONIAN

The smallest nontrivial bcc crystal contains two atoms. With periodic boundary conditions, a calculation using this crystal is equivalent to a restricted sampling of two points in the Brillouin zone of the infinite crystal. These two points, both of which have full cubic symmetry, are Γ (the zone center) and H (the point at the end of the cubic axes). There are five d orbitals per spin; in the presence of a cubic field they split into the triplet t_{2g} and the doublet e_g. (This is the origin of the two d bands referred to by Pauling.) The s electrons are not explicitly included in the Hamiltonian because they do not participate in

magnetism; however, they are important because they act as a reservoir of electrons. Thus, the number of d electrons is not fixed at the atomic value. Since the method allows only an integral number of particles in the cluster, and there are two atoms in the bcc clusters, we are restricted to integer and half-integer values for n, the number of d holes per atom. The earlier Fe work[11] was done with two d holes ($n=2$) per Fe atom; we now believe $n=3$ is more sensible for the "weak" ferromagnet Fe. We use $n=2$ for Co, and $n=2.5$ for the 50:50 Fe-Co alloy.

The model Hamiltonian contains both single-particle and two-particle terms:

$$H=\sum_{\substack{i,j;\mu,\nu;\sigma\\(i\neq j)}} t_{i\mu,j\nu}c^{\dagger}_{i\mu\sigma}c_{j\nu\sigma}+\sum_{i;\mu;\sigma} e_{\mu}c^{\dagger}_{i\mu\sigma}c_{i\mu\sigma} + \sum_{i;\mu,\nu,\lambda,\phi;\sigma,\sigma'} V_{\mu\nu\lambda\phi}c^{\dagger}_{i\mu\sigma}c^{\dagger}_{i\nu\sigma'}c_{i\lambda\sigma'}c_{i\phi\sigma} \ . \quad (1)$$

Here, i,j $(=1,2)$ label atoms, μ,ν,λ,ϕ label orbitals, and σ,σ' label spins. The single-particle hopping terms $t_{i\mu,j\nu}$ are parametrized according to the Slater-Koster tight-binding scheme. Note that this scheme allows for only nearest-neighbor hopping; in our restricted crystal, the second-nearest neighbor of an atom is itself. Intra-atomic Coulomb interactions $V_{\mu\nu\lambda\phi}$ are used; they include a direct Coulomb integral U, an average exchange integral

$$J=\tfrac{1}{2}[J(e_g,e_g)+J(t_{2g},t_{2g})] \ ,$$

and an exchange anisotropy

$$\Delta J=[J(e_g,e_g)-J(t_{2g},t_{2g})] \ .$$

Following Victora and Falicov,[10] a value for U is chosen and the other interaction parameters are set in the ratios $U:J:\Delta J=56:8:1$. (The results are insensitive to the exact values of these ratios.) The next-largest contribution is the nearest-neighbor Coulomb term, which makes a constant contribution and may be neglected.

Slater-Koster parameters for Fe and Co were initially taken from Victora's thesis.[12] The bcc Fe parameters were then adjusted to reproduce, in the absence of any interactions, the calculated paramagnetic local-density-approximation band structure[13] of Moruzzi *et al.* at the Γ and H points. In order to accomplish this, only the occupation energies of the e_g and t_{2g} bands [e_3 and e_5, respectively, in the second term of (1)] were changed. The relative shift in these energies is caused by hybridization between the d and sp bands, as well as second-neighbor hopping between the atoms. The occupation energies were then shifted further to obtain the correct ground state for Fe; the same shift was applied to the bcc Co parameters. The value of U for Fe was taken to be 4.9 eV; scaling the value for Co in the same ratio to Fe as in Victora's thesis[12] yields a value of 6.6 eV. Such large values of U (Ref. 14) are necessary because the screening of U is explicitly included in our treatment. Parameters for Fe-Co were obtained by averaging Fe and Co; this is essentially the virtual-crystal approximation. The parameters actually used in the calculation are summarized in Table I, which shows one-electron eigenvalues in the absence of the interactions as well as the interaction parameters. (In this paper, lower-case letters are used to denote the symmetry of single-particle energy levels.)

TABLE I. Hamiltonian parameters (units of Ry).

	Co	Fe-Co	Fe
γ_3	0.8829	0.8915	0.9000
γ_5	0.7022	0.7001	0.6990
h_3	0.5621	0.5495	0.5370
h_5	0.8939	0.9044	0.9160
U	0.4844	0.4220	0.3600
J	0.0692	0.0603	0.0514
ΔJ	0.0086	0.0075	0.0064

Since metallic Fe has a magnetic moment of $2.22\mu_B$/atom,[15] and the method only allows an integral number of holes in the cluster, the configuration chosen for Fe is six d holes in the neutral state of the cluster. (In this configuration there is an average of three holes per atom; therefore the maximum possible spin per atom is 3. A spin per atom of 2 is the closest possible correspondence in our theory to the experimental value of the magnetic moment and designates an unsaturated ferromagnetic state.) Simple combinatorial arguments yield 38 760 states in the cluster for this number of holes. Cobalt, with an experimental moment of $1.72\mu_B$/atom,[15] is modeled with four d holes (4845 states) in the cluster. (Again, a spin per atom of 2 is the closest possible correspondence to the experimental moment, but in this case designates a fully saturated ferromagnetic state. The experimental moment is for hcp cobalt rather than the calculated bcc cobalt.) Modeling Fe-Co requires five d holes (15 504 states) in the cluster.

Clearly, even the two-atom cluster model for Fe has a very large Hamiltonian. The symmetries inherent in the Hamiltonian (1) must be exploited to reduce further the size of the matrices to be diagonalized.

The space group of the two-atom bcc lattice contains 96 operations including the inversion i. The point group is $O_h=O\times i$. Since only d orbitals are involved, and they are even under i, the inversion operation may be ignored. A restricted set of 48 operations, with 10 irreducible representations (five each at Γ and H), is sufficient. The representations are shown in Table II, the character table of the space group. With a complete set of matrices that transform according to these irreducible representations,[16] it is possible to project out sets of symmetrized basis states. Since the representations cannot mix, this is equivalent to a block diagonalization of the Hamiltonian. In the case of six holes in the cluster, the largest block is 904×904, a considerable reduction from the original $38\,760\times 38\,760$ matrix.

The symmetry of the Hamiltonian also requires that the eigenstates have definite spin angular momentum. This symmetry may be exploited for further block diagonalization; the sizes of the reduced blocks for four, five, and six holes are shown in Table III. Of course, the solutions obtained by diagonalizing these blocks are exact solutions of the full Hamiltonian for the cluster.

TABLE II. Two-atom bcc space-group character table (inversion omitted).

		1 E	3 C_4^2	6 C_4	6 C_2	8 C_3	1 τ^a	3 τC_4^2	6 τC_4	6 τC_2	8 τC_3
s	Γ_1	1	1	1	1	1	1	1	1	1	1
	Γ_2	1	1	−1	−1	1	1	1	−1	−1	1
e_g	Γ_3	2	2	0	0	−1	2	2	0	0	−1
p	Γ_4	3	−1	1	−1	0	3	−1	1	−1	0
t_{2g}	Γ_5	3	−1	−1	1	0	3	−1	−1	1	0
s	H_1	1	1	1	1	1	−1	−1	−1	−1	−1
	H_2	1	1	−1	−1	1	−1	−1	1	1	−1
e_g	H_3	2	2	0	0	−1	−2	−2	0	0	1
p	H_4	3	−1	1	−1	0	−3	1	−1	1	0
t_{2g}	H_5	3	−1	−1	1	0	−3	1	1	−1	0

[a]The symbol τ stands for the operation that translates from one lattice site to the other.

III. EIGENVALUE SPECTRUM AND THERMODYNAMICS

The results of our calculations may be understood by making a Hubbard-model–like interpretation in which the single-particle $U=0$ levels of Table I are split by the exchange interaction J into single-particle majority- and minority-spin levels.[17] This is, of course, only an approximate picture, since in the full many-body approach configuration interaction mixes all one-particle levels; nevertheless, it is a useful exercise.

In all three cases, the highest one-electron level (the first to be "occupied" by holes) is h_5, which has t_{2g} symmetry and therefore can accommodate three holes of each spin. The next highest level is γ_3, which has e_g symmetry and can accommodate two holes of each spin. When the Coulomb interaction is turned on, the spin states are split by approximately J, which is sufficient to bring the h_5 majority-spin level below the γ_3 minority-spin level. (The h_3 and γ_5 levels are too far away to matter.)

In Co, three of the four holes go into the minority-spin h_5 level and the fourth goes into the minority-spin γ_3 level, yielding a fully-spin-polarized ferromagnetic ground state with a spin per atom of 2. This is consistent with our calculated ground state of ${}^5H_3$ symmetry. The fifth hole in Fe-Co also goes into the minority-spin γ_3 level, yielding a fully-spin-polarized ferromagnetic ground state with a spin per atom of 2.5, consistent with our calculated ground state of symmetry ${}^6H_1$. Iron has a sixth hole to accommodate in the cluster, but the minority-spin h_5 and γ_3 levels are already full, so it goes into the majority-spin h_5 level, consistent with our calculated ground state of ${}^5\Gamma_5$ symmetry. This state is an unsaturated (not fully-spin-polarized) ferromagnet, and would still remain so even if U were several times larger. Within the limitations of the finite cluster, the peak in the Slater-Pauling curve for the Fe-Co system is reproduced by our model. Although the Coulomb interaction is certainly a requirement for the formation of ferromagnetic ground states, it is clear that the one-electron parameters (band-structure effects) play an important role in determining the ground-state spin polarization.

The density of many-body states (MBDOS) is the best way to show the spectrum of energy eigenvalues of the Hamiltonian (1). At each eigenvalue[18] a peak of weight equal to the degeneracy at that energy is plotted. In a finite system, this results in a discrete set of spikes, which we have broadened artificially into Gaussian of 0.1 eV half-width, at half maximum.

TABLE III. Sizes of blocks of the various representations.

N	Spin	Γ_1	Γ_2	Γ_3	Γ_4	Γ_5	H_1	H_2	H_3	H_4	H_5
4	2	6	4	11	11	15	2	4	8	14	12
	1	16	22	37	67	59	20	22	40	64	62
	0	29	16	40	44	56	18	18	32	50	50
5	$\frac{5}{2}$	9	5	11	14	16	9	5	11	14	16
	$\frac{3}{2}$	37	39	76	117	115	37	39	76	117	115
	$\frac{1}{2}$	71	67	141	202	208	71	67	141	202	208
6	3	2	4	8	14	12	6	4	11	11	15
	2	52	46	102	138	48	148	46	99	141	145
	1	130	148	276	446	424	150	144	293	433	437
	0	128	98	222	290	320	108	102	205	303	307

The finite-cluster method can also provide the eigenstates, allowing one to compute various correlation functions. It is trivial to obtain the most obvious correlation, namely the magnitude of S^2 in the cluster. Two other functions, which require knowledge of the eigenstates, can help interpret the results. The first is

$$\Delta n^2 \equiv \left\langle \left[\sum_{\mu} (n_{1\mu\uparrow} + n_{1\mu\downarrow}) - (n_{2\mu\uparrow} + n_{2\mu\downarrow}) \right]^2 \right\rangle . \quad (2)$$

Here, $n_{i\mu\sigma} = c^{\dagger}_{i\mu\sigma} c_{i\mu\sigma}$. The quantity Δn^2 can be called the intracluster charge fluctuation because it is simply the average of the square of the difference between the occupations of the two sites. It is a measure of the polarity of the electronic charge in the cluster; a zero value indicates a neutral cluster, while a large value indicates large charge-density fluctuations. The second function is

$$\Delta \sigma^2 \equiv \left\langle \left[\sum_{\mu} (n_{1\mu\uparrow} - n_{1\mu\downarrow}) - (n_{2\mu\uparrow} - n_{2\mu\downarrow}) \right]^2 \right\rangle , \quad (3)$$

which is called the intracluster spin fluctuation. It is a measure of the spin imbalance between the two sites of the cluster. A zero value indicates a uniform spin distribution, while a large value indicates large spin-density fluctuations, or, equivalently, antiferromagnetic correlations.

These correlations may be plotted as functions of the temperature by simply calculating them for each eigenstate, multiplying by the appropriate Boltzmann factor, and adding.

The MBDOS and thermodynamic averages of total energy, $\langle S^2 \rangle$, Δn^2, and $\Delta \sigma^2$, are shown in Figs. 1 and 2 for Co, Figs. 3 and 4 for Fe-Co, and Figs. 5 and 6 for Fe. In each case the MBDOS shows that the ground state is clearly split off from the other low-lying states. There are no real surprises in the thermodynamic functions, although it is worth emphasizing that Fe exhibits a high value of $\Delta \sigma^2$, implying strong antiferromagnetic correlations.

IV. CONCLUSIONS

A many-body small-cluster model of the $3d$ electrons in bcc Fe, Co, and Fe-Co has been studied in detail. No perturbation theory was employed. Although the model is undoubtedly too simple to reproduce the rich electronic behaviors of these metals, it does give accurate and detailed information about some properties, and it illustrates a very important point: when realistic values for the electron-electron interaction are used, one-electron effects can dominate the ground-state properties. In particular, the formation of a magnetic ground state depends on the ability of J to split the one-electron levels enough to overlap the h_5 level, which can accommodate three electrons of each spin, and the γ_3 level, which can accommodate two electrons of each spin. (The other levels are too far away to matter.) Since $U/J=7$, a change of $\Delta e = e_5 - e_3$ is as efficient as a change $\Delta U = 7\Delta e$. If the relevant one-electron levels are separated by even 2 eV, an unphysically large U of 14 eV would be necessary to overlap the bands. Even if they are separated by an

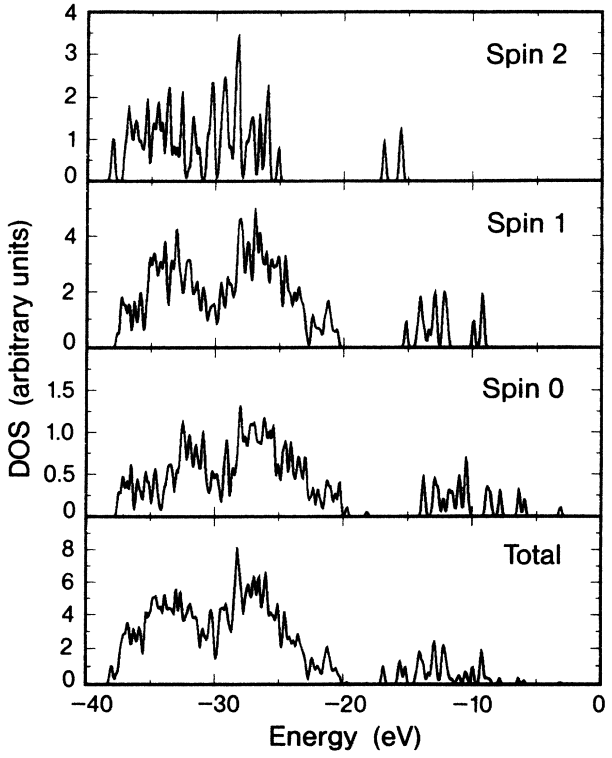

FIG. 1. Total and spin-resolved eigenvalue spectra (densities of many-body states) for bcc Co.

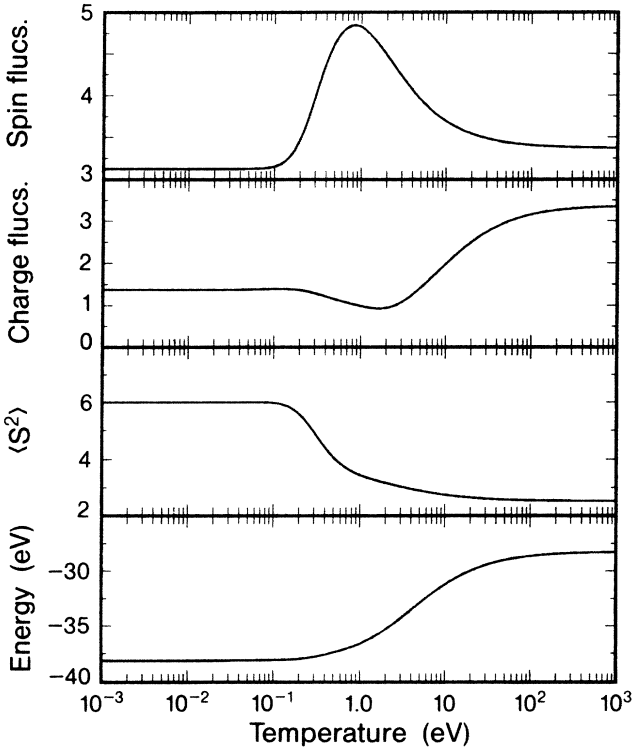

FIG. 2. Thermodynamic averages of energy, $\langle S^2 \rangle$, intracluster charge fluctuations, and intracluster spin fluctuations for bcc Co.

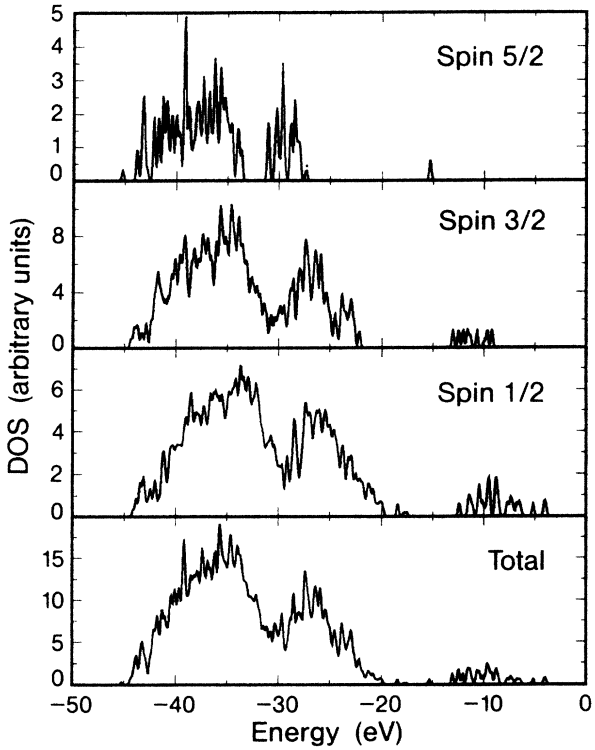

FIG. 3. Total and spin-resolved eigenvalue spectra (densities of many-body states) for bcc Fe-Co.

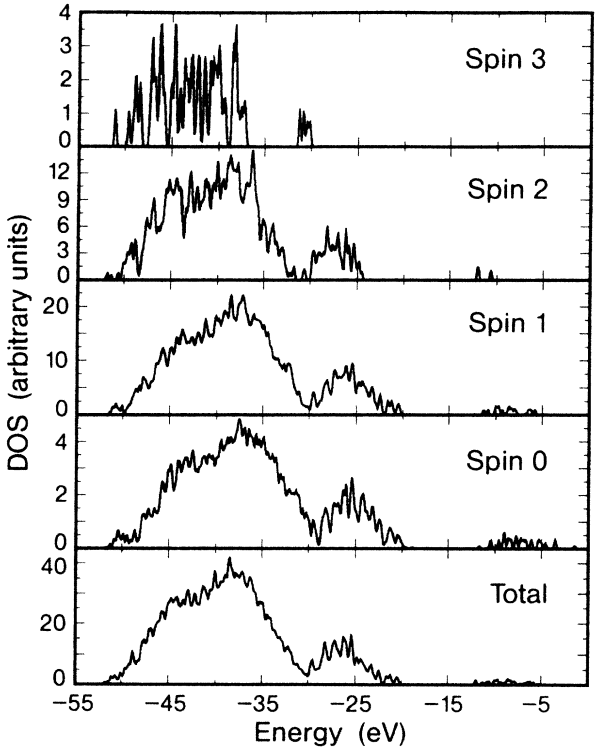

FIG. 5. Total and spin-resolved eigenvalue spectra (densities of many-body states) for bcc Fe.

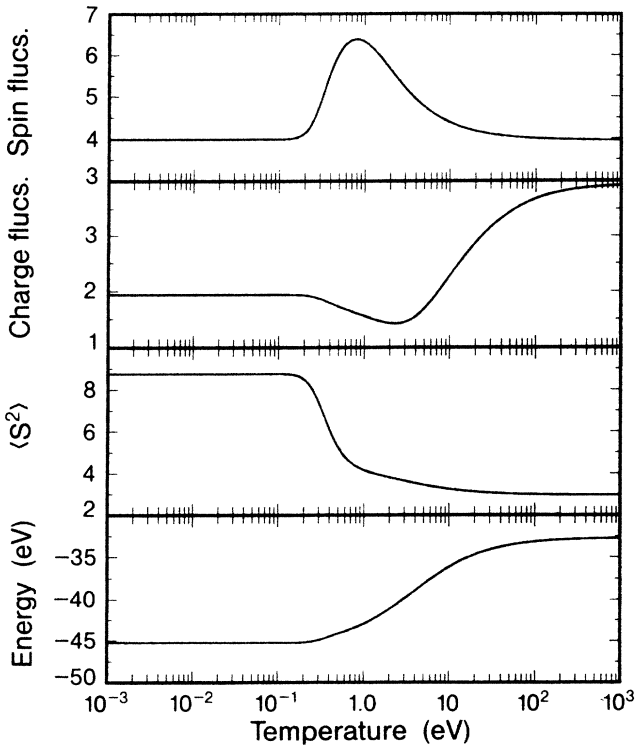

FIG. 4. Thermodynamic averages of energy, $\langle S^2 \rangle$, intracluster charge fluctuations, and intracluster spin fluctuations for bcc Fe-Co.

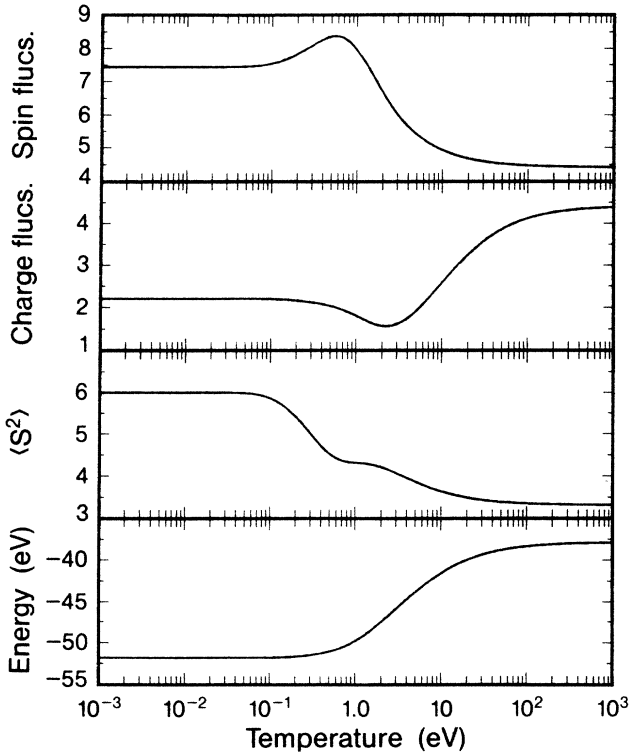

FIG. 6. Thermodynamic averages of energy, $\langle S^2 \rangle$, intracluster charge fluctuations; and intracluster spin fluctuations for bcc Fe.

amount small enough to be connected by J, the degree of spin polarization depends only on how many holes can fit into these levels. In our model, Fe is a weak ferromagnet not because U is smaller than in Co, but because only five holes of the same spin can be accommodated by these bands. In Pauling's language, the number of unbalanced d holes cannot exceed 2.5 per atom (five in the cluster), because the other electrons in the cluster belong to levels that cannot empty until all the higher levels empty. Obviously, a full calculation at more than two k points will change the exact details of the state counting, but the basic conclusion should remain valid.

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[14]We use U for the direct on-site Coulomb integral between orbitals of the same symmetry. Some authors use U for the same integral between orbitals of *different* symmetry, which we call U'. Atomic symmetry demands that $U'=U-2J$; our value of U for Fe is equivalent to $U'=3.5$ eV.

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[17]Any use of the words "majority" or "minority" in the context of spin orientation of an energy level refers to *electronic* spin, not to the spin of the hole. In particular, if the spin orientations of all the holes in a state are the same, these holes are in minority-spin levels.

[18]The MBDOS should not be confused with the usual single-particle DOS; here the eigenvalues are the energies of many-body states rather than single-particle excitation energies.