Electronically Driven Lattice Instabilities

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A general and physically simple model based on rigorous formulations of the dielectric function is presented and used to explain the phonon anomalies in niobium and niobium carbide. The model contains the explicit q dependence of both the electron-phonon and electron-electron interactions for localized states near the Fermi energy and appears quite useful for explaining the q dependence of phonon anomalies and lattice instabilities in various systems.

There exists a large class of interesting materials involving transition-metal atoms which exhibit actual or incipient lattice instabilities. These instabilities are usually associated with anomalies in the phonon spectra and are believed to be "electronically driven." Quite often, such materials are found to have a relatively high density of d states at the Fermi level, and also exhibit good superconducting properties. We show that in metals with an appreciable density of d states at the Fermi level, self-consistent field theory predicts a tendency towards a collective electron instability arising from charge fluctuations between the d shells. Because of electron-phonon coupling, however, the electronic instability does not actually occur, but rather initially produces an anomaly in the phonon spectrum, and in some cases eventually drives the lattice into a structural transformation. We illustrate our arguments with calculations for Nb and NbC. In our model, the quasi-localized nature of the d wave functions is crucial in promoting such an instability, which cannot be obtained from quasi-free-electron models without postulating a large electron-electron *attraction* to overcome the Coulomb repulsion. We sketch only the elements of our model from which a simple heuristic picture can be drawn, since the requisite theoretical apparatus has already been developed and thoroughly discussed.[1-4] Thus, we shall consider the simplified situation of a single d band at the Fermi level, thereby avoiding the cumbersome matrix notation used for the actual calculations.

In the localized-orbital representation,[1-3] the dielectric screening matrix may be written as

$$\epsilon(\vec{Q},\vec{Q}') = \epsilon_1(\vec{Q},\vec{Q}') + v(\vec{Q}) f_d(\vec{Q}) \chi_d(\vec{q}) f_d^*(\vec{Q}'), \tag{1}$$

where the second term arises from the d band and the first term denotes all other contributions. In Eq. (1), $f_d(\vec{Q})$ is the form factor associated with a d orbital on a single site,

$$\chi_d(\vec{q}) = \sum_{\vec{k}} (n_{\vec{k}d} - n_{\vec{k}+\vec{q}d})/(E_{\vec{k}+\vec{q}d} - E_{\vec{k}d}), \tag{2}$$

and $v(\vec{Q})$ is the Fourier transform of the electron-electron interaction. For our qualitative results, intersite overlap of the localized d orbitals is neglected. The inverse of the dielectric function is given by[4]

$$\epsilon^{-1}(\vec{Q},\vec{Q}') = \epsilon_1^{-1}(\vec{Q},\vec{Q}') - \sum_{\vec{Q}'',\vec{Q}'''} \epsilon_1^{-1}(\vec{Q},\vec{Q}'') v(\vec{Q}'') f_d(\vec{Q}'') S(\vec{q}) f_d^*(\vec{Q}''') \epsilon_1^{-1}(\vec{Q}''',\vec{Q}'), \tag{3}$$

where

$$S(\vec{q}) = [V(\vec{q}) + 1/\chi_d(\vec{q})]^{-1}. \tag{4}$$

$V(\vec{q})$ is most transparently written in a site representation as

$$V(\vec{q}) = \sum_{l \neq 0} \Phi(l) e^{i\vec{q}\cdot\vec{l}} + U, \tag{5}$$

where U is the intra-atomic Coulomb integral and $\Phi(l)$ is the (screened) Coulomb integral between d-

state densities on sites 0 and l. To leading order, exchange effects may be incorporated by subtracting from $\Phi(l)$ and U the corresponding exchange integrals. For many cases the screening by the ϵ_1 term may enable one to restrict the sum over l to nearest neighbors. In this case, $V(\vec{q})$ will attain a minimum negative value at the zone boundary, for $\vec{q}$ along directions of high symmetry. In general. $S(\vec{q})$, $V(\vec{q})$, $\Phi(l)$, etc., are $n^2\times n^2$ matrices (n is the number of localized orbitals in the band complex). From Eq. (2) $\chi_d(\vec{q})$ can be shown to be proportional to the density of states $n_d(E_\text{F})$ at the Fermi level. If $n_d(E_\text{F})$ is sufficiently large, $V(\vec{q})+\chi_d^{-1}(\vec{q})$ may become quite small and a tendency towards an electronic instability occurs. An analysis of the electron-density response function shows that a large value of the second term in Eq. (3) corresponds to a greater tendency for the d electrons to redistribute themselves on the atoms with a periodicity $\vec{q}$ in response to an external potential, i.e., to set up a charge-density wave. The $V(\vec{q})$ in Eq. (4) corresponds to the potential energy to set up such a charge-density wave (per unit amplitude), while $\chi_d^{-1}(\vec{q})$ corresponds to the kinetic energy. The coupling of the d electrons to the lattice may, however, cause softening of a phonon at a different $\vec{q}$, as shown below.

For the case of small intersite overlap of d orbitals we may obtain the main contribution to the electron-phonon interaction by assuming a local pseudopotential $W(r)$ between the ions and the electrons.[5] With use of the density response function obtained from Eq. (3), the contribution to the dynamical matrix from the second term can be written

$$\Delta D_{\alpha\beta}(\vec{q}) = -W_\alpha(\vec{q})S(\vec{q})W_\beta(\vec{q}), \tag{6}$$

where

$$W_\alpha(\vec{q}) = -\sum_l e^{i\vec{q}\cdot\vec{l}} \int d^3r\, n_d(\vec{r})\epsilon_1^{-1}(\vec{r},\vec{l})\nabla_\alpha W(\vec{r}-\vec{l}),$$

which may be written in the parametrized form

$$W_\alpha(\vec{q}) = i\sum_l e^{i\vec{q}\cdot\vec{l}} A(l)\hat{l}_\alpha,$$

where $n_d(\vec{r})$ is the electron density associated with the d orbital and $A(l)$ is a scalar associated with a particular ring of neighbors. (The only effect of nonlocal pseudopotentials will be to convert A to a second-rank tensor, without appreciably affecting the qualitative features of our model.) In a nearest-neighbor approximation, $W_\alpha(\vec{q})$ vanishes at the zone boundary, implying that the lattice cannot couple effectively to take advantage of the incipient charge-density wave at that $\vec{q}$. However, for longitudinal polarization, $W(\vec{q})$ peaks halfway to the zone boundary so that for metals where the denominator of $S(\vec{q})$ is small, there will be a dip in the longitudinal modes at the $\vec{q}$ where $W^2(\vec{q})S(\vec{q})$ is maximized. With a simple local electron-ion pseudopotential, no anomalies occur in the above model for the transverse branches, which require the overlapping d-orbital part of the electron-phonon matrix elements. From Eqs. (4) and (6), we note that anomalies in the phonon spectrum may also arise from structure in $\chi_d(\vec{q})$ itself (e.g., due to Fermi surface nesting features, etc.), and in one-dimensional materials, as is well known, such structure will play a crucial role. However, for our calculations, we find that the most important feature of $\chi_d(\vec{q})$ is its overall magnitude, which is adequately represented by $n_d(E_\text{F})$.

For our calculations on Nb, we have employed the full matrix version of the above model in which we considered a threefold complex of T_{2g}-type orbitals at E_F, and used the atomic Hartree-Fock-Slater 4d orbitals for Nb. The "E_g band" in Nb lies generally above the Fermi level and will contribute only to the interband part of the screening function. The screening function ϵ_1 was assumed free-electron-like with $k_\text{F}=0.2\times 2\pi/a$, and both hybridization and interband effects were ignored. The 9×9 $V(\vec{q})$ matrix was calculated using a complete reciprocal lattice sum, and $\chi_d(\vec{q})$ was evaluated using the actual augmented-plane-wave energy bands crossing E_F. The $\vec{q}$ dependence in $\chi_d(\vec{q})$ was found to be very small along [100], with some structure along [111], in excellent agreement with the calculations of Cooke, Davis, and Mostoller.[6] However, the size of $n_d(E_\text{F})$ was the crucial factor in determining the size of the anomaly. The intra-atomic (screened) Coulomb interaction U was taken as 2 eV, although, since it combines additively with $1/\chi_d(q)$, variation of U is simulated by variation in the size of χ_d. The electron-ion interaction was approximated by a local pseudopotential of the form

$$\begin{aligned} W(r) &= e^2Z_s/r \quad (r \geq r_\text{mt}), \\ &= e^2Z_s/r_\text{mt} \quad (r < r_\text{mt}), \end{aligned} \tag{7}$$

where r_mt is the muffin-tin radius, Ω the unit cell volume, and Z_s is an effective ionic charge.

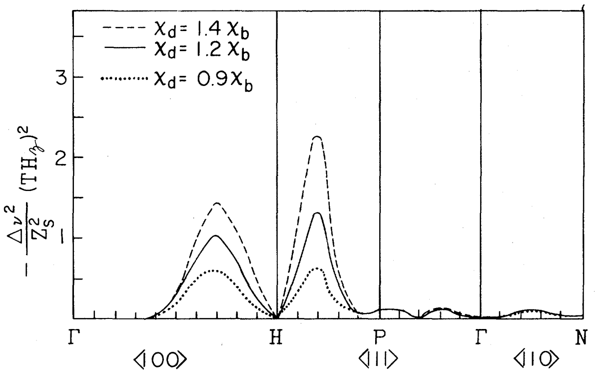

FIG. 1. The decrease in ν^2 for the longitudinal branches of Nb (in units of Z_s^2) due to the intra-d-band contributions to the dielectric function shown for different values of χ_d.

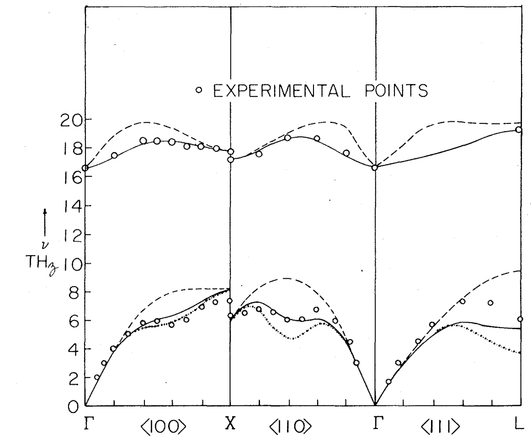

FIG. 2. Dispersion curves for longitudinal branches of NbC compared with measurements of Smith *et al.* Smooth curve corresponds to best-fit values within model. Dotted curve corresponds to 10% decrease in $A_{\mathrm{Nb}}, A_{\mathrm{C}}$. Dashed curve to $A_{\mathrm{Nb}}, A_{\mathrm{C}} \rightarrow \infty$. For the optic modes the smooth and dotted curves coincide.

The shift in the longitudinal phonon frequencies was calculated using the matrix generalization of Eq. (6). Figure 1 shows $-\Delta\nu^2$ expressed in terms of the square of the effective ionic charge Z_s for different values of α, where $\chi_d(\vec{q}) = \alpha\chi_b(\vec{q})$, $\chi_b(\vec{q})$ being the value of Eq. (2) calculated from the energy bands. The effect of α thus is to simulate a change of the magnitude of $\chi_d(\vec{q})$. We see that the effect of the screening associated with the "T_{2g} band" is to put dips into the longitudinal phonon branches at $(2\pi/a)(0.6,0,0)$ and $(2\pi/a)(0.8, 0.8, 0.8)$, whose magnitude goes rapidly to zero as χ_d decreases. The first anomaly is well known in Nb,[7,8] and the larger anomaly along [111] is probably masked by the dip that exists there in any simple bcc metal due to the direct ion-ion Coulomb interaction.[9] It is interesting to note that upon alloying Nb with Zr, an instability to the so-called ω phase is known to occur[10-12] which is characterized by a lattice displacement with $\vec{q} = (2\pi/a)(\frac{2}{3}, \frac{2}{3}, \frac{2}{3})$. The exact value of $\frac{2}{3}$ may be stabilized by third-order anharmonic terms in the free energy.

Finally, the longitudinal branches of NbC were calculated in similar fashion. However, in this case, the screening function ϵ_1 was taken to be a sum of a free-electron part (with only the Nb atoms assumed polarizable) *and* an interband part which was assumed to be of the generalized dipolar form.[4] It may be shown that the lattice equations of motion correspond to a generalization of the conventional "screened-shell-model" equations coupled to n^2 extra degrees of freedom representing the n^2 possible charge-fluctuation-type transitions between the orbitals in the d-band complex. Recent band calculations[13] show that this complex consists of T_{2g} d orbitals on the Nb atoms hybridized also with p orbitals on the C atoms. The latter were approximated by a single orbital on the C sites. If we completely neglect the $\vec{q}$ dependence of $\chi(\vec{q})$, and make approximations for the mixing coefficients of the T_{2g} Nb and C orbitals in the band complex, it may be shown that the second term of Eq. (3) may be expressed in terms of two parameters $A_{\mathrm{Nb}} = U_{\mathrm{Nb}} + 9/n_{\mathrm{Nb}}(E_{\mathrm{F}})$ and $A_{\mathrm{C}} = U_{\mathrm{C}} + 1/n_{\mathrm{C}}(E_{\mathrm{F}})$, where $n_{\mathrm{Nb}}(E_{\mathrm{F}})$ and $n_{\mathrm{C}}(E_{\mathrm{F}})$ are, respectively, the partial densities of states at E_{F} associated with the Nb and C orbitals. In the case where there is no appreciable density of localized states at E_{F}, A_{Nb} and $A_{\mathrm{C}} \rightarrow \infty$, and the effect due to these intraband transitions disappears. The shell-model parameters and the parameters A_{Nb}, A_{C} were fitted to the data of Smith and Glaser.[14] The results are shown in Fig. 2. Considering the simple model used in these calculations the agreement is quite gratifying. The dips were quite sensitive to the parameters A_{Nb}, A_{C} and could be made to disappear for large values of these parameters. The important point is that they always occurred at the observed $\vec{q}$ values, regardless of moderate changes in any of the parameters. We note that ZrC, which has a relatively small density of states at E_{F}, has similar dispersion curves but without the dips.[14] Weber has proposed an explanation of the phonon anomalies in the carbides in terms of a resonance in the electronic degrees of freedom. However, his model corresponds to an additional dipolar electronic fluctuation rather than charge fluctuation and consequently he must postulate an attractive direct electron-electron interaction between his supershells.[15]

The model proposed here may also explain the large superconducting transition temperatures found in many of the materials which possess anomalies in their phonon spectrum. The electron-phonon matrix elements are screened by the dielectric function of Eq. (3), and if $S(q)$ becomes large with $V(q)$ negative, the matrix elements for regions of k space coupled by this q will be considerably enhanced. Complete details and implications for superconductivity will be published in the more extended version of this work.

Our conclusion is simply that in metals with a relatively high density of localized states at E_F, anomalies in the phonon spectrum or even lattice instabilities may arise if the q-dependent electron-electron and electron-phonon interactions are favorable for an incipient charge-density wave to couple to the lattice. We have shown this to be true for Nb and NbC and believe the model to be applicable to many other materials. The effective electron-phonon coupling constant may be enhanced by such effects, giving rise to high superconducting transition temperatures. Full details will be published shortly.

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[1] W. Hanke, Phys. Rev. B 8, 4585 (1973).

[2] L. J. Sham, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1, Chap. 5.

[3] R. Pick, *Phonons* (Flammarion Press, Paris, 1971), p. 20.

[4] S. K. Sinha, R. P. Gupta, and D. L. Price, Phys. Rev. B 9, 2564, 2573 (1974).

[5] S. K. Sinha, Phys. Rev. 169, 477 (1968).

[6] J. F. Cooke, H. L. Davis, and Mark Mostoller, Phys. Rev. B 9, 2485 (1974).

[7] B. M. Powell, P. Martel, and A. D. B. Woods, Phys. Rev. 171, 727 (1968).

[8] B. N. Ganguly and R. F. Wood, Phys. Rev. Lett. 28, 681 (1972).

[9] D. L. Price, K. S. Singwi, and M. P. Tosi, Phys. Rev. B 2, 2983 (1970).

[10] J. C. Williams, D. de Fontaine, and N. E. Paton, Metall. Trans. 4, 2701 (1973).

[11] S. C. Moss, D. T. Keatings, and J. D. Axe, Solid State Commun. 13, 1465 (1973); H. W. Myron, S. C. Moss, and A. J. Freeman, to be published.

[12] C. W. Dawson and S. L. Sass, Metall. Trans. 1, 2225 (1970).

[13] D. J. Chadi and M. L. Cohen, Phys. Rev. B 10, 496 (1974).

[14] H. G. Smith and W. Glaser, in *Proceedings of the International Conference on Phonons, Rennes, France, 1971*, edited by M. A. Nusimovici (Flammarion, Paris, 1972), p. 145.

[15] W. Weber, Phys. Rev. B 8, 5082 (1973); W. Weber, H. Bilz, and U. Schröder, Phys. Rev. Lett. 28, 600 (1972).

Neutron-Scattering Study of the 38- and 54-K Phase Transitions in Deuterated Tetrathiafulvalene-Tetracyanoquinodimethane (TTF-TCNQ)

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Neutron-elastic-scattering experiments performed on deuterated TTF-TCNQ single crystals reveal two structural transformations at 38 ± 0.5 K and at 54 ± 1.0 K. Below 38 K, a $4\vec{a} \times 3.4\vec{b} \times \vec{c}$ modulation relative to the underlying undistorted lattice is established. At 38 K the modulation period in the $\vec{a}$ direction becomes incommensurate and displays an abrupt decrease from its low-temperature value of $4\vec{a}$ and gradually decreases with increasing temperature to $2\vec{a}$ near 51 K.

Recent x-ray diffuse-scattering experiments performed with photographic patterns, first clearly revealed the existence of a low-temperature long-range-ordered modulated lattice in the one-dimensional (1D) metal tetrathiafulvalene tetracyanoquinodimethane (TTF-TCNQ),[1] and suggest-