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Evidence of strong electron correlation effects on thermal expansion in transition metals

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The electronic contribution α_e to the thermal-expansion coefficient of Fe and Ni is investigated on the basis of a variational theory. This goes beyond the static approximation to the functional integral method by including electron correlations. The correlations greatly reduce the spontaneous volume magnetostriction in Fe and change the sign of the discontinuity of α_e at T_C in Ni: the results differ qualitatively from those of the static approximation.

There has been considerable progress[1-7] in the theory of magnetovolume effects in transition metals since Janak and Williams[8] demonstrated the failure of the Stoner model for the magnetovolume effect in α-Fe on the basis of first-principles local spin-density functional theory. Nevertheless, difficulties remain in explaining the small magnitude of the spontaneous volume magnetostriction (ω_s) in Fe and Ni (i.e., the volume expansion of the ferromagnetic state relative to the paramagnetic state).[9,10]

The essence of recent theories is the inclusion of thermal spin fluctuations or the persistence of local moments (LM) above T_C. A phenomenological theory of the magnetvolume effect in weak-ferromagnets has been developed by Moriya and Usami.[1] They derived a volume change proportional to the square of the amplitude of LM ($\langle m^2 \rangle$), assuming a small amplitude of spin fluctuations and a q-independent magnetovolume coupling constant. Their result is also known as the Shiga-Schlosser expression.[11,12] They estimated ω_s to be 0.004 for Fe from their expression and the experimental forced-volume-magnetostriction data. The application of the Shiga-Schlosser expression to Fe and Ni, however, lacks theoretical basis because they are obviously not weak ferromagnets.[13]

A microscopic theory was developed first by Kakehashi.[3,4] He derived general expressions for the electronic contribution to the thermal-expansion coefficient (α_e) and the forced volume magnetostriction. He adopted the single-site approximation (SSA) and static approximation (SA) to the functional integral method in the actual evaluation of the thermal average in α_e and obtained $\omega_s = 0.007$–0.02 in Fe, depending on s-d charge transfer. Hasegawa[6] has developed a single-site theory of the magnetovolume effect and obtained $\omega_s = 0.04$ for Fe, which was considered to be more than 10 times the experimental value.[7,14] The overestimation of ω_s in the SSA was interpreted as evidence of large magnetic short-range order in the paramagnetic state.[7] The thermal-expansion coefficient of Ni poses another problem: the SSA and SA together always give the wrong sign for the jump in the thermal-expansion coefficient of Ni at T_C.[2-4,6] Therefore, they do not explain the change of sign in Fe-Ni alloys with increasing Fe concentration.[5]

On the other hand, Korenman and Wyman[7] have developed a local-band theory. Starting from the free energy in the long-wavelength limit, they claim to find the right sign for ω_s in both Fe and Ni, i.e., $\omega_s > 0$ for Fe and $\omega_s < 0$ for Ni. Their theory, however, neglects the temperature dependence of the amplitude of LM. This assumption should always lead to negative ω_s, as can be seen from the general expression for α_e[4]. We have therefore checked their parameters and found that ω_s for Fe changes sign if we use a more accurate volume dependence for the d-band width (W),[15] i.e., γ ($\equiv -\partial \ln W / \partial \ln V) = 3.8/3$ instead of Heine's law ($\gamma = 5/3$).[16] Thus their theory has to be reconsidered.

In the present work we demonstrate that the inclusion of local electron correlations removes the main difficulties encountered in previous calculations[2-4,6] and therefore show that electron correlation is decisively important in the present problem.

So far the effect of local electron correlation on the thermal expansion has not been investigated. The SA reduces to the Hartree-Fock approximation at $T = 0$. Therefore, the magnetic energy and the magnetization are overestimated. To avoid this, one uses an effective Coulomb interaction U_{eff} ($< U$).[1-7] The reduction of U, however, leads to incorrect results for the correlation corrections to other physical quantities. The charge fluctuations $[\langle (\delta n)^2 \rangle]$ and the bonding energy ($-E_b$) are overestimated while the amplitude of LM ($\langle m^2 \rangle^{1/2}$) is underestimated. The local correlation effects mentioned above persist above T_C because the resulting energy gain is much larger than T_C. Therefore, the SA with U_{eff} underestimates the atomic character of d electrons in those quantities, even if it correctly reproduces the magnetization, the Curie temperature, and the susceptibility. In particular, the electronic contribution to the thermal-expansion coefficient is proportional to the temperature derivative of the bonding energy [see Eq. (5)]. Therefore, the thermal expansion should be treated in a theory which takes account of electron correlations at finite temperatures. Such a theory has been developed by Kakehashi and Fulde on the basis of a variational principle.[17] We adopt this theory for the present problem of thermal expansion.

In variational approach (VA) the free energy F_G reduces to a Gutzwiller-type ground-state energy at $T = 0$,[18,19] instead of the Hartree-Fock energy, and agrees with that of the SA in the high-temperature limit:[17]

$$F_G = -T \ln \int \left(\frac{\beta U}{4\pi} \right)^{1/2} d\xi \, e^{-\beta E_G(\xi,\zeta(\xi),\eta(\xi))} \tag{1}$$

$$E_G(\xi,\zeta(\xi),\eta(\xi)) = E_{\mathrm{st}}(\xi,\zeta(\xi)) + \langle Q\tilde{H}Q \rangle_{0\xi} \; . \tag{2}$$

Here we have used the single-band Hubbard model (or, more precisely, five-fold degenerate unhybridized bands with no interaction between them) and the SSA. $E_{\mathrm{st}}(\xi,\zeta(\xi))$ is the single-site energy functional, in the SA, of a scalar potential ξ and charge potential $\zeta(\xi)$ in an effective medium, and $\tilde{H} \equiv H - \langle H \rangle_{0\xi}$. The average $\langle \sim \rangle_{0\xi}$ is taken with respect to the one-electron state with exchange field ξ and charge potential $\zeta(\xi)$. The second term on the right-hand side of Eq. (2) describes the local electron correlations adiabatically. The projection operator Q partially suppresses states with double occupancy on a site and is of the Gutzwiller form:[18,19]

$$Q = \langle [1-\eta(\xi)O]^2 \rangle^{-1/2} [1-\eta(\xi)O] \; ,$$

where

$$O = (n_\uparrow - \langle n_\uparrow \rangle_{0\xi})(n_\downarrow - \langle n_\downarrow \rangle_{0\xi}) \; .$$

n_σ is the electron number operator for spin σ on a site. The best charge potential $\zeta(\xi)$ and best correlation parameter $\eta(\xi)$ are determined variationally:

$$\frac{\partial}{\partial \zeta(\xi)} E_G(\xi,\zeta(\xi),\eta(\xi)) = 0 \; , \tag{3}$$

$$\frac{\partial}{\partial \eta(\xi)} \langle Q\tilde{H}Q \rangle_{0\xi} = 0 \; . \tag{4}$$

In the previous calculation,[17] E_G in Eq. (3) is replaced by E_{st}. However, in the present calculation we solve Eq. (3) numerically. Other procedures are as before.[17] We use the following parameters: $n=7.2/5$, $W=0.45$ Ry, and $U=0.475$ for Fe; $n=9.0/5$, $W=0.35$ Ry, and $U=0.717$ Ry for Ni. Here n is the d-electron number, U is the intra-atomic Coulomb repulsion, and W is the d-band width as defined in Figs. 1 and 2. This fuller treatment of the charge potential further reduces the charge fluctuations and further modifies T_C. Figures 1 and 2 show the results for Fe and Ni, respectively.

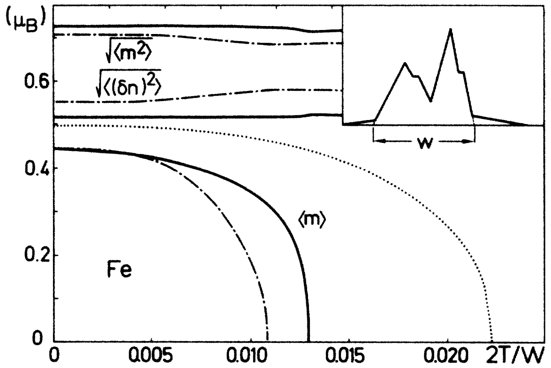

FIG. 1. Magnetization $\langle m \rangle$, amplitude of local moment $\langle m^2 \rangle^{1/2}$, and charge fluctuation $\langle (\delta n)^2 \rangle^{1/2}$ for Fe as a function of temperature. Solid line represents the variational approach. Dotted line represents $\langle m \rangle$ in the static approximation. Dashed-dotted lines represent the results in the static approximation but with $U_{\mathrm{eff}}=0.753\,U$. The inset shows the density of states.

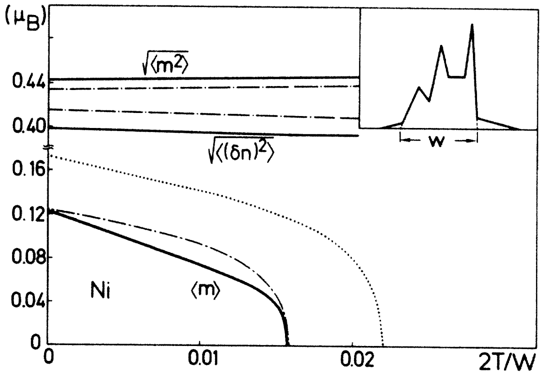

FIG. 2. Magnetization, amplitude of local moment, and charge fluctuation for Ni as a function of temperature. Notation as in Fig. 1. $U_{\mathrm{eff}}=0.685\,U$ is used.

The electronic contribution to the thermal-expansion coefficient $(V^{-1}\partial V/\partial T)$ is calculated from the expression[3,4]

$$\alpha_e = \frac{\dot{D}}{3BV} \frac{\partial E_b}{\partial T} \; . \tag{5}$$

Here we have neglected s-d charge transfer since we are interested in the d-electron correlation effects. $\dot{D}$ is the electron Grüneisen parameter, which is derived from the one-electron d-radial wave function at the Wigner-Seitz sphere.[20] It is 3.5 for Fe and 4.0 for Ni at the equilibrium lattice parameter.[21] B and V are the bulk modulus and the volume per atom respectively. We use the experimental room-temperature values, $3BV=2.79$ Ry for Fe and $3BV=2.92$ Ry for Ni.[22] In Eq. (5), E_b is the bonding energy. For the single-band Hubbard model it is

$$\tfrac{1}{5} E_b = \sum_{i,j,\sigma} t_{ij} \langle a_{i\sigma}^{\dagger} a_{j\sigma} \rangle \; , \tag{6}$$

where t_{ij} is the transfer integral between sites i and j, and $a_{i\sigma}^{\dagger}$ $(a_{i\sigma})$ is the electron creation (annihilation) operator for spin σ on site i. The thermal average is expressed by $\langle \; \rangle$. The bonding energy E_b in Eq. (6) is obtained by parameter differentiation of the free energy (1) (Ref. 3).

It is worth pointing out that, because of its generality, Eq. (5) includes well-known results as limiting cases. In the weak and classical limits Eq. (5) reduces to the Shiga-Schlosser expression if the Fermi-distribution function is replaced by a step function. [See Eq. (3.10) in Ref. 4.] Thus,

$$\alpha_e = \frac{\dot{D}}{3BV} U \frac{\partial \langle \mathbf{S}^2 \rangle}{\partial T} \; , \tag{7}$$

where U is the intra-atomic exchange interaction and $\mathbf{S}$ is the spin-density operator on a site. In the insulator limit our (5) agrees with a formula for the localized model,[23]

$$\alpha_e = \frac{1}{BV} \left(-\frac{\partial \ln J_{ij}}{\partial \ln V} \right) \frac{\partial}{\partial T} \left[-\sum_{\langle i,j \rangle} J_{ij} \langle \mathbf{S}_i \cdot \mathbf{S}_j \rangle \right] \; . \tag{8}$$

Here J_{ij} is Anderson's superexchange integral between sites i and j.[24] We have used the results that $\dot{D}=5$ and

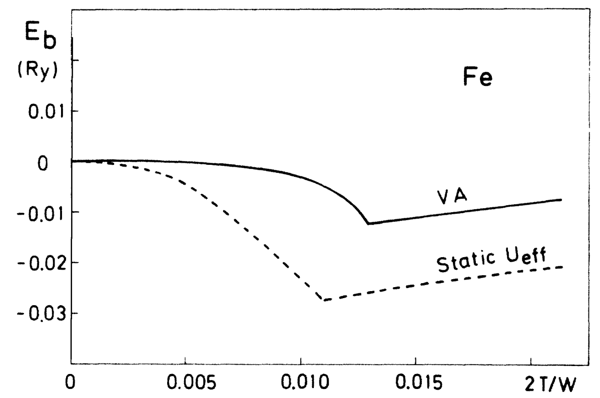

FIG. 3. Temperature variation of the bonding energy $E_b(T)-E_b(0)$ for Fe in the variational approach (solid curve) and in the static approximation with $U_{\rm eff}=0.753\,U$ (dashed curve).

$J_{ij} \propto |t_{ij}|^2 \propto V^{-10/3}$ in the insulator limit.[25]

Figure 3 shows the temperature dependence of the bonding energy in Fe. The local electron correlations strongly reduce the temperature dependence of the bonding energy, and therefore the thermal expansion. This can be understood from the following argument.

Let us consider ferromagnetic metals with nearly-half-filled bands and assume that the exchange splittings are the same on average in the SA with $U_{\rm eff}$ and in the VA. The above assumptions are not in fact necessary, but help to clarify the essential mechanism. The volume contraction is proportional to the electron-hopping rate $\langle a_{i\sigma}^{\dagger} a_{j\sigma} \rangle$ according to Eqs. (5) and (6). Even in the SA the hopping rate for spinup is suppressed because most of the surrounding sites are occupied by spin-up electrons due to the ferromagnetic exchange field. This effect is, however, weakened by spin disalignment with increasing temperature, because the number of empty levels with spinup at surrounding sites increases. Therefore, we obtain $\omega_s > 0$ in the SA. The small magnitude of the expansion above T_C in Fig. 3 is due to the suppression of hopping by temperature-induced local-exchange splittings. Correlations suppress electron hopping since hopping creates double occupancy on a site. This is suppressed by the large U. This effect is larger in the paramagnetic state than in the ferromagnetic state, since in the former more neighboring sites are occupied by opposite-spin electrons, so that electron hopping creates more double occupancy. Therefore, electron correlation effects tend to decrease ω_s.

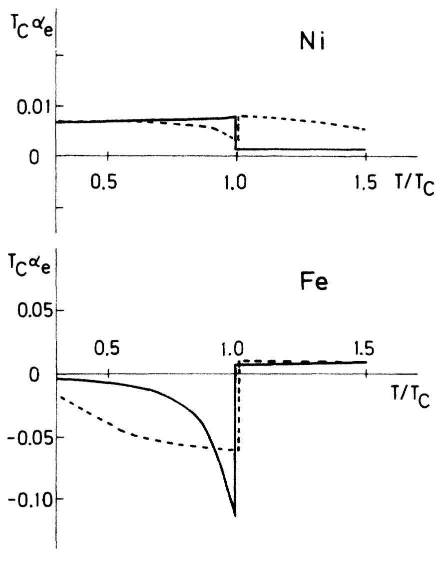

FIG. 4. Temperature dependence of the electronic contribution to the thermal-expansion coefficient for Ni and Fe. The solid (dashed) curves are the results in the variational approach (the static approximation with $U_{\rm eff}$).

TABLE I. Electronic contribution to the volume change $[V(T_C)-V(0)]/V(0)$ for Fe and Ni in various approximations. The model densities of states in Figs. 1 and 2 are used, and other parameters are as given in the text. The experimental values are of $[V(T)-V(0)]/V(0)$ with $T \gg T_C$.

	Stoner	Static $U_{\rm eff}$	VA	Expt.
α-Fe	-0.090 (-0.072)[b]	-0.035 (-0.040)[c]	-0.015	~ -0.005[a]
Ni	-0.008 (-0.005)[b]	0.007 (0.011)[c]	0.007	~ 0.004[d]

[a] Ridley and Stuart, Ref. 9.
[b] Janak and Williams, Ref. 8.
[c] Hasegawa, Ref. 6.
[d] Evaluated by the present authors from Fig. 4 in Ref. 7.

Figure 4 shows the temperature dependence of the electronic contribution to the thermal-expansion coefficient in Ni and Fe. The electron correlations change the sign of the jump of α_e at T_C in Ni, and therefore explain the observed behavior of the λ type.[10] The SA with reduced U overestimates delocalized character. Then the exchange splitting rises to rapidly with increasing temperature in the paramagnetic state, which leads to too large an α_e above T_C in Ni as seen in the figure. In Fe the electron correlations enhance the dip of α_e near T_C which is also consistent with experiment.[9] As seen in Eqs. (7) and (8), $\alpha_e(T)$ is determined by the temperature derivative of the amplitude of LM in weak magnets, which is negative below T_C, and by the specific heat in strong magnet, which is always positive. The behavior in transition metals is determined by the competition between the two effects. Fe is dominated by the former and Ni by the latter.[4]

The spontaneous volume magnetostrictions ω_s in Fe and Ni are tabulated in Table I. With the present densities of states (see Figs. 1 and 2) the Stoner model gives $\omega_s = 9.0\%$ in Fe. This value should be compared with 7.2% in a first-principles calculation.[1] The 20% overestimation by the former originates from the neglect of the spin dependence and the self-consistent change of the radial wave function in the derivation of Eq. (5). Thermal spin fluctuations within the static approximation reduce ω_s by a factor of 3. The local electron correlations reduce ω_s by a further factor of 2 and yield 1.5%. The latter should be compared with the experimental value $\sim 0.5\%$.[9] Ridley and Stuart[9] estimated ω_s in Fe to be 0.33% by integration of their magnetic contribution α_m up to 1058 K. However, this is certainly an underestimate because they neglected the contribution between 1058 and 1700 K, above which the magnetic contribution to the specific heat vanishes.[26] Thus we took, as a better value, the mean of 0.33% and their upper estimate 0.75%. In the case of Ni the Stoner model gives the wrong sign for ω_s. The static approximation gives the right sign for ω_s, but the wrong sign for the jump of α_e at T_C (see Fig. 4). The local electron correlations hardly change ω_s, but change the sign of the discontinuity in α_e.

The experimental value of ω_s in Ni is regarded as -0.0003 (Ref. 10). This is obtained by the integration of the magnetic contribution to α_e over a small temperature range of 200 K around T_C. However, some short-range magnetic order persists to 1200 K, or nearly $2T_C$, according to a specific-heat analysis.[27] Thus the above-mentioned value underestimates the magnitude of ω_s. We estimated ω_s by smoothly interpolating the paramagnetic contribution $\alpha_p(T)$ to the thermal-expansion coefficient from 1200 K in Kollie's data,[28] and obtained -0.4%. This should be compared with the theoretical result -0.7%. Although our interpolation for $\alpha_p(T)$ can cause an error of ± 0.002 in ω_s in Ni, the magnetic contribution $\alpha_m(T)=\alpha(T)-\alpha_p(T)$ which we estimated from Kollie's data satisfies the theoretical relation $\alpha_m=(\dot{D}/3BV)C_m$ for Ni, valid in the case of temperature-independent LM.[4] Here C_m is the magnetic contribution to the specific heat.[27]

In conclusion, we have shown that inclusion of local electron correlations resolves the main problems encountered in treatments of the magnetovolume effect by the SA: too large a spontaneous volume magnetostriction in Fe and the wrong sign of the jump in the thermal-expansion coefficient at T_C in Ni. This means that the giant magnetic short-range order above T_C advocated by Korenman *et al.*[7] is not needed to explain the thermal-expansion data in Fe and Ni.

Our conclusions do not depend sensitively on the density of states or other input parameters. For a quantitative comparison with the data we need to resolve the ambiguity (factor of 2 or 3) in the experimental values of ω_s due to uncertainty in the background phonon contribution. In the theory the effect of *s*-*d* charge transfer and five-fold degeneracy have to be taken into account. In the former, an *s*-*d* charge transfer $\delta n_s=0.01$ causes a volume change $\delta V/V=0.005$ in Fe.[3,4] The latter effect involves Hund's rule coupling. These effects should be included in future quantitative work.

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