Phenomenological Free-Energy Density Describing the Spin-Density-Wave State of Chromium

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Either the free-energy density describing the spin-density-wave state of chromium must be allowed to depend on the electron density and local state of strain of the crystal (as well as the order parameter) or highly nonlocal contributions to the free energy must be included. The theory describes the linear polarization of the spin-density-wave state of chromium, and other observable properties.

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A widely used phenomenological approach to incommensurable systems assumes that the free energy can be written as a volume integral of a local free-energy density, the free-energy density being expanded in powers of the order parameter. Such theories have been developed by Shimizu[1] for the spin-density-wave (SDW) state of chromium, and by McMillan[2] for the charge-density-wave state of the transition-metal dichalcogenides.

In the case of chromium, incommensurability manifests itself in a relatively slow spatial modulation of the basic antiferromagnetic structure, the modulation period being approximately 25 lattice constants near the Néel temperature.[3] The SDW state of chromium is thus inhomogeneous, and this paper argues that it is therefore essential to assume that the free-energy density is a function not only of the local value of the order parameter, but of local values of other variables (such as the local state of strain and the local conduction electron density) as well. It is true that the local electron density and strain tensor can be found as functions of the order parameter, and that the free energy can thus be expressed as a function of the order parameter only; however, when this is done the free energy is found to contain what we call highly nonlocal terms [see Eq. (9)] and thus has a radically different structure from what is usually assumed. The proposed theory is thus substantially different in its structure from previous theories.

The theory described below allows a second-order (within mean-field theory, cf. Bak and Mukamel[4]) transition to a linearly polarized SDW state and can thus describe the SDW state of chromium. On the other hand, Shimizu's approach allows a second-order transition only to a helical SDW state [see the discussion between Eqs. (11) and (12)] and it was a desire to correct this defect which provided the impetus for a reexamination of the basic structure of the theory.

The spin density in chromium will be written in the form

$$\vec{S}(\vec{x}) = \vec{n}(x) S_0(\vec{x}), \tag{1}$$

where $S_0(\vec{x})$ describes the spatial variation of the spin density of a commensurable antiferromagnetic state and $\vec{n}(\vec{x})$ describes a relatively slowly varying amplitude modulation of the basic antiferromagnetic structure. The free-energy density at a given point $\vec{x}$ will be assumed to depend on the order parameter $\vec{n}(\vec{x})$ and its spatial gradients, the local state of strain as described by the components $e_1(\vec{x}), e_2(\vec{x}), \ldots, e_6(\vec{x})$ of the strain tensor, and the conduction-electron density averaged over a unit cell, $\rho_e(\vec{x})$. Allowing the free-energy density to depend on $\rho_e(\vec{x})$ and taking account of the fact that the strain fields $e_1(\vec{x}), \ldots, e_6(\vec{x})$ are not all independent of each other [e.g., in arriving at Eq. (6) below] represent our principal extensions of Shimizu's approach. Strains will be measured relative to the state at the Néel temperature, T_{N0}, in zero stress; also, the conduction-electron density will be described in terms of the variable $e_7 = \rho_e - \rho_{e0}$, ρ_{e0} being the value of ρ_e at the Néel temperature at zero stress. Thus, close to the Néel temperature, an expansion in powers of the e_i's and n_α's yields, for the Helmholtz free energy,

$$F = F_0 + \int d^3x \{ \tfrac{1}{2} n_\alpha A(-i\nabla) n_\alpha + \tfrac{1}{4} B n^4 + \Lambda_{i'} e_{i'} + \tfrac{1}{2} c_{i'j'} e_{i'} e_{j'} + \tfrac{1}{2} G_{i'} e_{i'} n^2 \}, \tag{2}$$

where the conventions $\alpha, \beta = x, y, z$; $i, j, k, 1 = 1, 2, \ldots, 6$; $i', j', k', 1' = 1, 2, \ldots, 7$; and the summation convention are used. F_0 and the coefficients appearing in (2) are functions of temperature only. The nonzero values of the coefficients are easily found by symmetry arguments keeping in mind the cubic symmetry of chromium, the second-rank tensor nature of the e_i's, and the scalar nature of e_7. The independent nonzero $c_{i'j'}$'s are the three independent elastic constants of a cubic crystal, c_{11}, c_{12}, and c_{44}, together with the constant c_{17}. The independent nonzero values of the $\Lambda_{i'}$'s and $G_{i'}$'s are Λ_1, Λ_7, G_1, and G_7. The quantity $A(-i\nabla)$ is given by

$$A(\vec{\delta}) = A_0 + A_2\delta^2 + A_4'\delta^4 + A_4''(\delta_x{}^4 + \delta_y{}^4 + \delta_z{}^4). \tag{3}$$

In writing (2) spin-orbit coupling effects have been neglected, and the free-energy density is thus a function of the quantity $n^2 = n_\alpha n_\alpha = \vec{n}(\vec{x})\cdot\vec{n}(\vec{x})$ which is a scalar in spin space. Also, since $\vec{n}(\vec{x})$ is slowly varying, gradients of the terms in n^4 and $e_{i'}n^2$ have been neglected. A more detailed discussion[5] shows that these effects are indeed relatively small, although important for the interpretation of certain measurements. Thus, the free energy of Eq. (2) allows the principal thermodynamic properties of chromium to be accounted for, while keeping the derivations relatively simple.

Now write

$$e_{i'} = \langle e_{i'}\rangle + \delta e_{i'} \tag{4}$$

the angular brackets denoting a volume average, i.e., $\langle e_{i'}\rangle \equiv V_0{}^{-1}\int d^3x\, e_{i'}$, V_0 being the crystal volume. Note that $\langle e_7\rangle = 0$ since the number of electrons in the crystal is assumed fixed. The free energy thus becomes $F = F_1 + F_2$, where F_1 is F [of Eq. (2)] evaluated at $e_{i'} = \langle e_{i'}\rangle$ and

$$F_2 = \int d^3x \{\tfrac{1}{2}c_{i'j'}\,\delta e_{i'}\,\delta e_{j'} + \tfrac{1}{2}G_{i'}\,\delta e_{i'}\,n^2\}. \tag{5}$$

F_2 (and hence F) is now minimized with respect to δe_7 and to the displacement fields u_α occurring in $\delta e_{\alpha\beta} = \frac{1}{2}(\partial u_\alpha/\partial x_\beta + \partial u_\beta/\partial x_\alpha)$, giving

$$\partial[c_{\alpha\beta\gamma\delta}\,\delta e_{\gamma\delta} + c_{\alpha\beta;7}\,\delta e_7 + \tfrac{1}{2}G_{\alpha\beta}n^2]/\partial x_\beta = 0, \tag{6}$$

$$c_{\alpha\beta;7}\delta e_{\alpha\beta} + c_{77}\delta e_7 + \tfrac{1}{2}G_7[n^2 - \langle n^2\rangle] = 0. \tag{7}$$

The solution of Eq. (6) is simplified by assuming that all quantities $\delta e_{i'}$ and n_α depend only on a single coordinate, say z, as is appropriate for chromium. With this assumption, $\delta e_1 = \delta e_2 = \delta e_4 = \delta e_5 = \delta e_6 = 0$. Also, defining the 2×2 matrix $s_{st}{}^{(2)}$ to be the inverse of the matrix c_{st}, where s and t take the values 3 and 7 only, one finds

$$\delta e_s(z) = -\tfrac{1}{2}s_{st}{}^{(2)}G_t[n^2 - \langle n^2\rangle]. \tag{8}$$

Substituting (8) into (5) gives

$$F_2 = -\tfrac{1}{4}B''\int n^4\,d^3x + \tfrac{1}{4}B''V_0{}^{-1}\iint n^2(z)n^2(z')\,d^3x\,d^3x', \tag{9}$$

where $B'' = \frac{1}{2}G_s s_{st}{}^{(2)}G_t$. The last term in (9) will be called a highly nonlocal term; terms such as this have not been exhibited in previous theories of incommensurable systems, but have been noted in a discussion of the critical behavior of compressible magnets.[6] Such highly nonlocal terms have been derived[7] within the framework of microscopic theory (neglecting strains) by generalizing the method of Malaspinas and Rice.[8] It is clear from (9) that one can not neglect the dependence of the free-energy density on local variables such as the $e_{i'}$'s and still write the free energy as an integral of a local free-energy density, as has often been done (e.g. in Ref. 2).

Now assume that the order parameter has the form

$$\vec{n}(z) = \vec{S}e^{i\delta z} + \vec{S}^*e^{-i\delta z}. \tag{10}$$

The Gibbs free energy per unit volume, $G = (F/V_0) - \sigma_i\langle e_i\rangle$, is now found, with use of (2), (8), and (10), to be

$$G = G_0(T) - \tfrac{1}{2}\sigma_i s_{ij}\sigma_j + \sigma_i s_{ij}\Lambda_j + (A_\sigma + \sigma_i s_{ij}G_j)\vec{S}\cdot\vec{S}^* + B_\sigma'(\vec{S}\cdot\vec{S}^*)^2 + \tfrac{1}{2}B_\sigma''|\vec{S}\cdot\vec{S}|^2, \tag{11}$$

where s_{ij} is the inverse of c_{ij}, $B_\sigma' = B - \frac{1}{2}G_i s_{ij}G_j$, and $B_\sigma'' = B - \frac{1}{2}G_s s_{st}{}^{(2)}G_t$; A_σ is given by (2) with A_0 replaced by $A_{0\sigma} = A_0 - \frac{1}{2}\Lambda_i s_{ij}G_j$ and $\vec{\delta}$ in the z direction. A_σ can also be written $A_\sigma = a_\sigma(T - T_{\mathrm{N}0})$, $T_{\mathrm{N}0}$ being the Néel temperature at zero stress.

If $B_0'' > 0$ in Eq. (11) the helical state [e.g. $\vec{S} = (S_0, iS_0, 0)$] is stable, whereas if $B_\sigma'' < 0$, the linearly polarized state [e.g., $\vec{S} = (S_0, 0, 0)$] is stable. Thus, to have a second-order phase transition to a linearly polarized state as is appropriate for chromium, one must have both $B_\sigma'' < 0$ and $B_\sigma' + \frac{1}{2}B_\sigma'' > 0$; the definitions of B_σ' and B_σ'' given above allow this.

If the dependence of the free-energy density on the conduction-electron density is ignored, as has been done by Shimizu,[1] and as would be appropriate for a description of a localized Heisenberg model, the derivations proceed along similar lines, while now $B_\sigma' = B - \frac{3}{2}[G_1{}^2/(c_{11} + 2c_{12})]$ and $B_\sigma'' = \frac{1}{2}[B - \frac{1}{2}(G_1{}^2/c_{11})]$. Thus, if $B_\sigma'' < 0$, then $B_\sigma' < 0$ also (since $c_{11} > c_{12}$) and it is not possible for such a model to have a second-order phase transition to a linearly polarized state or to describe chromium.

A number of thermodynamic properties of chromium can be evaluated by use of Eq. (11) with $B_\sigma'' < 0$ and $B_\sigma \equiv 2B_\sigma' + B_\sigma'' > 0$. The Néel temperature, T_N, is found by setting the coefficient of $\vec{S}\cdot\vec{S}^*$ in Eq. (11) equal to zero; the stress derivative of T_N is then found to be

$$\partial T_N/\partial\sigma_i = -a_\sigma^{-1}(s_{11}+2s_{12})G_1, \quad i=1,2,3, \qquad (12)$$

and $\partial T_N/\partial\sigma_i = 0$, $i=4, 5, 6$. Since the Néel temperature decreases with increasing pressure, $G_1 < 0$.[9] The average strain is found using $\langle e_i\rangle = -\partial G/\partial\sigma_i$. The thermal expansion coefficients $\alpha_i \equiv \partial\langle e_i\rangle/\partial T$ have the discontinuities

$$\Delta\alpha_i = -a_\sigma B_\sigma^{-1}(s_{11}+2s_{12})G_1, \quad i=1,2,3, \qquad (13)$$

at the Néel temperature (the discontinuity in a quantity is the value just above T_N minus the value just below); also $\Delta\alpha_i = 0$ for $i=4, 5, 6$. Thus chromium should remain cubic (to a first approximation) below its Néel temperature and also $\Delta\alpha_1 > 0$, both predictions being in agreement with experiment.[10] The compliance matrix below T_N, s_{ij}^-, can be found using $s_{ij}^- = \partial\langle e_i\rangle/\partial\sigma_j$; the discontinuities in the s_{ij}'s at the Néel temperature are thus $\Delta s_{44} = 0$ while

$$\Delta s_{11} = \Delta s_{12} = -B_\sigma^{-1}(s_{11}+2s_{12})^2 G_1^2. \qquad (14)$$

The quantities in Eqs. (12), (13), and (14) satisfy the Ehrenfest-type relation

$$\Delta\alpha_i(\partial T_N/\partial\sigma_j) = -\Delta s_{ij}. \qquad (15)$$

The experimentally determined values $\Delta\alpha \sim 4\times10^{-6}$ K^{-1},[10] $\partial T_N/\partial\sigma_1 = -\frac{1}{3}(\partial T_N/\partial p) = 1.7\times10^{-9}$ K dyn^{-1} cm^2,[9] and $\Delta s_{11} = \Delta s_{12} = \Delta(E^{-1}) = -4\times10^{-15}$ dyn^{-1} cm^2 (Ref. 11; E is Young's modulus) satisfy (15) to within a factor of 2, which is all one can expect for a mean-field theory, such as the present one, which neglects critical fluctuations. As a final point note that the substitution of Eq. (10) into Eq. (8) shows that a charge-density wave and a longitudinally polarized strain wave at wave vector 2δ are predicted to accompany the SDW of wave vector δ, in agreement with experiment.[12] Furthermore, the amplitudes of these second-harmonic waves are proportional to $\vec{S}\cdot\vec{S}$ and their experimental observation[10] is clear evidence that the SDW in chromium is not helical (since $\vec{S}\cdot\vec{S}=0$ for a helical structure). Shimzu's approach[1] fails to predict the correct polarization of the strain wave.

The above theory has accounted for a number of properties of chromium not previously accounted for. A conclusion with regard to the principles of formulating phenomenological theories for incommensurable systems is that it is important to consider carefully what other local variables (such as strains or electron density) in addition to the order parameter, the free energy should be a function of. These other local variables can be neglected only at the expense of giving up the idea of a local free-energy density and including in the free energy such intrinsically nonlocal terms such as occur in Eq. (9), and perhaps others. These comments apply not only to the theory of the SDW state of chromium just discussed, but also to the widely used McMillan[2] theory of charge-density waves, and it appears desirable that the McMillan theory should be extended in a way similar to that described above.

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