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Charge-density distortions and lattice dynamics: A general theory and application to Nb

P. B. Allen
Department of Physics, State University of New York, Stony Brook, New York 11794
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A general formulation is given of phenomenological models for lattice dynamics which use localized electronic variables as additional adiabatic degrees of freedom. This formulation encompasses shell models of all types, bond-charge models, and charge-fluctuation models. Restrictions due to symmetry are discussed. In a specific application to Nb, Γ_1 (scalar), and $\Gamma_{25'}$ (quadrupolar) degrees of freedom are introduced. All symmetry-allowed parameters out to second-neighbor coupling are kept. The resulting 18-parameter model gives a good fit to the measured phonon dispersion, and a number of the parameters are found to be ignorable. The anomalies in the LA branches arise from interatomic-stabilized charge fluctuations, while the anomalies in TA branches are associated with dispersionless quadrupolar fluctuations. It is suggested that in a similar model for $A15$ metals, charge fluctuations alone might explain the TA anomalies.

I. INTRODUCTION

Many phenomenological models have been developed to interpret the lattice dynamics of ionic crystals.[1] A simplifying feature of ionic materials is localization of electronic charge around atoms. Distortion of electronic-charge clouds during lattice displacements can then be modeled with localized parameters. The shell model keeps only the induced electronic dipole moments. For nontransition metals the opposite situation holds: valence electrons are not localized, and charge-density distortions (CDD's) cannot be modeled with localized parameters. Fortunately, pseudopotential theory gives a good microscopic picture of induced CDD, making phenomenological models unnecessary. Covalent solids and d-band metals are intermediate cases. Microscopic theory is not yet able to calculate with sufficient accuracy the CDD's of these materials. On the other hand, since there is a fairly good degree of valence-charge localization (in the bonds between atoms for covalent materials, and around atoms for d-band metals), phenomenological descriptions with localized CDD parameters may be of some help in interpreting experiment and guiding microscopic theory. A number of steps in this direction have been taken, especially in the development of bond-charge models for covalent materials.[2] The situation for d-band metals is more obscure, partly because of the complexity of d-electron bonding, and partly because complex phonon spectra are observed, especially in materials with a high superconducting transition temperature.[3] Probably the best model for a truly complicated d-band metal is Weber's double-shell model[4] for NbC and TaC. However, it is not easy to understand the physical basis for this model.

This paper presents a general formulation of phenomenological models which differs somewhat in philosophy from most earlier work. An appealing feature of most phenomenological models is that they are based on well-defined notions of the relatively simple CDD's which are occurring; the new parameters and their coupling constants can usually be generated by intuition or inspection of a mechanical analog. However, the reliance on intuitively simple distortions may be a mistake in formulating models for d-band metals. The present formulation makes no reference to intuitive models, but is instead an analysis of a completely general set of local CDD parameters. The coupling constants are as general as symmetry allows. All phenomenological models known to me are contained as special cases of the present formulation.

The model is then specialized to body-centered cubic (bcc) transition metals. Niobium has been chosen as a test case because of all elements it seems to be the most challenging to theorists at this time.[5] The specific model used for Nb has two types of electronic CDD parameters, a scalar (Γ_1) and a three-component quadrupole ($\Gamma_{25'}$).

Scalar variables were first introduced in lattice dynamics as the breathing mode of the breathing-shell model.[6] A more general interpretation occurs in the deformable-shell model.[7] The first use of a scalar variable interpreted as a charge transfer was by Feldkamp.[8] Such a scalar variable is also implicit in the semimicroscopic work of Sinha and Harmon.[5] Quadrupole and higher-multipole models were first explicitly introduced by Bilz.[9,10] The present paper is a generalization of the ideas of Refs. 7–10. The specific model used for Nb differs from all previous models with CDD parameters in not having a Γ_{15} (dipolar) degree of freedom. After the research had been completed, a preprint was received from Wakabayashi[11] pro-

posing a model for Nb with a single Γ_1 (scalar) CDD, interpreted as a charge-transfer mode. The present work is essentially identical to Ref. 11 insofar as the treatment of LA modes is concerned.

II. GENERAL THEORY

The Hamiltonian for the lattice degrees of freedom in harmonic approximation is written in terms of the displacement $\vec{u}(l)$ and momentum $\vec{P}(l)$ operators of the lth atom as

$$\mathcal{H}_0=\frac{1}{2M}\sum_l [P_\alpha(l)]^2+\frac{1}{2}\sum_{lR} u_\alpha(l)K_{\alpha\beta}(R)u_\beta(l+R)\,. \quad (1)$$

In this formula, M is the atomic mass and α and β are indices for Cartesian components, with repeated Greek indices summed, and $K_{\alpha\beta}(R)$ is the Born–von Kármán force-constant matrix. There is one atom per cell. The solutions are propagating phonon modes described by quantum numbers $\vec{Q}\lambda$ (wave-vector and branch index) with polarization $\hat{\epsilon}_{Q\lambda}$ and frequency $\omega_{Q\lambda}$ given by the eigensolutions of the dynamical matrix $K_{\alpha\beta}(Q)$,

$$\begin{aligned} &M\omega_{Q\lambda}^2\epsilon_{Q\lambda\alpha}=K_{\alpha\beta}(Q)\epsilon_{Q\lambda\beta}\,,\\ &K_{\alpha\beta}(Q)=\sum_R K_{\alpha\beta}(R)e^{i\vec{Q}\cdot\vec{R}}\,. \end{aligned} \quad (2)$$

Microscopic considerations show that the force constants have two contributions—a direct force between the rigidly moving parts of the atom, and an indirect force coming from the CDD. The latter is responsible for the interesting long-range forces in metals and semiconductors.

One of the principal difficulties of the microscopic theory is that there is no clear definition of the entity which moves rigidly and the remaining charge density which distorts. The conceptual problem is especially severe for d-band metals. It is possible that phenomenological models may be of help in clarifying the situation. The essence of all phenomenological models is the assumed existence of parameters $\rho_{L\alpha}(l)$ which describe the amplitude of the $L\alpha$ component of the CDD on atom l. For example in NaCl, the dipole moment of the Cl^- ion is such a set of parameters, which could be labeled $\rho_{15,\alpha}$. The terminology $L=15$ corresponds to the fact that the dipole moment vector transforms according to the Γ_{15} irreducible representation of the point group of the crystal. The subscript α then runs over the three Cartesian components which are the partners for a basis of this irreducible representation.

Generalizing the idea of the shell model, we can write an additional term in the Hamiltonian describing an arbitrary collection of electronic coordinates $\rho_{L\alpha}(l)$

$$\begin{aligned} \mathcal{H}_1=&\sum_{LlR}\rho_{L\alpha}(l)A^L_{\alpha\beta}(R)u_\beta(l+R)\\ &+\frac{1}{2}\sum_{LL'lR}\rho_{L\alpha}(l)\Phi^{LL'}_{\alpha\beta}(R)\rho_{L'\beta}(l+R)\,. \end{aligned} \quad (3)$$

Here the phenomenological coupling constants Φ and A describe the CDD-CDD interactions and the CDD-displacement coupling forces, respectively. Unlike earlier models, ϕ need not be diagonal in LL'. There is no term in this theory corresponding to a momentum conjugate to $\rho_{L\alpha}$. Instead the dynamics of the CDD's are specified by the constraint

$$\frac{\partial\mathcal{H}_1}{\partial\rho_{L\alpha}(l)}=0\,. \quad (4)$$

This is the adiabatic approximation, i.e., whatever lattice displacements $u_\alpha(l)$ exist at a given time, the CDD amplitudes $\rho_{L\alpha}(l)$ instantly adjust themselves to minimize electronic energy. The resulting theory [Eqs. (1), (3), and (4)] then gives rise to a modified dynamical matrix

$$K^{\text{eff}}_{\alpha\beta}(Q)=K_{\alpha\beta}(Q)-\sum_{LL'}[A^L_{\gamma\alpha}(Q)]^\dagger[\Phi(Q)^{-1}]^{LL'}_{\gamma\delta}A^{L'}_{\delta\beta}(Q)\,, \quad (5)$$

where $A(Q)$ and $\phi(Q)$ are Fourier transforms of $A(R)$ and $\phi(R)$, respectively, just as in Eq. (2) for $K(Q)$. The dagger in (5) means complex-conjugate transpose. The matrix Φ which is inverted in Eq. (5) is the multidimensional matrix formed by the direct product of the (α,β)-labeled matrices $\phi^{LL'}_{\alpha\beta}$ for the various representations LL'. This theory describes long-range forces even when the coupling constants $K(R), A(R), \Phi(R)$ are short range.

As has been shown most clearly by Sham,[12] the structure of the phenomenological theory has a direct correspondence with the structure of microscopic theory. The total energy change U of a lattice with distortions $\vec{u}_l$ and charge deformation $\delta\rho(r)$ can be written to second order as

$$\begin{aligned} U=&\frac{1}{2}\sum_{ll'}\frac{\partial^2V_C(\vec{R}_l-\vec{R}_{l'})}{\partial\vec{R}_l\partial\vec{R}_{l'}}:\vec{u}_l\vec{u}_{l'}\\ &+\sum_l\int d\vec{r}\,\delta\rho(\vec{r})\frac{\partial V(\vec{r}-\vec{R}_l)}{\partial\vec{R}_l}\cdot\vec{u}_l\\ &+\frac{1}{2}\int d\vec{r}\,d\vec{r}'\,\delta\rho(\vec{r})\chi^{-1}(\vec{r},\vec{r}')\delta\rho(\vec{r}')\,. \end{aligned} \quad (6)$$

Here $V_C(\vec{R}_l-\vec{R}_{l'})$ is the direct Coulomb interaction with ionic positions denoted $\vec{R}_l=\vec{l}+\vec{u}_l$, $V(\vec{r}-\vec{R}_l)$ is the bare electron-ion potential, and $\chi(\vec{r},\vec{r}')$ is the

charge-density response at point $\vec{r}$ to an external scalar potential at point $\vec{r}'$. The derivatives by $\vec{R}_l$ and the susceptibility χ are to be evaluated at the undistorted lattice positions. The adiabatic approximation now says that $\delta\rho(r)$ instantly adjusts to minimize energy. Mathematically, the functional derivative $\delta U/\delta\rho(r)$ vanishes. Then $\delta\rho(r)$ can be eliminated from (6), giving

$$U=\frac{1}{2}\sum_{ll'}\vec{u}_l\cdot\left(\frac{\partial^2 V_C}{\partial\vec{R}_l\partial\vec{R}_{l'}}-\int d\vec{r}\,d\vec{r}'\frac{\partial V(\vec{r})}{\partial\vec{R}_l}\chi(rr')\frac{\partial V(\vec{r}')}{\partial\vec{R}_{l'}}\right)\cdot\vec{u}_{l'}. \tag{7}$$

This is the standard microscopic formula[12] for the force constants $\underline{K}(l-l')$. The microscopic formula (6) would translate directly into the phenomenological version (1) plus (3) if we could write

$$\delta\rho(r)=\sum_{L,l}\rho_{L\alpha}(l)f_{L\alpha}(r-l)\,, \tag{8}$$

where the CDD $\delta\rho(r)$ is expanded in a complete orthonormal set of functions $f_{L\alpha}(\vec{r}-\vec{l})$ with expansion coefficients $\rho_{L\alpha}$. Then the coupling constants Φ and A would be matrix elements of χ^{-1} and $\partial V/\partial R_{l\beta}$ with the basis function $f_{L\alpha}$. The Wannier functions are the simplest known complete orthonormal set, and are sometimes exploited for lattice-dynamical calculations.[13] However, so far such microscopic schemes have not proved easy to implement. Thus a purely phenomenological investigation seems warranted.

III. SYMMETRY CONSIDERATIONS

To fix a notation, let S stand for a general element of the point group, and $\underline{S}$ be the corresponding three-dimensional rotation matrix. Then if $\vec{R}$ is a lattice vector, $S\vec{R}=\vec{R}'$ is another lattice vector. The representation matrices for the Lth irreducible representation will be denoted $\Gamma^L_{\mu\nu}(S)$. Then under the rotation S of the point group, the displacements $\vec{u}(l)$ and CDD's $\rho(l)$ transform according to

$$\begin{aligned}u_\alpha(\underline{S}\vec{l})&=\Gamma^{15}_{\alpha\beta}(S)u_\beta(\vec{l})\,,\\ \rho_{L\alpha}(\underline{S}\vec{l})&=\Gamma^{L}_{\alpha\beta}(S)\rho_{L\beta}(\vec{l})\,.\end{aligned} \tag{9}$$

Rotational invariance of the Hamiltonian then implies the following transformation laws for the coupling constants:

$$\begin{aligned}K_{\alpha\beta}(\underline{S}\vec{R})&=\Gamma^{15}_{\alpha\alpha'}(S)K_{\alpha'\beta'}(\vec{R})\Gamma^{15}_{\beta'\beta}(S^{-1})\,,\\ A^L_{\alpha\beta}(\underline{S}\vec{R})&=\Gamma^{L}_{\alpha\alpha'}(S)A^L_{\alpha'\beta'}(\vec{R})\Gamma^{15}_{\beta'\beta}(S^{-1})\,,\\ \Phi^{LL'}_{\alpha\beta}(\underline{S}\vec{R})&=\Gamma^{L}_{\alpha\alpha'}(S)\Phi^{LL'}_{\alpha'\beta'}(\vec{R})\Gamma^{L'}_{\beta'\beta}(S^{-1})\,.\end{aligned} \tag{10}$$

The first of these is the familiar transformation law for force constants,[14] and the others are a simple generalization. The requirements (10) put severe restrictions on the form the coupling constants can take and the number of free parameters.

As a matter of practical necessity, one must minimize the number of new coordinates that are introduced. Choices are usually based on intuition, but symmetry considerations are helpful also. Consider the case of bcc Nb. It seems logical that the first electronic coordinate should have Γ_1 symmetry. This is partly because the lowest terms in an angular momentum expansion should have largest amplitude. But more important, intuition says that in a metal, flow of charge from one atom to another is the most fundamental distortion. Thus the *net* charge on an atom might be taken as the first electronic variable, and its symmetry is clearly Γ_1. As shown by Wakabayashi,[11] the addition of a parameter for the net charge allows an accurate few-parameter fit to the peculiar longitudinal modes of Nb. However, a Γ_1 CDD has no influence on transverse modes along symmetry directions. The reason is clear from group theory. The dynamical matrix (5) is block-diagonal along symmetry directions, corresponding to the various irreducible representations of the little group of $\vec{Q}$ which are compatible with the Γ^{15} representation at $\vec{Q}=0$. These are the Δ_1,Δ_5 representations along the Δ direction, $\Sigma_1,\Sigma_3,\Sigma_4$ along Σ, and Λ_1,Λ_3 along Λ. But a CDD of Γ_1 symmetry can only couple to the representations $\Delta_1,\Sigma_1,\Lambda_1$, which are compatible with Γ_1 at $Q=0$. These are the longitudinal branches.

One logical way to proceed would be to add new parameters $\rho_{L\alpha}$ corresponding first to $l=1$ (Γ_{15}), then $l=2$ ($\Gamma_{12}+\Gamma_{25'}$), and so forth. The $l=1$ terms have been studied extensively in the context of the shell model.[1] Simple shell models have not been successful for fitting complicated dispersion curves of metals, although some success has been achieved with shell[15] and breathing-shell[16] models for d-band metals such as Ni which have simple dispersion curves. Weber's double-shell model,[4] although very successful for TaC and NbC, is less successful when applied to Nb, Mo, and Nb-Mo alloys.[17] Because the shell-displacement symmetry is the same as the lattice-displacement symmetry, models of this type are permitted to couple to all phonons in bcc structure. However, experience has not given compelling evidence for the necessity of Γ_{15}-type parameters in Nb.

Several arguments can be made for consideration instead of a $\Gamma_{25'}$-type CDD parameter. Since $l=2$

distortions break into Γ_{12} and $\Gamma_{25'}$ symmetries, a $\Gamma_{25'}$-type distortion can be thought of as a special type of quadrupolar charge distortion, and will be referred to as a quadrupolar degree of freedom frequently in this paper.

The first argument rests on the nature of the experimentally observed anomalies[18] in the dispersion curves of Nb. All longitudinal branches are unusual, but these can be explained (as Wakabayashi[11] showed) by the Γ_1 CDD alone. All transverse branches except Σ_4 have sharp wiggles or anomalous inflection points. The $\Gamma_{25'}$ representation has the unique feature of coupling to (i.e., being compatible with) every transverse branch (TA) *except* Σ_4. Thus the experiments suggest an electronic mode of $\Gamma_{25'}$ symmetry. This mode also happens to couple to the longitudinal branches (LA) everywhere except along [100] (Δ_1), and at N and P.

A totally different reason for considering $\Gamma_{25'}$ CDD's lies in an analysis of the electronic charge density of Nb. This has been calculated from pseudopotential band theory by Ho *et al.*[19] There is a noticeable buildup of bonding valence charge between nearest-neighbor atoms, coming from electron states within 2 eV of the Fermi level. These bonds should be particularly susceptible to distortion when an atom is moved. Thus we might imagine making a bond-charge model for Nb, where the parameters $\rho_L(l)$ corresponded to the amount of charge in the ith bond about the lth atom. This idea is somewhat different from the bond-charge models which have recently been applied[2] with considerable success to covalent semiconductors. The model of Weber[2] uses the *position* of the bond charge as the electronic variable $\rho_{i\alpha}(l)$, whereas it is the *amplitude* of the bond charge which can be more naturally taken as the fluctuating variable for Nb. Thus we introduce four electronic parameters $\rho_i(l)$ per atom of Nb. (There are eight nearest neighbors, each sharing one bond charge.) These variables form the basis for a four-dimensional representation of the cubic point group, which is easily shown to reduce to $\Gamma_1 + \Gamma_{25'}$. Thus in the next section we make a model for Nb with a Γ_1 and a $\Gamma_{25'}$ set of CDD parameters. This model contains a bond-charge model as a special case. However, the choice of coupling constants will be as general as point symmetry allows, while a pure bond-charge model would no doubt involve restrictions relating Γ_1 and $\Gamma_{25'}$ coupling constants. Also it should be said that Wakabayashi's[11] charge-fluctuation model is less general than the most general Γ_1 model permitted by Eqs. (3) and (10), because his parameters A and ϕ are imagined to be derived from a scalar potential. However, for first and second neighbors in bcc structure, there is no difference between Wakabayashi's form and the present theory.

IV. A MODEL FOR Nb

In choosing specific forms for the coupling matrices K, A, and Φ, the parameters are allowed to be as general as point symmetry permits, with the restriction that the range should be short. Unfortunately, in bcc structure the second neighbor lies only 15% further away than the first neighbor. The third neighbor is 63% further away. Thus all coupling constants are truncated after second neighbors, but it does not seem *a priori* justifiable to omit any second-neighbor parameters while keeping first neighbors. It proves impossible to fit the experimental curves with this model, so that direct displacement-displacement matrix K is allowed to have centrally-symmetric third-neighbor components. A very satisfactory fit is then found.

An explicit form for each coupling constant out to second neighbor is given in Table I. The definitions of the coupling matrices are given in Eqs. (1) and (3), and the symmetries were determined from the rules (10). The zeroth-neighbor coupling constants are particularly simple. The charge-charge constants $\phi_{\alpha\beta}^{LL'}(0)$ are of the form $\phi_0\delta_{LL'}\delta_{\alpha\beta}$, while the charge-displacement matrices $A_{\alpha\beta}^{L}(0)$ all vanish unless $L=15$ in which case the result is $A_0\delta_{\alpha\beta}$. There is no $L=15$ (i.e., Γ^{15}-type) CDD in the present model. The reason behind these rules is that the $\vec{R}=0$ coupling matrices form a representation of the full point group and are thus block diagonal with no components coupling different irreducible representations (or different rows of the same one). By the same argument, the $R=0$ Born–von Kármán matrix $\underline{K}(0)$ should be proportional to the unit matrix. However, this matrix can be eliminated by the requirement of translational invariance

$$0=\sum_{\vec{R}} K_{\alpha\beta}(R)\,. \tag{11}$$

This constraint is built into the theory by redefining the Fourier transform of Eq. (2),

$$K_{\alpha\beta}(Q)=-\sum_{R\neq 0} K_{\alpha\beta}(R)[\cos(\vec{Q}\cdot\vec{R})-1]\,. \tag{12}$$

Use has also been made of the evenness of the matrix elements $K_{\alpha\beta}$ as a function of R. A sign change has also been introduced in Eq. (12) and in row one of Table I, so that positive values of $\hat{R}\cdot\underline{K}(R)\cdot\hat{R}$ will correspond to positive spring constants.

A similar restriction from translational invariance applies to the matrices $A_{\alpha\beta}^{L}(R)$, namely,

TABLE I. Definitions of the 16 coupling constants ($K_{1a}, K_{1b}, K_{2a}, K_{2b}$; ϕ_1, ϕ_2; $C_{1a}, C_{1b}, C_{2a}, C_{2b}$; D_1; A_1, A_2; B_{1a}, B_{1b}, B_2) allowed by symmetry in the scalar-quadrupolar model for bcc structure, out to second neighbor. The structure of the coupling matrices for each neighbor $\vec{R}$ is also given explicitly here.

	Zeroth neighbor	First neighbor $\vec{R}=\frac{1}{2}a(X,Y,Z)$, $(X,Y,Z)=(\pm1,\pm1,\pm1)$	Second neighbor $\vec{R}=a(X,Y,Z)$, $(X,Y,Z)=(\pm1,0,0)$, etc.
$-K_{\alpha\beta}(\vec{R})$	See text	$K_{1a}\delta_{\alpha\beta}+K_{1b}X_\alpha X_\beta(1-\delta_{\alpha\beta})$	$[K_{2a}+(K_{2b}-K_{2a})X_\alpha^2]\delta_{\alpha\beta}$
$\Phi^{1,1}(\vec{R})$	1	ϕ_1	ϕ_2
$\Phi_{\alpha\beta}^{25',25'}(\vec{R})$	$\delta_{\alpha\beta}$	$C_{1a}\delta_{\alpha\beta}+C_{1b}X_\alpha X_\beta(1-\delta_{\alpha\beta})$	$(C_{2a}+C_{2b}X_\alpha^2)\delta_{\alpha\beta}$
$\Phi_\alpha^{1,25'}(\vec{R})$	0	$D_1(YZ, ZX, XY)$	0
$A_\alpha^1(\vec{R})$	0	$A_1(X,Y,Z)$	$A_2(X,Y,Z)$
$A_{\alpha\beta}^{25'}(R)$	0	$\begin{pmatrix} B_{1a}XYZ & B_{1b}Z & B_{1b}Y \\ B_{1b}Z & B_{1a}XYZ & B_{1b}X \\ B_{1b}Y & B_{1b}X & B_{1a}XYZ \end{pmatrix}$	$B_2\begin{pmatrix} 0 & Z & Y \\ Z & 0 & X \\ Y & X & 0 \end{pmatrix}$

$$0=\sum_{\vec{R}} A_{\alpha\beta}^{L}(\vec{R}). \tag{13}$$

However, this places no restrictions on the matrices for $L=1$ or $25'$ or any other even representation, because for even representations L, $A_{\alpha\beta}^{L}(\vec{R})$ is an odd function of $\vec{R}$ and (13) is automatic. Because the present model has only even L, the Fourier transform matrices can be written

$$\begin{aligned} A_{\alpha\beta}^{L}(Q)&=\sum_R A_{\alpha\beta}^{L}(R)\sin(\vec{Q}\cdot\vec{R}), \\ \Phi_{\alpha\beta}^{LL'}(Q)&=\sum_R \Phi_{\alpha\beta}^{LL'}(R)\cos(\vec{Q}\cdot\vec{R}). \end{aligned} \tag{14}$$

The remaining nonvanishing zeroth-neighbor constants are $\Phi^{1,1}(0)$ (renamed ϕ_0) and $\Phi_{\alpha\alpha}^{25',25'}(0)$ (renamed C_0). These parameters can both be scaled to 1 without affecting phonon frequencies. The reason is that according to Eq. (5), only the factors $A^L A^{L'}(\phi^{-1})^{LL'}$ affect the frequencies ω_Q^2. Thus the frequencies are invariant under the scaling

$$\begin{aligned} [\Phi_{\alpha\beta}^{LL'}(R)]^*&=\Phi_{\alpha\beta}^{LL'}(R)/[\Phi_{\alpha\alpha}^{LL}(0)\Phi_{\beta\beta}^{L'L'}(0)]^{1/2}, \\ [A_{\alpha\beta}^{L}(R)]^*&=A_{\alpha\beta}^{L}(R)/[\Phi_{\alpha\alpha}^{L}(0)]^{1/2}. \end{aligned} \tag{15}$$

The parameters defined in Table I are to be interpreted as having been scaled as in (15), with the asterisks dropped for simplicity. Note that it is thus impossible to assign absolute magnitudes to the values of the CDD coupling constants A and Φ. Similarly it is impossible to learn the absolute sign of the coefficients A, although the relative signs are fixed. Furthermore, since the scalar-quadrupolar coupling constant $\Phi_x^{1,15}(R_1)\equiv D_1$ turns out to be small, the relative signs of A^1 and A^{15} coefficients are only weakly determined.

The model is now completely specified by Eqs. (5) and (12)–(15) and Table I, plus the following definition of the central-force third-neighbor spring constants, with $R=a(X,Y,Z)$ and $(X,Y,Z)=(\pm1,\pm1,0)$, etc.:

$$K_{\alpha\beta}^{(3)}(R)=K_{3a}\delta_{\alpha\beta}+K_{3b}X_\alpha X_\beta. \tag{16}$$

The 18 parameters have been chosen to minimize the mean-square deviation in ω_Q between theory and experiment for 155 frequencies as tabulated in Ref. 18 along the Δ, Λ, and Σ directions. Most of the data points are shown in Fig. 1.

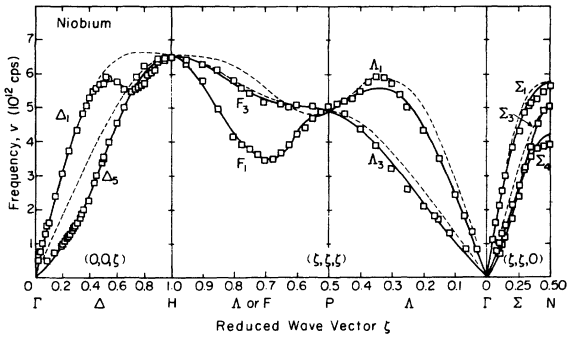

FIG. 1. Theoretical and measured phonon dispersion in Nb. Some of the data points (from Ref. 18, denoted by boxes) have been omitted for clarity. The solid curve is the best fit with the scalar-quadrupolar model. The dashed curve is the same theory with the displacement-scalar and displacement-quadrupolar coupling constants A^L set to zero. The Σ_4 branch is unaffected by the parameters A^L.

TABLE II. Fitted values of the parameters of the scalar-quadrupolar model of Nb.

Name of parameter		Units	Best value	Uncertainty
$\frac{K}{M}$	K_{1a}	$(10^{12}\ \mathrm{Hz})^2$	2.69	±0.24
	K_{1b}		0.98	±0.39
	K_{2a}		−0.48	±0.54
	K_{2b}		1.72	±1.05
	K_{3a}		−0.59	±0.29
	K_{3b}		1.08	±0.37
$\Phi^{LL'}$	ϕ_1	dimensionless	0.138	±0.12
	ϕ_2		0.076	±0.15
	C_{1a}		−0.027	±0.20
	C_{1b}		−0.057	±0.13
	C_{2a}		0.066	±0.14
	C_{2b}		0.214	±0.45
	D_1		−0.023	±0.11
$\frac{A^L}{(M)^{1/2}}$	A_1	10^{12} Hz	0.207	±0.18
	A_2		−0.522	±0.51
	B_{1a}		0.031	±0.09
	B_{1b}		0.377	±0.25
	B_2		0.038	±0.41

The fitting was done with the help of the program MINUIT from the CERN program library. The best fit has a root-mean-square deviation of 0.10 $\times 10^{12}$ cps, which is the size of the experimental uncertainty of ω_Q. The best values of the parameters are shown in Table II, and the theoretical dispersion is the solid line in Fig. 1. The fit, although quite good, is not decisively superior to a Born–von Kármán fit with an equal number of parameters. In particular, there are problems at the Λ_1 maximum, on the Δ_5 branch near Γ and near H, and in the Σ_1 and Σ_4 branches near N. These problems give rise to a large measure of uncertainty shown in Table II for most of the parameters. Relatively large excursions in parameter space are available which cause improvements in some branches and discrepancies elsewhere, with a small increase in mean-square deviation. The program MINUIT calculates an 18-dimensional hyperellipse in parameter space, centered about the minimum, on the surface of which the rms deviation is increased from 0.10×10^{12} to 0.13×10^{12} cps. This ellipse is rather eccentric, with a major axis tilted away from the parameter axes. The listed uncertainties are not the intersections but the projections of the extreme points onto the parameter axes. These results suggest that improvements might occur by eliminating (i.e., setting to zero) certain parameters, such as D_1, B_2, and possibly all four parameters C_i, and adding some new degrees of freedom.

The reason why third-neighbor Born–von Kármán terms were needed is that none of the scalar or quadrupolar degrees of freedom can couple at H or N. The four experimental frequencies at these points then put four constraints on the Born–von Kármán matrix, leaving no extra flexibility to fit elsewhere in Q space. This is disturbing in light of the fact that Varma and Weber[5] need only first- and second-neighbor Born–von Kármán constants plus electron-phonon terms. In retrospect, a Γ_{15} (dipolar) degree of freedom might be the physically most correct way to open up the extra needed flexibility. A Γ_{15} electronic parameter would couple at H and N, releasing some of the constraints on the Born–von Kármán terms. A full scalar-shell-quadrupolar theory with all allowed coupling constants out to second neighbors has 29 parameters, an almost prohibitive number (and this without third-neighbor Born–von Kármán terms). However, the present results strongly suggest that $\underline{\phi}^{LL'}(\vec{R})$ may be neglected when $L \neq L'$ and is of extremely short range (zeroth neighbor only?) for the $L = L' = 25'$ terms. The matrices $A^L(\vec{R})$ are somewhat longer range, but possibly only first neighbor is needed except for $L = 1$. Further development of the model along these lines is needed before it can be considered as a serious candidate for interpolation and data fitting.

In spite of these reservations, it is possible to draw several conclusions about the origin of phonon anomalies in Nb. The dip in the LA branch at $\zeta = 0.7$ in the [100] direction (Δ_1 branch) has been assigned both to topological features of the electron bands near the Fermi surface in $\vec{Q}$ space,[20] and to "resonant screening" corresponding to geometrical resonances in the local field in $\vec{R}$ space.[5] It is not entirely clear that these are distinct concepts, but in an extreme phrasing the former point of view maintains that the physics is in the band-structure-induced anomalies of the diagonal part $\epsilon(\vec{Q}+\vec{G},\vec{Q}+\vec{G})$ of the dielectric function, while the latter point of view claims this is unimportant compared to the geometric structure of the off-diagonal part $\epsilon(\vec{Q}+\vec{G},\vec{Q}+\vec{G}')$ and its inverse ϵ^{-1} which are related to resonances in the factor $[\Phi^{-1}(Q)]^{LL'}$ of phenomenological theory. The calculations presented here show clearly that resonances of $\Phi^{-1}(Q)$ coming from charge transfer give a natural explanation for the LA anomalies. On the other hand, interatomic quadrupolar-quadrupolar coupling, although capable of producing similar resonancelike behavior of $\phi^{-1}(Q)$ for the TA branches, is in fact unimportant.

To see these results more clearly, we can write out the explicit solution of Eq. (5) for the Δ_1 and Δ_5 branches,

$$M\omega^2(\Delta_1) = 16K_{1a}\sin^2 z + (4K_{2b} + 16K_{3a} + 16K_{3b})\sin^2 2z - (8A_1 \sin 2z + 2A_2 \sin 4z)^2/[1 + 8\phi_1 \cos 2z + \phi_2(4 + 2\cos 4z)], \tag{17}$$

$$M\omega^2(\Delta_5) = 16K_{1a}\sin^2 z + (4K_{2a} + 16K_{3a} + 8K_{3b})\sin^2 2z - (8B_{1b}\sin 2z + 2B_2 \sin 4z)^2/[1 + 8C_{1a}\cos 2z + C_{2a}(4 + 2\cos 4z) + 2C_{2b}], \tag{18}$$

where $z = \frac{1}{2}\pi\zeta$ and $Q = (2\pi/a)(\zeta, 0, 0)$. The last terms in (17) and (18) represent the effect of charge and quadrupolar fluctuations, respectively, in softening the LA and TA branches. The degree of softening is exhibited in Fig. 1 by comparing the dashed and solid lines. The dashed line (with the matrices A^L set to zero) shows the unsoftened Born–von Kármán curves, and the solid line is the complete fit. The denominators of the last terms in (17) and (18) have extrema at the zone boundary and zone center, with the possibility of other extrema in between. For the LA branch, the denominator in (17) is 2.56 at $Q = 0$ and 0.35 (seven times smaller) at $Q = 2\pi/a$, which are the absolute maximum and minimum, respectively, whereas for the TA branch, the denominator of (18) is almost constant. The physical interpretation is that these denominators represent the electronic restoring forces for charge and quadrupolar fluctuations. These forces are highly local for quadrupolar fluctuations giving a dispersionless denominator. For charge fluctuations the range is longer. First- and second-neighbor terms ϕ_1 and ϕ_2 help to stabilize charge fluctuations with large $\vec{Q}$ where near-neighbor atoms have opposite charge, while the on-site Coulomb term ϕ_0 discourages all fluctuations. Apparently a zone-boundary charge density wave in the [100] direction costs only about $(\frac{1}{7})^{1/2}$ as much energy as at $Q = 0$. The characteristic energy is roughly the plasma energy, about 20 eV. It would be interesting to see whether this effect could be observed in inelastic $Q \neq 0$ electron scattering. The reason for the minimum in $\omega^2(\Delta_1)$ occurring at $\zeta = 0.7$ instead of $\zeta = 1$ is because the numerator has a maximum at

$$\zeta = (1/\pi)\cos^{-1}[-\alpha - (\alpha^2 + \tfrac{1}{2})^{1/2}] = 0.68,$$

(where $\alpha = A_1/A_2$), and goes to zero at $\zeta = 1$. The position of the dip along Δ_1 is thus determined in this model primarily by the ratio A_1/A_2, and to get the right position this ratio must be about -0.4. It is uncertain whether the large value of A_2 relative to A_1 is physically meaningful.

V. CONCLUSIONS

In agreement with Wakabayashi,[11] the LA anomalies in Nb have a natural explanation from coupling of phonons to charge fluctuations. The large-Q charge fluctuations are softened by interatomic charge-charge interactions, and this in turn softens the phonons. The TA anomalies of Nb have a reasonably good explanation in terms of quadrupolar fluctuations with local ($\vec{R} = 0$) restoring forces. However, a dipolar degree of freedom might be helpful in improving the fit.

Wakabayashi has mentioned other types of crystals where charge-fluctuation models might be useful. The $A15$ metals can also be considered. The simplest model would have (in addition to the 24 lattice degrees of freedom which occur for eight atoms in a cell) six new variables corresponding to the magnitude of the charge on the six atoms which lie on linear chains. One of the interesting features of phonons in these materials is the soft TA ([110], [1$\bar{1}$0]) phonon known to occur in V_3Si and Nb_3Sn. If the model allowed transfer of charge only within a single chain, then there would be no coupling to this branch. A symmetry analysis shows that the soft TA branch in the [110] direction does couple to charge fluctuations *between* the [100] and [010] chains. The TA ([110], [001]) phonon does not couple to any charge fluctuation modes in this model. Thus a charge fluctuation model would be interesting to examine for $A15$ metals, and suggests the unorthodox view that interchain coupling may be necessary to explain the phonon anomalies.

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[1]Many recent review articles are available: (a) H. Bilz, B. Gliss, and W. Hanke, in *Dynamical Properties of Solids*, edited by G. K. Horton and A. A. Maradudin (North-Holland, Amsterdam, 1974), Vol. 1, p. 344; (b) J. R. Hardy, *ibid.*, p. 157; (c) A. N. Basu, D. Roy, and S. Sengupta, Phys. Stat. Sol. 23, 11 (1974); (d) S. K. Sinha, CRC Crit. Rev. Sol. State Sci. 4, 273 (1973); (e) W. Cochran, *ibid.* 2, 1 (1971); (f) G. Venkataraman, L. A. Feldkamp, and V. C. Sahni, *Dynamics of Perfect Crystals* (MIT, Cambridge, Mass., 1975).

[2]R. M. Martin, Phys. Rev. 186, 871 (1969); W. Weber, Phys. Rev. Lett. 33, 371 (1974).

[3]H. G. Smith, N. Wakabayashi, and M. Mostoller, in *Superconductivity in d- and f-Band Metals*, edited by D. H. Douglass (Plenum, New York, 1976), p. 223. An early and obscure attempt at a CDD phonon theory for *d*-band superconductors was given by B. T. Matthias, H. Suhl, and C. S. Ting, Phys. Rev. Lett. 27, 245 (1971).

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

[5]The first successful microscopic calculation for a *d*-band material is reported by C. M. Varma and W. Weber, Phys. Rev. Lett. 39, 1094 (1977). For earlier work on Nb, see (a) M. I. Korsunskii, Ya. E. Genkin, V. I. Markovnin, V. G. Zavodinskii, and V. V. Satsuk, Fiz. Tverd. Tela 13, 2138 (1971) [Sov. Phys.-Sol. State 13, 1793 (1972)]; (b) S. K. Sinha and B. N. Harmon, Phys. Rev. Lett. 35, 1515 (1975); and in Ref. 3, p. 269; (c) W. E. Pickett and P. B. Allen, Phys. Rev. B 16, 3127 (1977).

[6]U. Schroder, Sol. State Commun. 4, 347 (1966).

[7]A. N. Basu and S. Sengupta, Phys. Stat. Sol. 29, 367 (1968); S. S. Jaswal and V. D. Dilly, Phys. Rev. B 15, 2366 (1977).

[8]L. A. Feldkamp, J. Phys. Chem. Solids 33, 711 (1972).

[9]H. Bilz, in *Computational Solid State Physics*, edited by F. Herman, N. W. Dalton, and T. R. Koehler (Plenum, New York, 1972), p. 309.

[10]K. Fischer, H. Bilz, R. Haberkorn, and W. Weber, Phys. Stat. Sol. 54, 285 (1972).

[11]N. Wakabayashi, Solid State Commun. 23, 737 (1977).

[12]L. J. Sham, in *Modern Solid State Physics: Vol. 2, Phonons and their interactions*, edited by R. H. Erns and R. R. Haering (Gordon and Breach, New York, 1969), p. 143.

[13]W. Hanke, Phys. Rev. B 8, 4585, 4591 (1973); L. J. Sham, in Ref. 1(a), p. 301; R. Pick, in *Phonons*, edited by M. A. Nusinovici (Flammarion, Paris, 1971), p. 20.

[14]For example, see A. A. Maradudin, E. W. Montroll, G. H. Weiss, and I. P. Ipatova, *Solid State Physics Suppl. 3*, 2nd ed. (Academic, New York, 1971), p. 13.

[15]B. L. Fielek, J. Phys. F 5, 17 (1975).

[16]W. Hanke and H. Bilz, Z. Naturforsch, 26a, 585 (1971).

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

[18]Y. Nakagawa and A. D. B. Woods, in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, Oxford, 1965), p. 39.

[19]K. M. Ho, S. G. Louie, J. R. Chelikowsky, and M. L. Cohen, Phys. Rev. B 15, 1755 (1977).

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