ing a vacancy. It turns out that the barrier height would have to be of the order of 0.38 eV, i.e., 13 times less than the electrostatic interaction energy between neighboring ions. In reality the Coulomb interaction will be effectively screened by the very polarizable host lattice so that $2V_0$ must be correspondingly lower in order to remain consistent with the observed displacements.

It is beyond the scope of this Letter to elaborate on the consequences of this very peculiar situation. Barrier heights of tenths of electron volts are typical for superionic conductors; we therefore suggest that such a Coulomb-interaction-imposed order is characteristic of many solid electrolytes. It is evident that in a system with strong displacive short-range order, diffusion is by no means a single-particle process. For an understanding of the low-frequency and dc conductivity of superionic conductors, models have to be found which properly account for the constant trend to re-establish the short-range order during the diffusion of ions.

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[1] *Fast Ion Transport in Solids*, edited by W. Van Gool (North-Holland, Amsterdam, 1973).

[2] Proceedings of the International Conference on Superionic Conductors, Schenectady, New York, 10–12 May 1976 (Plenum Press, to be published).

[3] H. Sato and R. Kikuchi, J. Chem. Phys. 55, 677 (1971).

[4] G. E. Murch and R. J. Thorn, J. Electrochem. Soc. 123, No. 3, 77C (1976).

[5] H. R. Zeller, P. Brüesch, L. Pietronero, and S. Strässler, in Proceedings of the International Conference on Superionic Conductors, Schenectady, New York, 10–12 May 1976 (Plenum Press, to be published).

[6] Y. Le Cars, R. Comès, L. Deschamps, and J. Thery, Acta Crystallogr. A30, 305 (1974).

[7] D. B. McWhan, S. J. Allen, J. P. Remeika, and P. D. Dernier, Phys. Rev. Lett. 35, 953 (1975).

[8] T. Hibma, H. U. Beyeler, and H. R. Zeller, J. Phys. C 9, 1691 (1976).

[9] T. H. Holland, Rec. Geol. Surv. India 23, 98 (1906).

[10] A. Byström and A. M. Byström, Acta Crystallogr. 3, 146 (1950).

[11] J. Singer, H. E. Kautz, W. L. Fielder, and J. S. Fordyce, in *Fast Ion Transport in Solids*, edited by W. Van Gool (North-Holland, Amsterdam, 1973).

[12] R. A. Huggins, Technical Report No. AD-782 365 (National Technical Information Service, Springfield, Va., 1974).

[13] W. L. Roth and O. Muller, Technical Report No. N-74-26498 (National Technical Information Service, Springfield, Va., 1974).

[14] J. Singer, H. Kautz, W. Fielder, and J. Fordyce, National Aeronautics and Space Administration Report No. NASA TM x-71753 (National Technical Information Service, Springfield, Va., 1975).

[15] C. Schüler, unpublished.

[16] A. Guinier, *X-Ray Diffraction* (W. H. Freeman and Co., San Francisco, 1963), p. 154.

Phonon Anomalies and Superconductivity in Transition-Metal Compounds

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We present a physically simple but general argument that explains the phonon anomalies and their interrelation to high T_c's in transition-metal compounds. It is shown that covalent-bond formation due to hybridization of metal d (T_{2g}) states and nonmetal p states near E_F leads to a resonancelike increase of the nonlocal dielectric function. This anomalous increase of the screening produces the phonon softening and explains the interrelation with the high T_c's as resulting from a simultaneous increase of the electron-phonon matrix elements and a decrease in the phonon energies.

Neutron-scattering studies revealed the existence of phonon anomalies in superconducting transition-metal compounds (TMC) like carbides and nitrides,[1] thus establishing an empirical correlation between actual or incipient lattice instabilities and high transition temperatures, T_c. While several discussions of this correlation have been given,[2-8] it seems that there exists no microscopic theory which explains the interdependence of phonon softening and superconductivity.

We present a semiquantitative analysis based on a rigorous microscopic theory which, for the first time, describes both longitudinal and transverse phonon anomalies, and in particular explains their connection with high T_c's. It is shown that hybridization of metal d (T_{2g}) states and nonmetal p states near the Fermi level E_F leads to a resonancelike increase of the nonlocal screening function ϵ^{-1}. By using a simple band model and the microscopic screening approach, it is demonstrated for NbC that this anomalous screening causes phonon softening both in longitudinal and transverse branches. The relation with high T_c's can only be explained by incorporating nonlocal p-d screening simultaneously in the electron-phonon matrix elements and in the phonon energies entering the attractive interaction. This again is verified in a model calculation for NbC. Our theory predicts that disappearance of the resonancelike p-d screening in the oxides and in TMC systems with vacancies is due to dehybridization of nonmetal p states, so that lattice softening and high T_c's should not be expected. This is indeed what has been found experimentally.[9]

The nonlocal screening function ϵ^{-1} is determined by

$$\epsilon^{-1} = 1 + v\tilde{\chi}\epsilon^{-1}, \tag{1}$$

where $\tilde{\chi}$ denotes the proper polarization part and v the Fourier transform of the Coulomb potential. In a Wannier or linear combination of atomic orbitals representation for the electronic wave functions, the polarizability quite generally is of the separable form[10-12]

$$\tilde{\chi}(\vec{q}+\vec{G}, \vec{q}+\vec{G}'; \omega) = \sum_{ss'} A_s(\vec{q}+\vec{G}) N_{ss'}(\vec{q};\omega) A_{s'}^{+}(\vec{q}+\vec{G}') \tag{2a}$$

or, in matrix notation,

$$\tilde{\chi} \equiv ANA^{+}. \tag{2b}$$

In Eq. (2a) $\vec{G}$ and $\vec{G}'$ are reciprocal-lattice vectors and the index s stands for the quantum numbers of the Wannier functions. A_s may be interpreted as a form factor for a generalized charge-density wave. In a metal it is convenient to separate out a diagonal (in $\vec{G}$ and $\vec{G}'$) part $\tilde{\chi} = -(\epsilon_0 - 1)/v$ from the polarizability.[10,13] The inverse dielectric matrix then becomes[10-13]

$$\epsilon^{-1} = \epsilon_0^{-1} + v\epsilon_0^{-1} A (N^{-1} - A^{+} v \epsilon_0^{-1} A)^{-1} A^{+} \epsilon_0^{-1}. \tag{3}$$

Here N^{-1} may be viewed as the kinetic energy of the density waves, and $V = A^{+} v \epsilon_0^{-1} A$ as their Coulomb energy. The solution ϵ^{-1} of Eq. (3) allows for an explicit inclusion of local-field effects, which become important whenever electrons with localized character participate in the screening.[10-14]

In the local-pseudopotential approximation the second term in Eq. (3), i.e., the term containing the local-field corrections, gives the contribution to the dynamical matrix[10-13]

$$E_{\alpha\beta}(\vec{q}) = \sum_{ss'} F_\alpha{}^{s}(\vec{q}) [N^{-1}(\vec{q}) - V(\vec{q})]^{-1} F_\beta{}^{s'+}(\vec{q}), \tag{4}$$

where $F_\alpha{}^{s}$ is the force experienced by an ion in direction α due to coupling to the density wave s.

We have put forward the idea that phonon anomalies can be related to a resonancelike increase of the screening matrix $(N^{-1} - V)^{-1}$.[15] Employing metal (d) on-site interactions in a parameterized version of the microscopic screening formalism, Sinha and Harmon were in fact able to reproduce the anomalies in the longitudinal phonon branches in NbC.[16] In this work an important role was assigned to the density of d states $n_d(E_F)$ at the Fermi energy E_F. The transverse anomalies, which are decisive for lattice instabilities, cannot be attributed to d-d scattering.[17] In our theory a high density of states at E_F is helpful but not necessary for phonon softening. As shown in the following calculation for NbC, the driving mechanism in our description is the inversion procedure [i.e., the screening matrix $(N^{-1} - V)$, the determinant of which becomes very small at the "anomalous" q vectors]. The density of d metal and p nonmetal states plays the role of a proportionality constant in the nonlocal screening contribution to the dynamical matrix [Eq. (4)].

A successful phenomenological model for the phonon dispersion of TMC has been developed by Weber *et al.*[18,19] Here the phonon dips are described as due to a resonance in second-nearest-neighbor (snn) shell interactions in the metal sublattice, which are interpreted as d (T_{2g}) interactions. The following study shows that the basic ingredients of this model description, a planar snn interaction in the metal sublattice, produce the correct phase relations and symmetries also in microscopic theory. Here, however, it is an snn interaction between hybridized (p-d) orbitals, resulting effectively in an nn overlap between metal (d) and nonmetal (p) wave functions.

Band-structure calculations[20] of superconducting carbides like NbC have confirmed x-ray emission spectra[21] which show a strong p-d (T_{2g}) hybridization near the Fermi level. The hybridization can be described in form of a covalent-ionic bonding with most important contributions coming from planar (π-type) p-d interactions. We consider a simple band model with the "p"- and "d"-

band complexes (Γ_{15} and $\Gamma_{25'}$ at the Γ point) constructed out of linear combinations of bonding and antibonding $(d+p)_\pi$ and $(d-p)_\pi$ hybrides. A bonding or antibonding hybrid located at $\vec{R}\equiv 0$ is formed by adding (bonding) or subtracting (antibonding), for example, a d_{xy} orbital at $\vec{R}\equiv 0$ and a p_y orbital at nn position $\vec{\tau}=(a/2)(100)$, where a is the lattice constant. Numerical analysis, based on our model for NbC, then shows that the dominant p-d contributions to the polarizability come from the diagonal terms $A_sN_{ss}A_s^+$, which are proportional to the phase factor $\sin^2(\vec{q}\cdot\vec{R}/2)$; here s stands for $(\vec{R},\pi)$, where $\vec{R}$ is the distance between the two hybrids in the plane π forming the matrix element A_s. Thus the nn p-d overlap contribution to the polarizability stems from snn hybrid overlap. The corresponding contribution to the dynamical matrix [Eq. (4)] peaks at positions $q_\alpha=\frac{1}{2}$ in reduced units. Higher-than-snn hybrid overlap tends to shift the peaks in ⟨100⟩ and ⟨110⟩ symmetry directions towards the zone boundary, in agreement with the experimental phonon dispersion.[1]

In our simplified model calculation in NbC, the p-d polarizability is treated in the nonlocal form ANA^+, confining p-d overlap to nn. All other contributions to the polarizability are approximated in a diagonal form $\tilde{\chi}_0$, with d-d metal and p-p nonmetal overlaps taken into account up to nn in the fcc sublattice. The p and d orbitals are expressed in Gaussian expansions of the corresponding Hartree-Fock-Slater atomic orbitals. We neglect the dependence of the polarizability matrix N on the eigenvectors of the band complex.[10] This "bare" susceptibility in the random phase approximation recently has been calculated by Gupta and Freeman for the three bands crossing the Fermi surface, using accurate augmented-plane-wave band-structure results.[22] Similar calculations for TaC have been performed by Klein, Papaconstantopoulos, and Boyer.[23] The intraband contribution to $N(q)$ shows maxima at the measured positions of the phonon anomalies. However, the interband contributions are large and, to some extent, anticorrelate with the intraband contributions[23]; i.e., they tend to diminish the pronounced maxima. Furthermore, recent work by Gupta and Freeman[24] demonstrates the importance of matrix elements which again tend to diminish structure in the polarizability. We evaluate $N(\vec{q})$ in the effective-mass model with the band parameters taken from the calculations of Schwarz.[25] It should be mentioned that about 20% of the total density of states at E_F is p-like. Thus in our theory, contrary to the work of Sinha and Harmon, the screening matrix $(N^{-1}-V)$ plays the dominant role in promoting phonon anomalies.

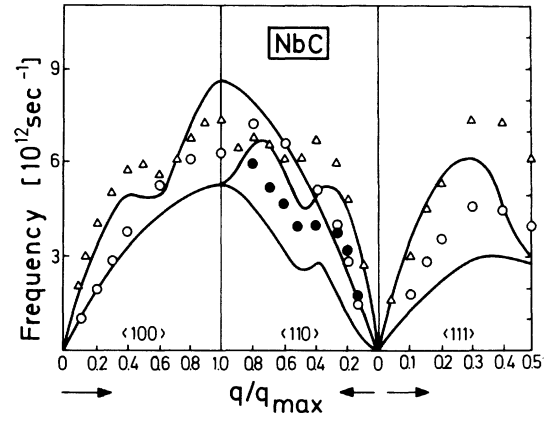

FIG. 1. Dispersion curves for acoustic phonon branches in NbC. Circles and triangles are the measured values of Smith and Gläser (Ref. 1).

We confine our phonon calculation in NbC to acoustic modes, which correspond predominantly to metal-atom vibrations.[19] In the results of Fig. 1, only the Nb vibrations are considered. Two parameters enter our calculation in form of a parametrized, local pseudopotential.[10] The parameters are adjusted so as to best reproduce the elastic constants C_{11} and C_{44}. The overall shape of the phonon dispersion is determined by d-d and p-p screening with a scalar response function $\tilde{\chi}_0$. The p-d screening causes the local minima in both longitudinal and transverse branches. The strength of the minima is diminished by dehybridization. It is essential to take the nonlocality of p-d screening into account; if we put the "local-field factor" $V=0$ in the screening matrix $(N^{-1}-V)^{-1}$, the phonon dips vanish on the scale of Fig. 1.

At the anomalous $\vec{q}$ vectors, the determinant $\det|N^{-1}-V|$ has a minimum giving rise to a sharp increase of the screening. Since $\det|N^{-1}-V|=0$ would correspond to a plasmon condition, we can interpret the softening mechanism as a tendency of the p-d waves to move collectively. An oscillator coupling between a bare phonon mode (screened only by ϵ_0^{-1}) and an actual plasmon mode can cause a lattice instability. A very effective coupling would arise, provided an "acoustical plasmon mode" exists.[2,5] With the help of Eq. (3), it can be shown that due to the local-field effect the plasmon frequency at $\vec{q}=0$ remains finite and corresponds to the energy required to make a rigid translation of the localized electrons.

To investigate the interrelation of phonon softening and high T_c's, we have expressed the phonon-induced electron-electron interaction in the strong-coupling approach in terms of the nonlocal dielectric function of Eq. (3).[26] The basic quantity entering is the electron-phonon spectral function $\alpha^2F(\omega)$ which, in the local-pseudopotential approximation, is given by

$$\alpha^2F(\omega) = \frac{\hbar}{4Mn(E_F)N}\, 2 \sum_{l,l'} \sum_{t,t'} \sum_{k,q} \exp(i\vec{k}\cdot\vec{R}_l)\exp[i(\vec{k}+\vec{q})\cdot\vec{R}_{l'}](1-VS^{-1})_{lt}[\vec{F}^t(\vec{q})\cdot\vec{e}(q)][\vec{F}^{t'}(\vec{q})\cdot\vec{e}(q)]$$
$$\times(1-VS^{-1})_{t'l'}\delta[E(k)-E_F]\delta[E(k+q)-E_F]\delta[\omega-\omega(q)]. \quad (5)$$

Here S is the screening matrix $(N^{-1}-V)$, M is the mass of an ion, and $\vec{q}=\vec{k}-\vec{k}'$. $\omega(q)$ and $E(k)$ denote phonon and electron energies, with q standing for the momentum and polarization of a phonon with polarization vector $\vec{e}(q)$ and k running over N wave numbers and band indices.

The relation between superconductivity and phonon anomalies usually is discussed in terms of the parameter[4] λ given by

$$\lambda = 2\int_0^\infty d\omega\, \alpha^2F(\omega)/\omega. \quad (6)$$

It is common practice to factorize λ into an averaged electron-phonon interaction and the phonon moment $\langle\omega^2\rangle$ which is calculated using the experimental dispersion.[27] It has been shown that the variation of the moment $\langle\omega^2\rangle$ caused by the anomalies is not enough to explain the variation of λ.[7]

The electron-phonon matrix elements which enter α^2F and λ show a significant enhancement at the anomalies due to the resonancelike increase of the p-d screening described by the matrix VS^{-1} in Eq. (5). Since simultaneously the matrix elements increase and the phonon frequencies decrease, we expect a pronounced enhancement of λ due to the (p-d) local-field effect. Using our simple model of the electron-phonon coupling in NbC we have evaluated λ for three different cases: In (a) the local field effects are neglected ($V=0$) both in the matrix elements and in the frequencies, in (b) these effects are included in calculating the phonon frequencies, and in (c) the p-d local field effects are taken into account simultaneously in the matrix elements and in the frequencies. The value for the coupling constant in case (a) is $\lambda=0.4$, in case (b) is $\lambda=0.5$, and in case (c) is $\lambda=0.6$. While these absolute values in view of our simplified model (and because we consider metal-sublattice interactions) are rather crude, the relative changes should be more reliable. With use of the standard expression[28] which relates T_c to λ with a Coulomb repulsion $\mu=0.1$, the relative change in T_c can be calculated. The change $\Delta\lambda=0.1$ due to neglect of local field effects in the matrix elements reduces the experimental T_c value of 11.1°K to 6.2°K. The further neglect of these effects in $\omega(q)$ brings T_c down to 2.7°K.

For one specific transition metal, when we go from the carbides to the oxides, band-structure calculations show a decrease in the nonmetal(p)-metal(d) hybridization.[20] Although the total density of states is larger for the oxides, our formalism explains the low T_c values for the oxides, contrary to previous theories. Similarly the very low T_c values and the absense of phonon anomalies in TMC with vacancies can be understood, since the empty p states which are essential for the hybridization mechanism are no longer available.[29]

In summary, we have described a simple model based on rigorous formulations of the microscopic theory which, for the first time, explains both phonon anomalies and high T_c's in TMC as resulting from a sharp increase of the nonlocal screening due to covalent-bond formation near E_F. Our results suggest p-d hybridization and the screening resonance to be quite generally the decisive mechanism for phonon softening and its interrelation with high-temperature superconductivity in a large class of materials involving transition-metal atoms.

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[1] H. G. Smith and W. Gläser, Phys. Rev. Lett. 25, 1611 (1970), and 29, 353 (1972).

[2] H. Fröhlich, Phys. Lett. A26, 169 (1968).

[3] H. R. Zeller, Phys. Rev. B 5, 1813 (1972).

[4] P. B. Allen and M. L. Cohen, Phys. Rev. Lett. 29, 1593 (1972).

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

[6] J. C. Phillips, in *Superconductivity in d- and f-Band Materials*, AIP Conference Proceedings No. 4, edited by D. H. Douglass (American Institute of Physics, New York, 1972).

[7] W. Weber, Phys. Rev. B 8, 5093 (1973).

[8] S. T. Chui, Phys. Rev. B 9, 3300 (1974).

[9] A. L. Giorgi, E. G. Szklarz, E. K. Storms, A. L. Bowman, and B. T. Matthias, Phys. Rev. 125, 837 (1962).

[10] W. Hanke, Phys. Rev. B 8, 4585, 4591 (1973).

[11] 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.

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

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

[14] W. Hanke and L. J. Sham, Phys. Rev. B 12, 4501 (1975).

[15] W. Hanke and H. Bilz, in *Proceedings of the International Conference on Inelastic Scattering of Neutrons* (International Atomic Energy Agency, Vienna, 1971).

[16] S. K. Sinha and B. H. Harmon, Phys. Rev. Lett. 35, 1515 (1975).

[17] W. Hanke, J. Hafner, and H. Bilz, in Proceedings of the International Conferenc on Low-Lying Vibrational Modes and their Relation to Superconductivity and Ferroelectricity, San Juan, Puerto Rico, 1975 (to be published).

[18] W. Weber, H. Bilz, and U. Schröder, Phys. Rev. Lett. 28, 600 (1972).

[19] W. Weber, Phys. Rev. B 8, 5082 (1973).

[20] A. Neckel, P. Raste, R. Eibler, P. Weinberger, and K. H. Schwarz, J. Phys. C 9, 579 (1976).

[21] L. Ramqvist, B. Ekstig, E. Källne, E. Noreland, and R. Manne, J. Chem. Phys. Solids 32, 149 (1971).

[22] M. Gupta and A. J. Freeman, Phys. Rev. Lett. 37, 364 (1976).

[23] B. M. Klein, D. A. Papaconstantopoulos, and L. L. Boyer, in Proceedings of the Second Rochester Conference on Superconductivity in *d*- and *f*-Band Metals Rochester, New York, 1976 (to be published).

[24] R. P. Gupta and A. J. Freeman, Phys. Rev. B 13, 4316 (1976).

[25] K. H. Schwarz, J. Phys. C 8, 809 (1975).

[26] J. Bar-Sagi and W. Hanke, in Proceedings of the International Conference on Low-Lying Vibrational Modes and their Relation to Superconductivity and Ferroelectricity, San Juan, Puerto Rico, 1975 (to be published).

[27] B. M. Klein and D. A. Papaconstantopoulos, Phys. Rev. Lett. 32, 1193 (1974).

[28] R. C. Dynes, Solid State Commun. 10, 615 (1972).

[29] K. H. Schwarz and N. Rösch, J. Phys. F 6, L433 (1976).

Charge Transfer in Amorphous Colored WO_3 Films Observed by X-Ray Photoelectron Spectroscopy

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X-ray photoemission spectra of W core levels and valence band in transparent and *in situ* uv-colored amorphous WO_3 films show that coloration is related to the existence of occupied electronic W^{5+} states situated ~ 2 eV above the valence band and localized on some tungsten sites. It is shown that x-ray photoelectron spectroscopy and optical data are understood if one considers the formation of a hydrogen-tungsten-bronze–like compound during uv irradiation.

Amorphous tungsten oxide thin films prepared by thermal evaporation under vacuum of WO_3 powder exhibit two stable states—the first one is transparent and highly resistive and the second one is blue and less resistive. Virgin layers are transparent. The blue coloration arises from a broad absorption band with a maximum at 900 nm (1.38 eV) and can be induced either by uv irradiation[1] ($h\nu > 3.4$ eV), by application of an electrical field[1] ($E \sim 10^4$ V/cm), or by proton injection.[2,3] Different models have been put forward on the origin of the absorption band.[1-3] In the earlier model, Deb[1] suggests F-center–like absorption between the fundamental and the excited states of an electron trapped in an oxygen vacancy. Later models[2,3] attribute the coloration to the existence of a hydrogen-tungsten-bronze H_xWO_3 formed by proton injection; Faughnan, Crandall, and McGee[2] suggest intervalence electron transfer between W^{5+} and W^{6+} valence states as a microscopic mechanism.

From optical measurements, the concentration of optical centers amounts to about 5×10^{20} and 10^{22} cm^{-3}, respectively, for uv coloration[1-4] and proton injection[2]; thus, x-ray photoelectron spectroscopy (XPS) demonstrates sufficient sensitivi-