Lattice dynamics of layered transition-metal dihalides

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We present an extended-shell-model (ESM) calculation of the dispersion relations and of the phonon density of crystals with either CdI₂ or CdCl₂ structure, namely, of V, Mn, Fe, Co, and Ni dichlorides and dibromides. The dynamical matrix, including the Coulomb and short-range contributions originating from the anion static dipoles, is constructed from model interionic potentials. While anion-anion Born-Mayer repulsion and van der Waals interactions are taken as in alkali halides, the parameters of metal-halogen short-range potential are obtained from equilibrium nearest-neighbor distance and cohesive energy. To this purpose we have derived an expression for the cohesive energy suitable to crystals with reduced ionicity and open d-shell configurations. A transverse metal-metal force constant and a correction to the transverse anion-anion interlayer force constant are added in order to fulfill the rotational invariance conditions. The three electrostatic parameters, net charge Z, anion shell charge Y, and anion shell-core displacement w_0 , are adjustable and are best-fitted to the experimental Raman and far-infrared data. A reliable scale of ionicities ranging from Z = 0.71 of NiBr₂ to 0.91 of MnCl₂ is obtained, and the theoretical dynamical charges and elastic constants are reported. The calculated dispersion curves are in good agreement with the few available neutron data. For MnCl₂, where a complete comparison with neutron data is possible, we show how the various ESM contributions influence the dynamical anisotropy and the lattice stability. Finally, we discuss the role of central metal-metal interaction, three-body forces, monopolar and quadrupolar metal-ion breathing (all neglected in the calculations) in order to explain the residual discrepancies.

I. INTRODUCTION

Layered crystals with $CdCl_2$ (C19) or CdI_2 (C6) structure form an ample class of binary compounds. Several of them, involving transition metals, present interesting magnetic properties; some are today the object of numerous studies on metal-insulator transition, charge density waves, superionic conductivity.¹⁻⁵ Transition-metal dihalides, which still have a relatively large ionicity, also show interesting and complex vibronic features in the region of crystal field transitions.⁴⁻⁹ All these aspects, widely investigated in recent years, have increased the need of knowing quantitatively the lattice dynamics of layer structures. Until now, however, the effort made along this direction, although represented by some excellent work, was not adequate to the importance of these materials.¹⁰

As Schmid has remarked in his review article,¹¹ layer structures present the challenging feature of combining a simple chemical formula with a nonsimple dynamical structure, the latter mainly originating from anisotropy. A single chemical bond (or two, if we consider to a further approximation the metal-metal bonding) is the main unknown which is expected to account for nine dispersion curves. This is a good test for the various shell models, because of the existence of dynamical features which cancel in isotropic crystals. However, a good philosophy is approaching this dynamical problem cannot consist of a mathematical game where parameters of a shell model are forced to fit a given set of neutron data, but in building the dynamical matrix from physical interatomic potentials, which, first of all, account for the equilibrium configuration of the lattice. In doing this, attention must be paid to all those interactions which cause static and dynamical anisotropy.

Since in the ideal (trigonally undistorted) C19 structure the anions form an fcc lattice, one can realize that, in the point-ion approximation, the dynamical matrix block for zone-center oddsymmetry modes is formally identical to that of an NaCl lattice at the Γ point, while the block for zone-center even-symmetry modes corresponds to that of NaCl-lattice L point. Such a similarity (approximately holding also for C6 structure) suggests the helpful distinction of the various physical interaction into isotropy factors. like monopole Coulomb forces, and anisotropy factors, like dipolar, van der Waals (vdW), and short-range interactions due to Born-Mayer repulsion (BM), and covalency. For instance, dipolar forces are peculiarly responsible for the anisotropy in LO-TO splitting, as previously found by Frey and Zeyher,^{13,14} while anisotropy in acoustical branches (which is smaller, the larger being the monopole Coulomb interaction) receives an important contribution from the vdW interaction. Indeed, without vdW forces, the price for reproducing the experimental acoustic branches along the c axis would be an unphysically low

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monopole interaction, 14,15 whereas the ionicity of 3d metal halides is known to be quite high.

II. GENERAL CONCEPTS ON THE MODEL

This work is devoted to 3d metal dihalides with either C6 or C19 structure.¹⁶ Their respective symmetry classes are D_{3d}^3 and D_{3d}^5 , and the metal ions are centers of D_{3d} symmetry in both structures (Fig. 1). We have selected those crystals for which Raman scattering (RS)¹⁷⁻²⁰ and infrared (ir) data^{20,21} are available, namely the chlorides and bromides of V, Mn, Fe, Co, and Ni and VI₂. The C6 lattice has a single molecule per unit cell, whereas C19 is built up by three molecules per cell. They have in common the same sandwich structure, and differ only for the stacking of sandwiches. Since both monopole and dipole parts of the Madelung constant are the same in the two lattices within the first three digits,²² C19 crystals can be treated to a good approximation with the same dynamical model used for the simpler C6 structure. Indeed, apart from the irrelevant folding of the dispersion curves along the c axis. the dynamical structure of C19 and C6 lattices are very close. The Brillouin zone (BZ) of C6 lattice is shown in Fig. 1.

We have used an extended-shell-model (ESM)



FIG. 1. (a) The octahedral cage of anions surrounding the metal ion in C6 and C19 structures. (b) Brillouin zone of a lattice with $CdI_2(C6)$ structure. With respect to the origin Γ , the points K, M, and A have coordinates $(4\pi/3a, 0, 0)$, $(0, 2\pi/\sqrt{3a}, 0)$ or $(2\pi/a, 0, 0)$, and $(0, 0, 2\pi/c)$, respectively, where a and c are the distances between neighbor metal ions along the x and z directions, respectively.

version including Coulomb interactions of anion static dipoles and halogen-halogen vdW force constants. The dipole-dipole vdW coefficient c_{dd} is derived from the London formula.²³ Shortrange repulsion between halogen ions is described by a Born-Mayer potential $b \exp(-r/\rho)$ whose parameters b and ρ for a closed-shell configuration are known in the literature.²³

The metal-halogen nearest-neighbor (nn) repulsion is also described by a Born-Mayer potential $b_0 \exp(-r/\rho_0)$. The exponent parameter ρ_0 is, however, allowed to be different from ρ in order to take into account that 3d metal ions have open shells and that bonding is partially covalent. The two metal-halogen repulsive parameters, b_0 and ρ_0 , are directly fitted to the experimental equilibrium interionic distance r_0 and cohesive energy. The fitting is performed taking into account that we are dealing with not completely ionic crystals, the net halogen charge being -eZ, with Z < 1. This implies that the expression of the "experimental" cohesive energy, as obtained from the Born-Haber cycle, contains Z-dependent effective metal ionization and halogen affinity energies, plus a Z-dependent resonance energy, representing the covalency contribution in a valence-bond picture. Z is used as a disposable parameter. The polarizability of transition-metal ions in view of their small size is neglected, whereas for the halide ions we have used the polarizabilities reported by Tessmann, Kahn, and Shockley (TKS).24 Therefore, in this model the adjustable parameters are three: Z, the anion shell charge Y, and the anion static shell-core displacement w_0 . In principle these reduce to only two since Y and w_0 should reproduce the equilibrium static dipole moment. However, the static dipole moment is in turn dependent on Z, which makes the exact optimization of the two parameters rather lengthy. Furthermore, the static dipole is quite sensitive to the value of u (whose deviation from $\frac{1}{4}$ represents the trigonal distortion of the sandwich), which is not yet known with sufficient precision in most of the present crystals. Therefore, we were content to report a set of results where w_0 is kept fixed for all crystals and only Z and Y are disposable: we shall show that the fitted static dipoles are fairly consistent with the theoretical values for the undistorted configuration $(u = \frac{1}{4})$.

In spite of such internal consistency concerning the static dipolar structure of the lattice, the interionic potential model we use is not expected to reproduce exactly the equilibrium trigonal distortion, whose parameters c/a and u, on the other hand, are used as input data in the calculation. In other words the set of force constants directly derived from the above potentials might not be ro-

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tationally invariant. The application of the rotational invariance conditions,²⁵ equivalent to the equilibrium conditions for c/a and u, yields a correction of the transverse interlayer anionanion force constant $B_{AA'}$ and the addition of a transverse metal-metal force constant B_{MM} . Although there is clear evidence that metal-metal interaction is not completely negligible in PbI_{2} ,¹² we have not included the radial metal-metal force constant A_{WW} in this model, as at present we have no a priori information on this parameter. However, in Sec. VIII we shall discuss its role in MnCl₂, for which we have a complete set of neutron dispersion curves. Finally, owing to the relatively large ionicity of the compounds, we have neglected three-body forces. Indeed, the three-body anglebonding force constants ψ_{θ} and $\psi_{\theta,r}$ entering a valence-force-field (VFF) model^{26,27} fitted on the experimental optical frequencies turn out to be, respectively, of the order of $\frac{1}{8}$ and $\frac{1}{50}$ of the nn force constant A_{MA} .²¹

III. THE EXTENDED-SHELL MODEL

In the extended shell model, in addition to the effect of dynamical dipoles, the contribution due to the static polarization is taken into account.²⁸ Static dipoles arise at anions, as they are not centers of inversion symmetry. The centers of mass of core and shells are displaced by w_0 (Fig. 1), and therefore the elements of the dynamical matrix must be evaluated for the actual core and shell positions. In particular, the shell-core (C^{sc}) and shell-shell (C^{ss}) Coulomb elements do not coincide with the core-core (C^{cc}) Coulomb force constant, but differ from it by amounts related to their anharmonic parts.

The ESM dynamical equations read

$$M\omega^2 u = Au + Bw, \qquad (1)$$

$$\mathbf{0} = B^{\dagger} \boldsymbol{u} + D \boldsymbol{w} , \qquad (1')$$

where u and w are core and shell displacement vectors, respectively, M is the mass matrix, and ω the phonon angular frequency. The matrices A, B, and D are expressed in terms of the shortrange shell-shell matrix R and Coulomb matrices as

$$A = R + XC^{CC}X + XC^{CS}Y + Y(C^{CS})^{\dagger}X + YC^{SS}Y,$$
(2a)

$$B = R + XC^{\operatorname{cs}} Y + YC^{\operatorname{ss}} Y. \tag{2b}$$

$$D = R + Y C^{SS} Y, \qquad (2c)$$

where X and Y are core and shell charge matrices. The elements of the matrices A, etc., are denoted by $A_{\alpha\beta}(\kappa^{\bar{q}}\kappa')$, etc., where \bar{q} is the wave vector, $\alpha, \beta = x, y, z$ are Cartesian indices (z direction along the c axis), and $\kappa, \kappa' = 1, 2, 3$ denote the atoms of the unit cell (Fig. 1).

Since the adjustable parameters of our model are best-fitted to the available experimental frequencies of the optical modes $[\omega(A_{1g}) \text{ and } \omega(E_g) \text{ from}$ RS, and $\omega(A_{2u}, \text{TO})$, $\omega(A_{2u}, \text{LO})$, $\omega(E_u, \text{TO})$, and $\omega(E_u, \text{LO})$ from ir measurements], we seek an explicit form for the frequencies. In the longwavelength limit ($\bar{q} = 0$) Eq. (1) can be block diagonalized, and the optical mode frequencies can be written as an analytical expression

$$\omega_{i,\alpha}^{2}(0) = A_{i,\alpha} + f_{i}B_{i,\alpha}B_{i,\alpha}^{\dagger}(D_{i,\alpha} + Y_{1}^{2}\alpha_{A}^{-1})^{-1}, \quad (3)$$

where i = g, *u* denotes the parity of the modes, and α_A is the (isotropic) anion polarizability.²⁴ For the odd modes (A_{2u} for $\alpha = z$ and E_u for $\alpha = x, y$) we have

$$\bar{A}_{\boldsymbol{u},\,\boldsymbol{\alpha}} = A_{\,\boldsymbol{\alpha}\,\boldsymbol{\alpha}} \begin{pmatrix} {}^{0}_{2} \end{pmatrix}, \quad \bar{B}_{\,\boldsymbol{u},\,\boldsymbol{\alpha}} = B_{\,\boldsymbol{\alpha}\,\boldsymbol{\alpha}} \begin{pmatrix} {}^{0}_{2} \end{pmatrix},
\tilde{D}_{\,\boldsymbol{u},\,\boldsymbol{\alpha}} = D_{\,\boldsymbol{\alpha}\,\boldsymbol{\alpha}} \begin{pmatrix} {}^{0}_{2} \end{pmatrix}, \quad f_{\,\boldsymbol{u}} = 2.$$
(4)

For the even modes $(A_{1g} \text{ for } \alpha = z \text{ and } E_g \text{ for } \alpha = x, y)$

$$\begin{split} \tilde{A}_{\boldsymbol{g},\alpha} &= 2A_{\alpha\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix} + A_{\alpha\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \\ \tilde{B}_{\boldsymbol{g},\alpha} &= 2B_{\alpha\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix} + B_{\alpha\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \\ \tilde{D}_{\boldsymbol{g},\alpha} &= 2D_{\alpha\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix} + D_{\alpha\alpha} \begin{pmatrix} 0 \\ 1 \end{pmatrix}, \\ f_{\boldsymbol{g}} &= 1. \end{split}$$
(5)

The matrix element $A_{\alpha\alpha}({}_{1}^{0}{}_{2})$ is given by

$$A_{\alpha\alpha}({}_{1}^{0}{}_{2}) = R_{\alpha\alpha}({}_{1}^{0}{}_{2}) + Z_{1}C_{\alpha\alpha}^{CC}({}_{1}^{0}{}_{2})Z_{2} + Y_{1}Y_{2}\Delta_{\alpha,12}^{SS},$$
(6)

where

$$\Delta_{\alpha,\kappa\kappa'}^{JJ'} = C_{\alpha\alpha}^{JJ'} \begin{pmatrix} 0\\ \kappa & \kappa' \end{pmatrix} - C_{\alpha\alpha}^{CC} \begin{pmatrix} 0\\ \kappa & \kappa' \end{pmatrix}$$
(7)

is the "anharmonic" part of the Coulomb force constant, and $Z_{\kappa} = X_{\kappa} + Y_{\kappa}$ is the net charge. Analogously we have

$$A_{\alpha\alpha} {\binom{1}{3}} = R_{\alpha\alpha} {\binom{1}{3}} + Z_1 C^{CC}_{\alpha\alpha} {\binom{1}{3}} Z_3 + Y_1^2 \Delta^{SS}_{\alpha_1 13} + 2Y_1 X_1 \Delta^{CS}_{\alpha_1 13}, \qquad (8)$$

 $B_{\alpha\alpha}({}^{0}_{\kappa'}), B^{\dagger}_{\alpha\alpha}({}^{0}_{\kappa'}), \text{ and } D_{\alpha\alpha}({}^{0}_{\kappa'}) \text{ are obtained just}$ by replacing in the expression of $A_{\alpha\alpha}({}^{0}_{\kappa'}), \text{ re-}$ spectively, $Z_{\kappa'}$ with $Y_{\kappa'}, Z_{\kappa}$ with Y_{κ} , and both $Z_{\kappa}, Z_{\kappa'}$ with $Y_{\kappa'}, Y_{\kappa'}$. It is useful to explain the specific role of $\Delta^{JJ}_{\alpha,13}$, which accounts for the existence of static dipoles, and distinguishes the ESM from the ordinary shell models. Since $\Delta^{JJ'}_{\alpha,13}$ is negative, the effect of this term on the ir-active modes is to enhance the polarization part essentially by reducing the denominator of Eq. (3). On the other hand, for RS-active modes, this effect is nearly absent because of the almost complete cancellation of the two last terms in the righthand side of Eq. (8). This behavior will be clearly displayed in the numerical results reported in Sec. VI.

IV. EQUILIBRIUM CONDITIONS

The equilibrium positions of cores and shells are fully defined by the four parameters a, c, u, and w_0 . Thus we have four equilibrium conditions, which yield three constraints on the set of the transverse force constants, and an equation for the static dipole $\mu_0 = eY_1w_0$. The first three equations state that the derivatives of the Coulomb (monopole and dipole) potential $\partial_{a_i}\psi_{\sigma}$ with respect to any lattice parameters a_i must be equal to the corresponding components of the short-range (Born-Mayer plus van der Waals) forces, namely:

$$\partial_a \psi_c = a (6B_{AA} + B_{AA'} + B_{AB''} + 2B_{MA} + 3B_{MM}),$$
(9a)

$$\partial_c \psi_c = 3c \left(1 - 2u\right) B_{AA'} , \qquad (9b)$$

$$\partial_{u}\psi_{c} = 3uc^{2}(2B_{MA} + B_{AA''}) - 9c(1 - 2u)B_{AA'}, \quad (9c)$$

where B_{AA} , $B_{AA'}$, and $B_{AA''}$ are, respectively, the anion-anion horizontal, oblique interlayer, and oblique intralayer transverse force constants, B_{MA} the metal-anion, and B_{MM} the metal-metal transverse force constants. Here we have used Eqs. (9) for defining $B_{AA'}$, B_{MM} , and B_{MA} . In the absence of trigonal distortion $[c/a = (\frac{B}{3})^{1/2}$ and $u = \frac{1}{4}]$ they are given by the approximate (but general) expressions

$$B_{AA'} = 0.039 Z^2 (e^2/a^3), \qquad (10a)$$

$$B_{MM} = 2.147 Z^2 (e^2/a^3) + B_{AA''} - 2B_{AA} , \qquad (10b)$$

$$B_{MA} = -4.082 Z^2 (e^2/a^3) - 2B_{AA''}. \qquad (10c)$$

We note that $B_{AA'}$ for the undistorted configuration could be obtained directly from the given BM and vdW potentials. The fact that such an a priori value might differ from that given by Eq. (10a) simply means that the undistorted lattice is not in equilibrium. In Eq. (10b) B_{MM} could have been neglected for simplicity and $B_{AA'}$, defined by this equation itself.^{14,15} We have two good reasons for also including the metal-metal transverse force constant in the model. First, a weak covalent bonding between neighboring d-metal ions was recognized to occur in layer structures.²⁹ Second, B_{MM} plays a role in the stability of E acoustic branches at the K point.^{12,13} We shall discuss the inclusion of a physical metal-metal interaction (i.e., the addition of the radial force constant A_{MM}) in Sec. VIII. Equation (10c), combined with the cohesive energy equation, is used for deriving the unknown Born-Mayer parameters b_0 and ρ_0 . The electrostatic equation of the shell-core displacement vector $\mathbf{\bar{w}}_0(1) = (0, 0, w_0) = -\mathbf{\bar{w}}_0(3)$ reads

$$Y_{1}^{2}\alpha_{A}^{-1}\vec{\mathbf{w}}_{0}(1) = X_{1}\sum_{\boldsymbol{l}'\boldsymbol{\kappa}'} \left(Y_{\boldsymbol{\kappa}}\cdot\vec{\nabla} \left| \vec{\mathbf{r}}(\boldsymbol{l}'\boldsymbol{\kappa}') + \vec{\mathbf{w}}_{0}(\boldsymbol{\kappa}') - \vec{\mathbf{r}}(\boldsymbol{l}1) \right|^{-1} + X_{\boldsymbol{\kappa}}\cdot\vec{\nabla} \left| \vec{\mathbf{r}}(\boldsymbol{l}'\boldsymbol{\kappa}') - \vec{\mathbf{r}}(\boldsymbol{l}1) \right|^{-1} \right), \quad (11)$$

where the sum extends over all atomic positions $\dot{r}(l'\kappa')$ with $(l',\kappa') \neq (l, 1)$. Since $\vec{w}_0(\kappa')$ also appear on the right-hand side, Eq. (11) needs an iteration procedure to be solved. Owing to the slow convergence and to the fact that Eqs. (11) and (10) are coupled to each other in principle via the presence of dipolar terms in $\partial_{a_i}\psi_o$ and the actual equilibrium positions in (11), the self-consistent solution of the system of Eqs. (10) and (11), with the best fit of $Z \equiv -Z_1$ and $Y \equiv Y_1$ to the optical frequencies [Eqs. (3)], is quite lengthy. It is perhaps too lengthy if compared with the modest amount of additional physical information involved. We preferred to use w_0 as a disposable parameter, taking as an initial value that of the first iteration

$$\bar{\bar{w}}_{0}(1) \simeq \frac{X_{1} \sum_{l'\kappa'} Z_{\kappa'} \bar{\nabla} \left| \bar{r}(l'\kappa') - \bar{r}(l1) \right|^{-1}}{Y_{1}^{2} \alpha_{A}^{-1} - X_{1} Y_{1} \left[C_{zz}^{CC} \begin{pmatrix} 0 \\ 1 \end{pmatrix} - C_{zz}^{CC} \begin{pmatrix} 0 \\ 1 \end{pmatrix} \right]}, \quad (12)$$

obtained by keeping only the linear term in the expansion of Eq. (11) with respect to \bar{w}_0 . In PbI₂ (Ref. 13) and VI₂, where the iteration procedure was accomplished, the final value is somewhat smaller than the first-step value, Eq. (12). On the other hand, when \bar{w}_0 is adjustable, the fitted value also turns out to be smaller than the first iteration value of \bar{w}_0 . This might indicate that the fitting procedure is not far from self-consistency. In VI₂ fitted and self-consistent \bar{w}_0 are effectively in good agreement (Table I).

We note that for $Y_1 \sim -X_1$ (namely $Z \ll |Y_1|$) Eq. (12) reduces to that reported by van der Valk and Haas for the static dipole moment.³⁰

V. COHESIVE ENERGY

The cohesive energy,³¹ as deduced from the Born-Haber cycle, is useful information for the dynamical model. However, in a partially ionic crystal the concept of cohesive energy is not straightforward, as it depends on the definition of the dissociated phase. The instantaneous dissociation of a lattice MX_2 (M=metal, X=halogen) into its atomic components yields a gaseous mixture of the ionic and atomic species M^{2*} , M^{1*} , M^0 , X^{-1} , X^0 , and X^{*1} .

By defining the ionicity Z as the probability of finding an additional electron on the halogen atom, the corresponding probabilities for the above species turn out to be Z^2 , 2Z(1-Z), $(1-Z)^2$, $(1+Z)^2/4$, $(1-Z^2)/2$, and $(1-Z)^2/4$, respectively. Hence we define an effective metal ionization potential

$$I(Z) = Z^{2}(I_{1} + I_{2}) + 2Z(1 - Z)I_{1}$$

= $I_{1} + I_{2} - I_{1}(1 - Z)^{2} - I_{2}(1 - Z^{2}),$ (13)

where I_1 and I_2 are the metal first and second ionization energies, and an effective halogen affinity

$$A(Z) = \frac{1}{4}A_{1}(1+Z)^{2} - \frac{1}{4}I_{a}(1-Z)^{2} + \frac{1}{4}(I_{a}-A_{1})(1-Z^{2}) = A_{1} + \frac{1}{2}(Z^{2}+Z-2)A_{1} + \frac{1}{2}Z(1-Z)I_{a}, \quad (14)$$

where A_1 is the first affinity and I_a the first ionization potential of the halogen atom.

According to the Born-Haber cycle, we write the cohesive energy up to small zero-point and thermal energy corrections as

$$U_{0}(Z) = H_{f} + H_{s} + D + I(Z) - 2A(Z) + 4\beta(1 - Z^{2})^{1/2} - E_{s} = U_{0} - I_{1}(1 - Z)^{2} - I_{2}(1 - Z^{2}) + (2 - Z - Z^{2})A_{1} - Z(1 - Z)I_{a} + 4\beta(1 - Z^{2})^{1/2} - E_{s} ,$$
(15)

where H_{f} , H_{s} , and D are salt formation, metal sublimation, and halogen molecule dissociation entalpies, respectively,³² and U_0 is the cohesive energy for the ideal ionic lattice. Two additional terms, peculiar to a system with open shells, are incorporated in the definition of $U_0(Z)$: the resonant energy associated with the overlapping parts of atoms, β being the Coulomb integral between nn ions, and the stabilization energy E_s , i.e., the lowering of the d-metal ion ground state due to the crystal field splitting of the d^n levels.³³ For the configuration $t_{2g}^m e_g^{n-m}$ such a lowering is given by (6n-10m)Dq, where Dq is the cubic crystalfield constant.³⁴ Why the resonance and stabilization energies are added to the Z-dependent affinity and ionization potentials becomes clear from the meaning of $U_0(Z)$ itself. $U_0(Z)$ is the energy recovered when the free ions combine to form the lattice. For closed-shell ions such a condensation occurs without any significant change of the electronic structure, the only effect being the rigid shift of levels produced by the Madelung monopole field. For open shells, instead, the condensation has three important effects. The first is the incomplete charge transfer from metal to halogen atoms. The second is the mixing of the halogen s and p orbitals occupied by bonding electrons with metal d orbitals, induced by the nondiagonal Coulomb interaction. The third is the rearrangement of the valence d electrons due to the crystal field. Such modifications, taking place with the change of the interionic distance, could be accounted for by some appropriate potentials: for instance, the valence-force-field potential^{26,27} for the covalency effect, and the quadrupolar Madelung potential for the *d* electron stabilization effect (quadrupolar-breathing-shell model). Since these (small) contributions are explicitly neglected in the present model potential, the ions in the gaseous phase should be "prepared" in the electronic configuration they shall have in the lattice, in order to keep such a configuration unchanged during condensation. The corrections to U_0 in Eq. (15) represent just the required overall preparation energy.

Within this approximation, we equate $U_0(Z)$ to a sum of two-body potentials valid for closed shells, namely

$$- U_{0}(Z) = 6b_{0}e^{-r_{0}/\rho_{0}} + 6be^{-a/\rho} + 3be^{-a'/\rho} + 3be^{-a''/\rho} - S_{6}c_{dd}/a^{6} - \mathbf{a}^{*}Z^{2}e^{2}/r_{0},$$
(16)

where b_0 and ρ_0 are the metal-halogen repulsive parameters, and r_0 the metal-halogen equilibrium distance. For the halogen-halogen repulsive parameters b and ρ we use the values known in alkali halides ($\rho = 0.3394$ Å, $\ln b = 7.8184$ for chlorides and 8.5709 for bromides, with b given in units of 10^{-19} J).²³ In nonideal (trigonally distorted) structures there are three different distances between neighbor halogen ions: that between ions in the same xy plane (a), and those between out-of-plane ions in the same layer (a") and in different adjacent layers (a').

The constant of the dipole-dipole vdW interaction between halogen ions, c_{dd} , is derived from the approximate London equation²³

$$c_{dd} = \frac{3}{4} E_D \alpha_A^2 , \qquad (17)$$

where E_p is an average halogen-ion excitation energy. We consider as an appropriate value for E_D the first peak of the D band,³⁵ corresponding to the transition from the outermost p orbital of the halogen to the 4s orbital of the transition metal. This transition, yielding the most prominent structure of the charge-transfer edge in uv absorption,³⁵ reflectivity,^{36,37} and soft x-ray spectra,³⁸ occurs nearly at the same energy in chlorides $(E_p = 8.32 \pm 0.16 \text{ eV})$ and bromides $(E_p = 8.32 \pm 0.16 \text{ eV})$ = 7.81 ± 0.05 eV). Thus a single average value c_{dd} $= 88 \times 10^{-79} \text{ Jm}^{-6}$ for chlorides, and $c_{dd} = 160$ $\times 10^{-79}$ J m⁻⁶ for bromides is used. Owing to the relative smallness of vdW contribution, we use for the lattice sum the same approximate value $S_{\rm g} = 14.454$ for all crystals: this corresponds to the undistorted C19 structure. in which the halogen ions form an fcc sublattice.²³

The Madelung constant entering the Coulomb term of Eq. 16 is the sum $\mathbf{a}^* = \mathbf{a}_N + \mathbf{a}_D$ of

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	a _M	a _D	c/aª	a ^a (Å)	Z	$w_0 Y \qquad \mu_0^{(1)}$ (Å)		U ₀ (10 ⁻¹⁹ J/mol)	ρ ₀ (Å)	$\ln\left(\frac{b_0}{10^{-19} \text{ J}}\right)$
VCl ₂	4.379	0.632	1.620	3.601	0.79	0.26	0.41	42.39	0.2089	11.2628
MnCl ₂ ^b	4.419	0.668	1.580	3.686	0.91	0.34	0.45	41.51	0.3373	7.4812
FeCl ₂ ^b	4.366	0.774	1.633	3.579	0.86	0.35	0.44	43.13	0.2948	8.1194
CoCl ₂ ^b	4.359	0.877	1.639	3.544	0.80	0.37	0.42	44.74	0.2567	9.0503
NiCl ₂ ^b	4.435	0.985	1.665	3.483	0.73	0.40	0.40	45.73	0.2276	9.9034
VBr_2	4.358	0.633	1.640	3.768	0.78	0.28	0.46	40.67	0.2155	11.3743
MnBr ₂	4.379	0.774	1.620	3.820	0.91	0.40	0.54	40.12	0.3075	8.3000
$FeBr_2$	4.348	0.875	1.650	3.740	0.83	0.40	0.51	42.02	0.2815	8.7490
$CoBr_2$	4.334	0.956	1.663	3.680	0.77	0.41	0.48	42.97	0.2490	9,5500
NiBr ₂ ^b	4.353	1.158	1.645	3.708	0.71	0.42	0.45	43.56	0.2300	10.2000
TiCl2	4.348		1.649	3.561				40.79		
$TiBr_2$	4.186		1.788	3.629				40.11		
TiI ₂	4.377		1.659	4.11				38.53		
VI ₂	4.329	0.804	1.666	4.057	0.75	0.348	0.326 °	39.83	0.1719	14.72
MnI ₂	4.358		1.639	4.16				39.38		
FeI ₂	4.325		1.670	4.04				41.19		
CoI ₂	4.315		1.679	3.96				42.32		
NiI ₂ ^b	4.431		1.539	3.892				43.53		

TABLE I. Crystal data of layer 3d-metal dihalides of either C6 or C19 structure.

^aAll crystal data are taken from Ref. 16, except those of NiCl₂ (u=0.235) and NiI₂ (u=0.233) taken from Ref. 39, and of VI₂ (u=0.240) from Ref. 47.

^bC19 structure.

^c From self-consistent calculation (Ref. 42).

monopole $(\mathbf{a}_{\mathcal{H}})$ and dipolar $(\mathbf{a}_{\mathcal{D}})$ contributions. a_p is a simple function of $\alpha_A/r_0^{3,39}$ taking values smaller than unity for all our crystals (except NiBr₂). Since the Coulomb energy is the main contribution in $U_0(Z)$, \mathbf{a}_M and \mathbf{a}_D have to be carefully calculated for the actual equilibrium configuration of the lattice and for the best-fitted values of the electrostatic constants w_0 , Y, and Z. In Table I we list only Z and Yw_0 , since w_0 was chosen to be - 0.1 Å for all crystals, except VCl₂ ($w_0 = -0.08$ Å) and VBr₂ ($w_0 = -0.09$ Å). The fitted static dipole Yw_0 is compared with the first iteration value $\mu_0^{(1)}$ calculated for the undistorted configuration. As explained in the previous section, $\mu_0^{(1)}$ turns out systematically larger than Yw_0 . C_M computed for all layered 3d-metal dihalides should be compared with the value for the ideal C6 ($\mathbf{G}_{M}^{0} = 4.366$) or C19 ($\mathbf{G}_{M}^{0} = 4.369$) structure.²² The deviation $\mathbf{a}_{\mu} - \mathbf{a}_{\mu}^{0}$ appears to be proportional to the deviation of the corresponding c/a from the ideal value $\left(\frac{8}{3}\right)^{1/2} = 1.633.^{40}$ For FeCl₂, having the ideal c/a value, the effect of the layer-distortion parameter u on \mathbf{a}_{N} and \mathbf{a}_{D} is also shown

in Table II. We note that \mathbf{G}_{u} depends rather strongly on u. This would be an unpleasant circumstance since u is not yet well known in most of the present compounds. Luckily, the variation of \mathbf{G}_{u} with u is compensated to a large extent by the opposite variation of \mathbf{G}_{D} , so that the indetermination of u has only a minor effect on the fitting to cohesive energy.

In this fitting procedure, the most serious lack of information concerns the resonant integral $\beta = \langle \psi_M | H | \psi_A \rangle$ between metal (ψ_M) and halogen (ψ_A) orbitals. Our main difficulty is to know how β

TABLE II. Madelung constants as function of u in FeCl₂.

FeCl ₂	u	Ct _M	a _D
	0.23	4.487	0.691
$w_0 = -0.10 \text{ Å}$	0.24	4.429	0.733
Y = -3.5	0.25	4.366	0.774
Z = 0.86	0.26	4.297	0.813
c/a = 1.633	0.27	4.222	0.851

implicitly depends on Z through its dependence on the interionic distance. Considering the bonding and antibonding combinations of atomic orbitals

$$\left|\psi_{b}\right\rangle = \sin\gamma \left|\psi_{M}\right\rangle + \cos\gamma \left|\psi_{A}\right\rangle, \qquad (18)$$

$$\left|\psi_{a}\right\rangle = \cos\gamma \left|\psi_{M}\right\rangle - \sin\gamma \left|\psi_{A}\right\rangle, \qquad (18')$$

with $\cos 2\gamma = Z$ and the diagonality condition

$$= \frac{1}{2}(E_{\mu} - E_{A})(1 - Z^{2})^{1/2} + Z\beta,$$

 $0 = \langle \psi_{\mathbf{h}} | \mathbf{3} \mathbf{C} | \psi_{\mathbf{n}} \rangle$

we have

$$2\beta = -(E_M - E_A)(1 - Z^2)^{1/2}/Z, \qquad (20)$$

where $E_M = \langle \psi_M | \mathcal{K} | \psi_M \rangle$ and $E_A = \langle \psi_A | \mathcal{K} | \psi_A \rangle$ are the

Coulomb integrals. Pearson and Gray,⁴¹ in their theory of ionicity of the free molecule, have established the following empirical relationships between the Coulomb integrals and the macroscopic parameters:

$$E_{M} = -ZI_{2} - \frac{1}{2}(1-Z)(I_{1}+I_{2}) + \frac{1}{2}\epsilon_{p} , \qquad (21a)$$

$$E_{A} = -(1 - Z)I_{a} - \frac{1}{2}Z(I_{a} + A) - \frac{1}{2}\mathbf{a}^{*}Ze^{2}/r_{0}, \quad (21b)$$

where ϵ_{p} is the promotional energy to the lowest *sd*-orbital bonding configuration. We borrow these equations just by reinterpreting \mathbf{a}^{*} as the crystalline rather than molecular Madelung constant. Inserting Eqs. (20) and (21) into Eq. (15), we rewrite $U_{0}(Z)$ as

$$U_0(Z) = U_0 - E_s + \frac{1}{Z} \left[(1 - Z)^2 I_1 + (1 - Z^2) I_2 + Z(1 - Z) A_1 - (2 - Z - Z^2) I_a - (1 - Z^2) \epsilon_p \right] - (1 - Z^2) \mathfrak{a}^* e^2 / r_0.$$
(22)

(19)

This is an interesting form of $U_0(Z)$, because it shows what is lost by reducing the Madelung energy [via the net charge reduction, the last term of Eq. (22)] and what is gained in the formation of the partially covalent bond.

The values of $\ln b_0$, with b_0 in units of 10^{-19} J, and ρ_0 obtained from Eqs. (10c) and (16) are also shown in Table I together with U_0 . The set of the short-range radial and transverse force constants is collected in Table III.

VI. DISPERSION CURVES

The dispersion curves calculated along the main symmetry directions (Fig. 1) for V, Mn, Fe, Co, and Ni dichlorides and dibromides are plotted in Figs. 2-11. (The results on VI₂ were already reported in a previous communication.⁴²) The modes having no transverse component parallel to the plan of the layers are represented by dashed lines.

The available neutron data for $MnCl_{2}$, ⁴³ FeCl₂, ⁴⁴ and CoCl₂, ⁴⁵ and the experimental optical modes are superimposed onto the dispersion curves for a comparison. Taking into account that neutron data were not used for the determination of the model parameters, we consider the agreement between experimental and calculated results to be very satisfactory. The comparison for MnCl₂, whose optical branches also have been measured, will be discussed more extensively below.

In order to appreciate the quality of the fitting of Z, Y, and w_0 to the experimental optical frequencies,¹⁹⁻²¹ in Table IV they are compared with the calculated values. Again the overall agreement is rather good. Moreover, the ionicity scale given by the fitted values of Z looks very reasonable (Fig. 12). The descending values from Mn to Ni compounds and the lower ionicity found in bromides with respect to chlorides are well consistent with what would be expected from gen-

TABLE III. Calculated short-range-force constants in units of e^2/v_0 , where $v_0 = \sqrt{3} ca^2/2$ is the cell volume; e^2/v_0 (last column) gives for comparison a measure of Coulomb force constants. In this model $A_{MM} = 0$.

	A _{MA}	B _{MA}	A _{AA}	B _{AA}	A _{AA} ,	B _{AA} ,	A _{AA} .,	В _{АА} ,,	B _{MM}	$e^2/v_0 ~({\rm Jm^{-2}})^{\rm a}$
VCl ₂	32.95	-2.75	1,512	-0.142	1.088	-0.0168	2,329	-0.228	0.984	3.511
MnCl ₂	26.14	-3.49	1.231	-0.113	0.959	-0.0234	2.496	-0.246	1.268	3.356
FeCl ₂	24.61	-2.93	1.596	-0.151	0.978	-0.0198	2,573	-0.255	1.135	3.548
CoCl ₂	25.13	-2.63	1.725	-0.165	1.029	-0.0167	2.709	-0.271	0.977	3.640
NiCl ₂	24.40	-2.29	1.191	-0.194	1.063	-0.0134	2.813	-0.283	0.841	3.775
VBr_2	32.82	-2.702	2.275	-0.205	1.422	-0.0195	3.383	-0.316	1.170	3.027
$MnBr_2$	27.15	-3.165	2.009	-0.178	1.307	-0.0267	3.430	-0.319	1.507	2.941
FeBr ₂	25.43	-2.757	2.430	-0.220	1.380	-0.0213	3.642	-0.343	1.266	3.077
$CoBr_2$	24.08	-2.341	2.785	-0.256	1.490	-0.0176	3.944	-0.375	1.103	3.205
NiBr ₂	22.14	-2.072	2.459	-0.225	2.428	-0.0143	4.785	-0.466	0.771	3.167

^aSince we adopt SI units, electrical expressions are intended to be multiplied by $1/4\pi\epsilon_0$. This factor is omitted for simplicity.



FIG. 2. Dispersion curves of VCl₂ (C6 structure). The wave-vector units are shown in parentheses for each symmetry direction. The point groups, whose irreducible representations label the phonon branches, are D_{3d} at Γ and A, C_{2h} at M, D_3 at K, C_{3v} along Δ , C_s along Σ , and C_2 along T(T'). The irreducible representations at A are the same as in Γ ; TA modes are E_u and LA mode is A_{2u} . The dashed lines refer to modes having no transverse component parallel to the plan of the layers. Black triangles are experimental RS and ir frequencies (Ref. 20).

eral chemical arguments. The same trend is found for free 3d-metal dichloride molecules (Fig. 12),⁴¹ whose ionicities however, are systematically lower than those of the correspondent crystals. This is essentially due to the shorter interionic distance occurring in molecules. Such a qualitative relationship between interionic distance and ionicity explains the exception of vanadium salts which are more covalent than manganous salts in the crystal and less covalent in the free molecule state. In fact the lattice distances of Mn dihalides are the largest of the series. On the other hand, the cohesive energy of manganous dihalides is a minimum along the 3d-metal series, a well known fact explained for the past twenty years in terms of crystal-field stabilization.³²

Some indication of the relatively high ionicity of $MnCl_2$ and $MnBr_2$ was obtained many years ago by Stout from the fitting of crystal-field spectra.³³ The values reported in that work (Z = 0.87 and 0.85, respectively) are consistent with the present results.

It would be interesting to compare this ionicity scale with some direct experimental information on the ionicity, e.g., the neutron data on the transferred hyperfine interaction (THFI).⁴⁶ For this class of crystals THFI measurements have been reported only for VI₂.⁴⁷ These data are found



FIG. 3. Dispersion curves of MnCl₂ (C19). Experimental neutron data (black points) from Ref. 43; RS and ir data (black triangles) from Refs. 19 and 21.



FIG. 4. Dispersion curves of FeCl₂ (C19). Experimental neutron data (black points) from Ref. 44; RS and ir data (black triangles) from Refs. 19 and 21.

to be consistent with the calculated value Z = 0.75 obtained for VI₂ within the present model.⁴²

In spite of the relatively high ionicity of these compounds, the dynamical charges (Szigeti and effective charges) as deduced from this ESM calculation (Table V) are rather small, indicating a relatively large charge transfer associated with optical polar vibrations. As expected for layer structures,³⁰ the anisotropy of $Z_{\alpha\alpha}^{eff}$ and $\epsilon_{\alpha\alpha}^{s}$ is also rather large, whereas the Szigeti charge $Z_{\alpha\alpha}^{s}$ turns out to be almost isotropic.

In Table V we list the calculated elastic constants. Only for $CoCl_2$ is some experimental information on the elastic constants available. The calculated values are in fair agreement with the data deduced from neutron dispersion curves.⁴⁵

The dynamical structure of a layered ionic

crystal is characterized by the complex interplay of various long- and short-range contributions, so that it is not easy to relate some features such as anisotropy, LO-TO splittings, etc., to welldefined terms of the dynamical matrix. Therefore, it is convenient to analyze the structure of the dispersion curves by showing in which manner the various kinds of interaction contribute to the eigenfrequencies in different high-symmetry points of the Brillouin zone.

In Figs. 13-16 we show how the frequencies of $MnCl_2$, calculated at the points Γ , M, K, and A for a rigid-ion model (Born-Mayer repulsion plus monopole Coulomb interaction) are modified by the addition of the various ESM contributions and, finally, of the vdW interaction.

In the rigid-ion model (first column of each



FIG. 5. Dispersion curves of CoCl₂ (C19). Experimental neutron data (black points) from Ref. 45; RS and ir data (black triangles) from Refs. 19 and 21.



FIG. 6. Dispersion curves of NiCl₂ (C19). RS and ir data (black triangles) from Refs. 19 and 21.

diagram) the most relevant feature, occurring at the Γ point, consists in the very small A_{2u} - E_u splitting and, consequently, in a practically isotropic LO-TO splitting. The latter splitting, on the other hand, is very largely due to the great ionic character of this compound.

The first ESM contribution (second column of the diagrams) is that due to the dynamical polarizabilities of the negative ions. Since the static dipoles are still neglected, we have now an ordinary shell model. The ion softening produces a general decrease of the frequencies, with a striking effect at the points M and K (and therefore in a wide short-wavelength region): the frequencies of the lower TA mode of B_u or A_2 symmetry, respectively, become imaginary, yielding a lattice instability with in-layer reconstruction.

Such a result, however, is originated by an internal inconsistency of the model because polariizable anions must have also a static dipole. When static dipoles are allowed in the model, two distinct effects are considered: one is the switching of long-range pole-dipole and dipole-dipole interactions (third column); the other effect, of shortrange character, is the change of Born-Mayer interaction due to the shell displacement (fourth column). The static displacement also produces a change in the application point of Coulomb forces, namely a Coulomb force constant change via its anharmonic part (see Sec. II). This effect is also included in the short-range dipolar term.

The long-range part of the dipolar interaction removes the instability at M and K. This is due to a large increase of the acoustic frequencies, which is accompanied by an overall decrease of the higher optical frequencies. Such a spectral narrowing occurring at M and K is compensated by an opposite behavior at the points A and Γ . This consists essentially in the appearance of wide $A_{2u}-E_u$ and $A_{1e}-E_e$ splittings. Indeed, as al-



FIG. 7. Dispersion curves of VBr₂ (C6). RS and ir data (black triangles) from Ref. 20.



FIG. 8. Dispersion curves of MnBr₂ (C6). RS and ir data (black triangles) from Refs. 19 and 21.

ready pointed out,^{12,13} the optical-mode anisotropy is mainly due to the long-range dipolar interaction.

As concerns the short-range dipolar term, we note that only a small increase of the optical frequencies and a decrease of the acoustic one are produced all over the Brillouin zone. Analogously, the vdW attractive forces (last column) are responsible for a general frequency softening. This effect, however, is rather small for all modes, except for the acoustic A_{2u} branch along the c axis (see the A_{2u} mode at the point A) whose lowering is relatively larger.

The specific effect of vdW forces on the acoustic A_{2u} branch is important for obtaining good agreement with neutron dispersion curves. When a model neglecting vdW interaction is forced to fit the neutron acoustic branches in Z direction, poor results for the optical branches and unphysical values for Z would be obtained. This might explain the very low values of Z (0.06 for FeCl₂ and 0.41 for CoCl₂) found by Pasternak.^{14,15}

VII. PHONON DENSITIES

The one-phonon frequency densities were calculated over a grid of 256 264 points in the BZ generated by means of a tetrahedral linear interpolation method from a set of 75 values of q uniformly distributed in the irreducible part (one twenty-fourth) of the BZ.

The density of Mn to Ni dichlorides and dibromides are shown in Figs. 17 and 18, respectively. The superposition of the spectra with the frequency scale normalized to the maximum frequency ω_M enables one to note the gradual modifications due to different metal ions. The effects on the phonon densities due to change of the anions is shown in Fig. 19 for V dihalides.

All crystals present rather sharp peaks in the phonon density, which means they have a pronounced molecular character.

When the cation is changed from Mn to Ni, a general narrowing of the phonon bands, correlated



FIG. 9. Dispersion curves of FeBr₂ (C6). RS and ir data (black triangles) from Refs. 19 and 21.



FIG. 10. Dispersion curves of CoBr₂ (C6). RS and ir data (black triangles) from Refs. 19 and 21.

with the opening of gaps, is observed both in chlorides and bromides. Such a band narrowing is related to the increasing covalency, and occurs also when chlorine is replaced by heavier anions.

Vanadium dihalide spectra (Fig. 19), compared with the other chlorides and bromides, display even sharper bands and larger gaps, as if they would be more covalent than Ni compounds. This apparently contradicts the fact that Z is larger in V than in Ni dihalides. Actually, the dynamical charges are responsible for the dispersion. While in Mn to Ni dihalides Z_{as}^{off} turns out to be close to the net charge, in V compounds Z_{as}^{off} is considerably smaller than Z (see Table V). Particularly in VI₂, which still has a relatively high ionicity, both Szigeti and effective charges are remarkably low; this is clearly reflected by the sharp features and the wide gap between optical branches occurring in the phonon density.

Another aspect of the relatively higher dynamical covalency of V dihalides is the relatively small LO-TO splitting of A_{24} modes (as in some di-

chalcogenides and di-iodides^{30,48}). As a consequence, their maximum frequency occurs at the M point, whereas in the other compounds ω_M is always the $A_{2\mu}$ (LO) frequency. Since the modes with ω close to $\omega(A_{2u}, LO)$ have a q value included in a very narrow cone around the c axis (due to the nonanalytical behavior of the Coulomb matrix elements for $\vec{q} \rightarrow 0$). Mn to Ni dihalides display a long and weak tail in the LO density, which is absent in VX_2 . This effect, however, seems to be overestimated in the present calculation, since the experimental $\omega(A_{2\mu}, LO)$ of MnCl₂ is 19 cm⁻¹ below the calculated value. It is interesting to note that ω_M decreases from MnBr₂ to NiBr₂ and increases from MnCl₂ to NiCl₂. This is easily explained by considering the competing effects of the increasing covalency (which yields a contraction of the unit cell and a strengthening of the force constants), and of the increasing metal mass. In the A_{2*} mode of dibromides the metal ion vibrates practically alone, whereas in dichlorides the anions take part of the motion: in the latter the



FIG. 11. Dispersion curves of NiBr₂ (C19). RS and ir data (black triangles) from Refs. 19 and 21.

$\omega(\Gamma)$ (cm ⁻¹ or 2π 0.03 THz)												
	A	18	E_{g}		$A_{2u}(LO)$		$A_{2u}(\mathrm{TO})$		$E_{u}(LO)$		$E_u(TO)$	
Г	expt.	cale.	expt.	calc.	expt.	cale.	expt.	calc.	expt.	calc.	expt.	calc.
VCl ₂	247	242	198	198		338	320	315	325	321	286	287
MnCl ₂	235	224	144	145		308	255	255		276	185	180
FeCl ₂	250	233	150	148		315	270	271		271	192	185
CoCl ₂	253	240	156	161		317	277	281		272	206	206
NiCl ₂	269	247	173	167		324	293	295		270	225	217
VBr_2	158	150	120	122		266	261	254	256	250	231	232
$MnBr_2$	151	152	90	96		263	234	226		225	143	150
$FeBr_2$	159	154	94	99		259	231	230		218	154	158
$CoBr_2$	162	155	9 8	104		253	230	227		212	161	167
NiBr ₂	168	163	106	116		248	230	230		212	181	181

TABLE IV. Room temperature experimental (from Refs. 19–21)^a and calculated frequencies of the optical modes at the point Γ .

^aA limited number of low-temperature Raman and infrared data is available. For a comparison see Refs. 17-19.

metal mass has a weaker influence on the optical frequencies.

A final remark: in all dichlorides, except VCl₂, the even- and odd-symmetry optical branches cross each other, so that the $E_u(TO)$ modes is always below the A_{1g} mode, while in bromides and V dihalides there is a complete separation between even- and odd-symmetry branches. In the latter compounds (see, e.g., NiBr₂) the bands of even modes present three sharp peaks (four peaks in NiCl₂), and those in the middle are associated with the A_g modes at the M point. This structure is clearly seen in the two-phonon infrared absorption of V dihalides.²⁰

VIII. DISCUSSION

In view of the small number of adjustable parameters used in this ESM version, the reliability



FIG. 12. Fitted net ionic charge of crystal 3d-metal dihalides compared with calculated free-molecule values (from Pearson and Gray, Ref. 41; these authors did not report any value for the VCl₂ molecule). We recall that CrX_2 crystals have structures other than C6 or C19.

of their values, and the reasonable agreement with the available neutron data, we consider this shell-model approach to the lattice dynamics of layer compounds as quite successful. Nevertheless, we are conscious of the fact that a complete comparison with the experimental data is done only for the most ionic compound of the series, $MnCl_2$. The important discrepancy found at the K point for the acoustic E mode (146 cm⁻¹ against the experimental value 118 cm⁻¹) is probably a common feature of the model and should occur also in the other crystals.

Moreover, we expect such discrepancy to increase with the crystal covalency, a point which should be verified as soon as more complete neutron-dispersion curves will be disposable. However, we have observed that the acoustic E mode at the K point is strongly affected by the central metal-metal interaction. When A_{MM} is allowed to be different from zero, one finds that the discrepancy is practically removed for $A_{MM} = -2B_{MM}$. If we believe in such a numerical correspondence, we infer that metal-metal force constants can be derived from an attractive, soft Coulomb-type potential, which results in a sensible reduction of the metal-metal monopole repulsion. This argument, however, sounds quite artificial, since it is a mere two-body transcription of the metal-metal covalent bonding which has a marked three-body character. As in superexchange the unpaired delectrons of neighboring metal ions take part of a "90° supercovalent" bond via the partially open anion shells. As a consequence, the smaller Zis, the larger should be the metal-metal interaction.

There is some hint that three-body forces play a non-negligible role also in these relatively

								(10^7 N m^{-1})						
	Ζ	Z_{xx}^S	Z^{S}_{zz}	$Z_{\rm xx}^{\rm eff}$	$Z_{zz}^{\rm eff}$	€ [∞] _{xx}	€ _{ZE}	<i>C</i> ₁₁	C ₃₃	C ₄₄	C ₆₆	<i>C</i> ₁₄	C ₁₃	
VCl ₂	0.79	0.435	0.484	0.720	0.616	2.567	2.527	61	24	6.5	25	-6.6	17	
MnCl ₂	0.91	0.659	0.726	1.104	0.893	2.560	2.501	57	18	4.7	26	-6.5	12	
FeCL	0.86	0.615	0.659	1.050	0.856	2.710	2.623	61	22	5.0	26	-6.6	13	
CoCl,	0.80	0.549	0.590	0.956	0.772	2.784	2.697	62	25	5.4	28	-7.4	16	
NiCL	0.73	0.492	0.521	0.875	0.707	2.919	2.812	63	28	5.6	2 8	-8.1	18	
VBr ₂	0.79	0.346	0.398	0.637	0.519	2.954	2.867	56	26	7.1	24	-5.2	18	
MnBr,	0.91	0.635	0.687	1.205	0.939	3.158	3.042	51	23	5.3	25	-6.6	9.7	
FeBr,	0.83	0.559	0.598	1.093	0.854	3.344	3.194	54	27	6.1	25	-6.8	12	
CoBr,	0.77	0.498	0.530	1.006	0.778	3.524	3.342	57	32	7.1	26	-7.2	14	
NiBr,	0.71	0.424	0.487	0.915	0.680	3.638	3.635	59	37	8.0	22	-8.9	15	
VI ₂	0.75	0.224	0.276	0.510	0.347	3.703	3.480	55	37	7.5	27	-4.5	16	

TABLE V. Macroscopic constants.

ionic compounds. Nearest-neighbor angle-bending force constants, which produce anisotropy in the short-range repulsive interaction,^{26,27} can by themselves remove the residual discrepancies between experimental and calculated optical frequencies.²¹ We note in Table IV that the experimental anisotropy of even modes given by $\omega(A_{ig}) - \omega(E_g)$ is slightly larger than the theoretical one, with deviations increasing from Mn to Ni. Such deviations (5–18 cm⁻¹) could be regarded as an estimate of the effect of three-body forces.

Other terms in the dynamical matrix which were

explicitly neglected are those coming from the crystal-field stabilization energy E_{g} . The adiabatic modulation of the d^{n} -electron ground-state energy due to even symmetry displacements of neighbors yields monopole and quadrupole breathing force constants. To give an idea on the order of magnitude of these contributions we have derived the central force constants for cubic (A_{1g}^{0}) , tetragonal (E_{g}^{0}) , and trigonal (T_{2g}^{0}) deformations of the nn octahedral cage (apex O labels O_{h} irreducible representations). This calculation can be easily done by considering the six nearest neighbors as point ions and using the axial field



FIG. 13. Effect of the various ESM contributions on the optical phonon frequencies of $MnCl_2$ at Γ point.



FIG. 14. Effect of the various ESM contributions on the phonon frequencies of $MnCl_2$ at M point.



FIG. 15. Effect of the various ESM contributions on the phonon frequencies of $MnCl_2$ at K point.

matrix elements between t_{2g} or e_g d-electron states reported by Sugano et al.⁴⁶ For a groundstate configuration $t_{2g}^m e_g^{n-m}$ we find

$$\frac{\partial^2 E_s}{\partial u (A_{1q}^0)^2} = 10(3n - 5m) \frac{Dq}{r_0^2} , \qquad (23)$$



FIG. 16. Effect of the various ESM contributions on the phonon frequencies of $MnCl_2$ at A point.



FIG. 17. Phonon frequency density (arbitrary units) of 3d-metal dichlorides.

$$\frac{\partial^2 E_s}{\partial u(E_g^0)^2} = 25(n-2m) \frac{Dt}{r_0^2} - 2(4n-m) \frac{Ds}{r_0^2} , \qquad (24)$$

$$\frac{\partial^2 E_{\bullet}}{\partial u (T_{2_{\theta}}^0)^2} = 5(n-6m) \frac{Dt}{r_0^2} + \frac{1}{2} (2n-5m) \frac{Ds}{r_0^2}, \quad (25)$$

where



FIG. 18. Phonon frequency density (arbitrary units) of 3d-metal dibromides.



FIG. 19. Phonon frequency density (arbitrary units) of V dihalides.

$$Dq = \frac{e^2 \langle r_{\theta}^4 \rangle}{6r_0^5}, \ Ds = \frac{e^2 \langle r_{\theta}^2 \rangle}{14r_0^3}, \ Dt = -\frac{3}{28} Dq , \qquad (26)$$

and $\langle r_{e}^{n} \rangle$ is the *n*th momentum of the 3*d*-electron radial distribution. The monopole breathing term Eq. (23), often the only one taken into account, vanishes for the Mn²⁺ ground state (n = 5, m = 3)and this was the reason why we did not find it convenient to include the breathing contributions in the model. However, in NiCl₂ $(Dq = 692 \text{ cm}^{-1})^{34}$ the monopole breathing force constant is -3.52 e^{2}/v_{0} , which is comparable to B_{NA} . Such a term is quite appreciable; we feel that, as soon as a detailed comparison with neutron dispersion curves will be possible, breathing force constants should be included in the dynamical model.

With regard to quadrupole breathing terms [Eqs. (24) and (25)], we cannot say much, as the expressions of Ds and Dt Eqs. (26), valid in the point-ion approximation, are not very reliable, owing to the omission of the (large) overlap effects. However, in a future work Eqs. (24) and (25) could be used with Ds taken as a disposable parameter, and with Dt related to the experimental Dq via Eq. (26).

Incidentally we note that Eqs. (23)-(25), when

used for excited d configurations, enable us to know the relaxation-induced renormalization of the force constants. For example, they could account for the difference between the groundstate phonon frequencies obtained by Raman or infrared techniques and those derived from the vibronic sidebands in crystal-field absorption spectra which refer to the excited state.^{21,49}

In recent years it was recognized that a considerable amount of information on lattice dynamics and electron-phonon interaction can be extracted from the spectroscopy of crystal-field transitions in 3d-metal layer compounds.^{18, 19, 21} Their low-temperature absorption spectra show an unusual wealth of vibronic structures, whose sharpness as well as their repetitive character to high orders recall molecular spectra.^{19,21} The physical basis of such highly resolved many-phonon patterns is now apparent from some peculiarities of the calculated phonon densities, such as the occurrence of sharp peaks, associated with different symmetries and intercalated by three or even four gaps. This distinctive feature, reaching the highest degree in V and Ni dihalides, takes its source from the combination of partial covalency with large-gap insulator properties. A quality which should disappear in layered transition-metal chalcogenides, 50-52 where the conduction-electron screening via the q-dependent charge transfer⁵³ supplies a strong dispersion factor for the optical branches.

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