Anomalies caused in the lattice properties of band magnetic materials by features of the electronic structure

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Particular features of the electronic structure of band magnetic materials near the Fermi level play an important role in the magnetovolume and magnetoelastic anomalies. Explicit expressions are derived for the corresponding contributions to the thermal expansion coefficient and the elastic moduli. An explanation is proposed for the anomalies observed in $ZrZn_2$ and Cr.

The anomalies in the lattice properties of ferromagnets and antiferromagnets have attracted considerable interest because of their importance in reaching an understanding of the nature of the magnetism of specific systems (in deciding whether a localized or itinerant picture is valid) and also because of practical applications (in alloys of the Invar and Elinvar types).[1,2] The approaches which have been taken to describe these anomalies[1,3,4] have ignored two important circumstances: that the details of the electronic structure near the Fermi level, E_F [the Van Hove singularities (VHSs) in the density of states $N(E)$], are important to the magnetism[5,6] and that these structural features play a governing role in shaping the phonon spectra and the lattice properties.[7,8] In the present study it has been shown, for the first time, that anomalies arise in the temperature dependence of the thermal expansion coefficient, $\beta(T)$, and the elastic moduli, $C_{ij}(T)$, in weak band ferromagnets such as $ZrZn_2$, MnSi, and Ni_3Al and also antiferromagnets (chromium) because of particular features of the electronic structure of these materials.

An important prerequisite for the occurrence of ferromagnetism in *d* metals and alloys (except in narrow-band ferromagnets of the $Fe_{1-x}Co_xS_2$ type) is that E_F be close to the peak in $N(E)$ in the paramagnetic phase. In typical cases (including the free-electron approximation) these peaks arise upon the coalescence of two 3D square root VHSs, which are associated with critical points which lie on a line l (Ref. 9; in iron, l is the PN line[6]). The $N(E)$ peak then has an effective 2D VHS:[9] $\delta N(E) \propto \ln|E-E_c|$. If the quantity $\eta = E_c - E_F$ is small in the paramagnetic phase, the Stoner condition for ferromagnetism holds. In the Stoner picture, the electron spectrum in the ferromagnetic phase is split by $\Delta = IM(T)$, where M is the magnetization, and I the Stoner parameter. For magnetic materials with well-defined local moments with an amplitude S_L we have[10] $\Delta = IS_L(T)$. In any case, we can assume that the E_c feature splits in two, and the resulting components are separated from E_F by $\eta_\pm = \eta \pm \Delta/2$. There is no change in the shape of the $N(E)$ peaks. As temperature is varied, the structural features then shift by virtue of the $\Delta(T)$ dependence. Virtual transitions from peaks at the Fermi level and back lead to anomalies in the polarization operator and in the dynamic matrix $D_{\alpha\beta}(\mathbf{q})$ ($\mathbf{q}$ is the phonon wave vector) and thus in the phonon part of the free energy, F_{ph}, and in the lattice properties.[7,8] Virtual transitions between peaks with spin up and spin down can be ignored since the spin–orbit coupling is weak (we are excluding from consideration here the actinide systems, for example).

Anomalous contributions to the lattice properties in the limit $\eta \to 0$ have been found[8] in the model of nearly free electrons for a standard root VHS. Since the energy remains constant along line l in this case, only the dispersion in the perpendicular direction is important. We thus consider the 2D case; correspondingly, we are dealing with an effective logarithmic VHS in a 3D system. For definiteness we assume that l lies at the boundary of the Brillouin zone [this is true for both Fe (Ref. 6) and $ZrZn_2$ (Ref. 5)]. As was shown in Ref. 8, the most singular contributions to the dynamic matrix are then independent of $\mathbf{q}$:

$$D_{\alpha\beta}^{\text{sing}} = -\frac{1}{M} g\alpha g\beta |V(\mathbf{g})|^2 (\Pi_{\mathbf{g},\mathbf{g}}^{\text{sing}} - \Pi_{\mathbf{g},-\mathbf{g}}^{\text{sing}}) , \tag{1}$$

where M is the mass of the ion, $\mathbf{g}$ is the reciprocal-lattice vector for the given face, $V(g)$ is a Fourier component of the crystal potential, and $\hat{\Pi}$ is the polarization operator. Separating out the singularities in

$$F_{ph} = T \sum_{\mathbf{q}\nu} \ln\left(2 \sinh \frac{\omega\mathbf{q}\nu}{2T}\right) \tag{2}$$

($\omega\mathbf{q}\nu$ is the phonon spectrum), we find the anomalous contributions to

$$\beta_{ph}(T) = \frac{\partial^2 F_{ph}}{\partial T \partial P}, \quad C_{ij}^{ph}(T) = \frac{1}{\Omega} \frac{\partial^2 F_{ph}}{\partial u_i \partial u_j}, \tag{3}$$

where Ω is the atomic volume, P is the pressure, and u_i are strain parameters. The electron contributions β^e and C_{ij}^e can be expressed directly in terms of either $N(E)$ or $\hat{\Pi}$ (Ref. 8).

In the two-wave model (the simplest one), which incorporates a mixing of the electron states $|\mathbf{k}\rangle$ and $|\mathbf{k}-\mathbf{g}\rangle$ for only a single $\mathbf{g}$, the singular contributions to the observable quantities are

$$\delta N(E_F) = -\frac{1}{4\pi^2 E_0} \left(\frac{v}{2}\right)^{1/2} \ln|\alpha + v|, \tag{4}$$

$$\delta C_{ij}^e = -\frac{E_0}{\sqrt{2}\Omega} \frac{\partial(\alpha+v)}{\partial u_i} \frac{\partial(\alpha+v)}{\partial u_j} \delta N(E_F), \tag{5}$$

$$\delta\omega_{\mathbf{q}\nu}^2 = \frac{\sqrt{2}}{M} |\mathbf{g}\mathbf{e}_{\mathbf{q}\nu}|^2 E_0 v^{3/2} (\alpha + v) \ln|\alpha + v| . \tag{6}$$

Here $\mathbf{e}_{\mathbf{q}\nu}$ is a polarization vector; $E_0 = g^2/(8m^*)$ (m^* is the effective mass); $v = |V(\mathbf{g})|/E_0$; and $\alpha = (E_F - E_0)/E_0$ ($\alpha + v \equiv -\eta/E_0 \to 0$). It can be shown that the nature of the singularities in terms of η remains the same in the general case of a logarithmic VHS.

It follows from (5) and (6) that, as in the case in Ref. 8, the singularity in the phonon frequencies at values of $\mathbf{q}$ which are not too small is weaker by one power of η than in the acoustic region, where we have $\delta\omega^2_{\mathbf{q}\nu} \sim \delta C_{ii}\mathbf{q}^2 \sim \mathbf{q}^2 \ln|\eta|$. The nature of the singularity changes at

$$q_s \sim g|V(g)\eta|^{1/2}/E_0. \tag{7}$$

The corresponding characteristic temperature for the lattice properties is $T_s = T_D q_s/g$, where T_D is the Debye temperature.

In the case of a ferromagnet we have a sum of singular contributions with $\eta \to \eta_\pm = \eta \pm \Delta/2$. In typical cases (except in the close vicinity of T_C) the relation $|\eta| \ll \Delta$ holds. A calculation of the electron and phonon singular contributions to $\beta(T)$ and of the temperature-dependent part of C_{ii} yields

$$\delta\beta_e(T) \sim T \sum_{\sigma=\pm} \frac{\partial \ln|\eta_\sigma|}{\partial P} \sim \frac{T}{\Delta}\frac{\partial\Delta}{\partial P}, \tag{8}$$

$$\delta C^e_{ii}(T) \sim -\frac{1}{\Omega}\left(\frac{T}{\Delta}\right)^2\left(\frac{\partial\Delta}{\partial u_i}\right)^2, \tag{9}$$

$$\delta\beta_{ph}(T) \sim \begin{cases} \left(\dfrac{T}{T_D}\right)^3 \dfrac{1}{\Delta}\dfrac{\partial\Delta}{\partial P}, & T \ll T_s, \\ T^3 \sum\limits_\sigma \dfrac{\partial\eta_\sigma}{\partial P}\ln\left|\dfrac{\eta_\sigma}{E_F}\right| \sim T^3 \dfrac{\partial\eta}{\partial P}\ln\dfrac{\Delta}{E_F}, & T_s \ll T \ll T_D, \\ \sum\limits_\sigma \dfrac{\partial\eta_\sigma}{\partial P}\ln\left|\dfrac{\eta_\sigma}{E_F}\right| \sim \dfrac{\partial\eta}{\partial P}\ln\dfrac{\Delta}{E_F}, & T > T_D, \end{cases} \tag{10}$$

$$\Omega\delta C^{ph}_{ii}(T) \sim \begin{cases} -\left(\dfrac{T}{T_D}\right)^4 \dfrac{1}{\Delta^2}\left(\dfrac{\partial\Delta}{\partial u_i}\right)^2, & T \ll T_s, \\ T^4 \dfrac{\partial\eta}{\partial u_i}\dfrac{1}{\Delta}\dfrac{\partial\Delta}{\partial u_i}, & T_s \ll T \ll T_D, \\ T \dfrac{\partial\eta}{\partial u_i}\dfrac{1}{\Delta}\dfrac{\partial\Delta}{\partial u_i}, & T > T_D. \end{cases} \tag{11}$$

As an example we consider magnetovolume anomalies in the weak band ferromagnetic $ZrZn_2$, where we have $\beta(T < T_c) < 0$, and where there is a sharp anomaly at T_c (Ref. 11). A corresponding behavior is seen in MnSi (Ref. 12). The explanation offered in Ref. 1 is unconvincing, since it is based on the assumption that $S_L(T)$ has a minimum at $T = T_c$; this assumption is not supported by the more systematic analysis of Ref. 13, which leads to a minimum at $T^* \sim T_c^2/E_F$. On the other hand, expression (10) leads immediately to the required behavior $\beta_{ph}(T)$, when we note that we have $\partial\Delta/\partial P<0$ and $\partial\eta/\partial P>0$ according to the fact that the ferromagnetism is suppressed with increasing P (Ref. 14)and also according to an analysis of the results of a band-theory calculation.[5] In contrast with Ref. 1, expression (10) allows the magnetic contribution to $\beta(T)$ to have either sign, depending on the sign of $\partial\eta/\partial P$.

We turn now to the case of band antiferromagnetism. In contrast with ferromagnetism, there may be no well-expressed VHS near E_F (as in Cr, for example), but there frequently is (e.g., as in UPt_3). A VHS definitely does exist in those antiferromagnets which are inclined toward a transition to a ferromagnetic state (e.g., FeRh and alloys of the Invar type). If we ignore the contribution of spin–flip processes to $\hat{D}(\mathbf{q})$ (the spin–orbit coupling is slight), then in calculating the anomalous contributions to F_{ph} we should treat the antiferromagnetism vector of the structure, **Q**, as a vector of "general position," in the sense that Umklapp processes involving **Q** do not lead to any important anomalies in $\Pi\mathbf{g},\mathbf{g}'$, regardless of **g** and **g**$'$. [In the opposite case, for an antiferromagnetic structure with a period doubling, the role of **g** in $\hat{D}(\mathbf{q})$ is played by the magnetic vectors of the reciprocal lattice.] We then have[7,8]

$$\delta F_{ph}\sim-\delta\,\bar{\Pi}\equiv-\delta\sum_{\mathbf{q}}\Pi(\mathbf{q}),\tag{12}$$

where $\Pi(\mathbf{q})$ is the static polarization operator in the RPA. For simplicity we adopt a "nesting" model, $\epsilon_{\mathbf{k}}=-\epsilon_{\mathbf{k}+\mathbf{Q}}$, where $\epsilon_{\mathbf{k}}$ is the electron spectrum reckoned from E_F. In the antiferromagnetic phase, with a spectrum $E_{\mathbf{k}}=\pm(\epsilon_{\mathbf{k}}^2+\Delta^2)^{1/2}$ (Δ is the direct antiferromagnetic gap), we then find

$$\bar{\Pi}=\sum_{\mathbf{k}\mathbf{k}'}\frac{2\epsilon_{\mathbf{k}}^2}{E_{\mathbf{k}}}\frac{1}{\epsilon_{\mathbf{k}}^2-\epsilon_{\mathbf{k}'}^2}\tanh\frac{E_{\mathbf{k}}}{2T},\quad \bar{\Pi}\,(T\ll\Delta)=\sum_{\mathbf{k}\mathbf{k}'}\frac{1}{E_{\mathbf{k}}+E_{\mathbf{k}'}}\left(1+\frac{\Delta^2}{E_{\mathbf{k}}E_{\mathbf{k}'}}\right).\tag{13}$$

At $T\ll\Delta\ll W=Q^2/2m^*$ we find from (13)

$$\frac{\partial\bar{\Pi}}{\partial\Delta}=4N(0)\Delta\int_{-\infty}^{\infty}\frac{d\epsilon}{(\epsilon^2+\Delta^2)^{1/2}}\ln\left[\frac{\epsilon+(\epsilon^2+\Delta^2)^{12}}{\Delta}\right]\frac{\partial N(\epsilon)}{\partial\epsilon}.\tag{14}$$

If the seed density of state, $N(\epsilon)$, is a regular function near $\epsilon=0$, we can distinguish a singularity in $\bar{\Pi}$ and thus in F_{ph} on the order of $\pm\Delta^2\ln\Delta$. The corresponding contributions to the lattice properties are

$$\delta\beta_{ph}\sim\pm\frac{\partial\Delta^2}{\partial P}\ln\frac{\Delta}{W},\quad \delta C_{ii}(T)\sim\pm\frac{1}{\Delta^2}\left(\frac{\partial\Delta^2}{\partial u_i}\right)^2.\tag{15}$$

This result differs from the usual electron contribution in having a large logarithmic factor, which is associated with particular features of the band structure in the antiferromagnetic phase (the formation of a gap). Under the condition $\Delta\ll T$ (in a small neighborhood of the Néel point) we have $\ln\Delta\to\ln T_N$. The result in (15) leads to a qualitative explanation of the magnetovolume and magnetoelastic anomalies in Cr as $T\to T_N-0$ [the negative values of $\beta(T)$ and the sharp decrease in the compressional modulus[15]]. The weaker anomalies as $T\to T_N+0$ are apparently associated with a short-range antiferromagnetic order.

If $N(\epsilon)$ has an ordinary root VHS at $\epsilon=0$, then we find $\delta F_{ph} \sim \pm \Delta^{3/2}$ from (14). If it has a logarithmic VHS (as in the case of a square lattice at the center of the band), then the singularity is greatly strengthened: $\delta F_{ph} \sim \pm \Delta \ln \Delta$. The anomalies in β_{ph} and C_{ii} are strengthened in a corresponding way.

In summary, pronounced anomalies in the lattice properties are characteristic of cases in which Δ varies rapidly upon a variation in external parameters. This case is typical near points of rapid changes in local moments, in particular, for alloys of the Invar type, in which there is furthermore an antiferromagnetic-ferromagnetic transition. The pronounced magnetoelastic anomalies in the paramagnetic phase of the antiferromagnetic Cu–Mn system are also interesting.[16]

Actinide systems also exhibit some clearly expressed magnetoelastic and magnetovolume anomalies.[17,18] In this case, relativistic processes with spin flip are important in the analysis, and all the singularities should be stronger: In (5) we have $\ln \Delta \rightarrow 1/\Delta$, and in the case of an antiferromagnet we should examine, instead of the anomalies in $\bar{\Pi}$ in (12), the stronger anomalies associated with Umklapp processes, as in the case of a ferromagnet.

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