Valence force fields and the lattice dynamics of beryllium oxide

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The lattice dynamics of beryllium oxide have been studied using a rigid-ion model, with short-range forces represented by a valence force field. Various existing calculations on group-IV elements using such a field have been examined as a prelude to transference of force constants from diamond to beryllium oxide. The effects of ionicity on the force constants have been included in the form of scale factors. It is shown that no satisfactory fit to the long-wavelength data on BeO can be found with transferred force constants. However, adequate least-squares fits can be found both with four- and six-parameter valence force fields, the discrepancy with experiment being large only for one optical mode at the Brillouin-zone center. Dispersion curves along Δ and Σ are presented and are in fair agreement with experiment, deviations arising essentially from the quality of the fit to the long-wavelength data. The bond-bending interactions are found to play a significant role and arguments have been presented to show that the inclusion of further angle-angle interactions would yield a very satisfactory picture of the dynamics.

I. INTRODUCTION

We have recently concluded a series of investigations of the lattice dynamics of graphite, boron nitride, and beryllium oxide. The objectives have been twofold: (a) to investigate the range of applicability of valence force fields to these crystals and (b) to study the extent to which force constants could be transferred from molecules to solids and from one solid to another. The work on graphite[1,2] has shown that a very satisfactory fit to the dispersion curves of graphite can be obtained by direct transference of the main force constants from naphthalene.

A similar study for BeO necessitated a critical examination of the use of valence force fields in diamond, and other crystals with the same structure, namely, Si and Ge. It was also found necessary to study the effect of the ionicity on the force constants in transferring the results on diamond to BeO. Further, the role of the angle-angle interactions indicated that the extent to which they were included made significant differences to the final results. In view of the recent interest in angle interactions in tetrahedrally coordinated solids,[3,4] we present here a discussion of the valence forces in the Group-IV elements, along with a calculation of the dynamics of BeO.

II. VALENCE FORCE FIELDS

In this section we summarize, for future reference, the description of the valence force field (VFF). The distortion energy per unit cell of the crystal, in this scheme, is written

$$\phi = \frac{1}{2}\sum_{i=1}^{4} k_r(\Delta r_i)^2 + \sum_{s=1}^{2}\left(\frac{1}{2}\sum_{i,j>i} r_0^2 k_\theta^{(s)}(\Delta\theta_{ij}^s)^2\right.$$

$$\left. + \sum_{i,j\neq i} r_0 k_{r\theta}^{(s)}(\Delta r_i)(\Delta\theta_{ij}^s) + \sum_{i,j>1} r_0^2 k_{rr}^{(s)}(\Delta r_i)(\Delta r_j)\right). \tag{1}$$

As it stands, the expression is valid for a structure containing two atoms per cell with tetrahedral coordination, and can easily be generalized for any other structure. The notation is that of Martin[5] and Musgrave and Pople,[6] with the various symbols having the following meaning: (a) r_0 is the equilibrium bond length; (b) Δr_i is the change in the length of the ith bond; (c) $\Delta\theta_{ij}^s$ is the change in the angle between the ith and jth bonds emanating from the sth atom.

In the last two terms in Eq. (1), the bonds considered meet at the sth atom. The various k's are the valence force constants connected with bond-stretching, bond-bending, bond-angle, and bond-bond interactions, in the order in which they appear in the equation.

In the course of analyzing the long-wavelength data for the diamond structure, one can determine only an average bond-bending force constant

$$k_\theta = \frac{1}{2}(k_\theta^{(1)} + k_\theta^{(2)}). \tag{2}$$

Though this is not so for the wurtzite structure, we shall quote only k_θ unless specifically necessary. Similar arguments hold true for the $k_{r\theta}$ and k_{rr} interactions.

In a number of applications of VFF's to diamond, Si, and Ge, other terms of the type

$$r_0^2 k_{\theta\theta}'\sum_{s=1}^{2}\sum_{j,i\neq k}(\Delta\theta_{ij}^s)(\Delta\theta_{jk}^s) + r_0^2 k_{\theta\theta}''$$

$$\times \sum_{s,s'\neq s}\sum_{j,i\neq k}(\Delta\theta_{ij}^s)(\Delta\theta_{jk}^{s'})\cdots \tag{3}$$

are added to Eq. (1). The first term in Eq. (3) represents interactions between angles centered

at the same atom. In the second term the angles are centered at different atoms, with the provision that all four atoms involved are coplanar. Further refinements of the force field are possible,[7] but result in a proliferation of parameters and are ignored in the present study.

The dynamics can now be worked out in one of two ways. In the first, the dynamical matrix can be set up in the standard Born–von Kármán scheme,[8] involving tensor force constants (TFC's); the relations between the TFC's and the valence force constants (VFC's) being obtained by standard methods. In the second, the secular equation can be written directly in terms of the valence co-ordinates[9] and then diagonalized. The final results are the same in both methods and we have used whichever one is most suitable for the purpose at hand.

It is helpful to know the contribution of the VFC's to the TFC's between different neighbors. All the constants given in Eqs. (1) and (3) effectively contribute to first- and second-neighbor interactions. The $k''_{\theta\theta}$ interaction in Eq. (3) further contributes to the TFC's between fifth neighbors in the case of the diamond structure, and to the TFC's between third and fifth neighbors in the wurtzite structure.

III. VALENCE FORCE CONSTANTS FOR THE GROUP-IV ELEMENTS

The VFF concept as outlined earlier has been used to study the dynamics of diamond,[9,10] silicon,[7,10,11] and germanium.[10] In addition, Martin[5] has used the Keating model[12] to study the long-wavelength properties of a range of tetrahedrally coordinated crystals.

In Table I, we list the VFC's for diamond as obtained by several workers. It is to be noted that there is a difference of $\sqrt{2}$ in the definition of $k_{r\theta}$ between Martin's values and those of the others,

TABLE I. VFC's for diamond (in 10^5 dyn cm^{-1}) from different workers.

VFC	Ref. 9	Ref. 10	Ref. 13[a]	Ref. 5
k_r	3.89	3.831	4.307	4.3037
k_θ	0.3582	0.3676	0.454	0.565
k_{rr}	0.1373	0.164	0.138	0.071
$k_{r\theta}$	0.1982	0.18	0.185	0.1998
$k'_{\theta\theta}$	−0.008	−0.0062	0.018	0.0
$k''_{\theta\theta}$	0.0895	0.0729	0.0365	0.0

[a]Values obtained from a vibrational analysis of paraffins.

TABLE II. Experimental and calculated values of long-wavelength data for diamond.

	Expt.[a]	Ref. 9	Ref. 10	Ref. 13	Ref. 5
c_{11}	107.6	106.0	104.3	103.4	107.9
c_{12}	12.5	13.01	15.6	20.5	12.55
c_{44}	57.58	55.9	53.2	58.1	54.1
ω_R	1332	1336	1334	1410	1636
Δ_{rms} (%)	...	2.62	13.06	32.20	11.8

[a]Experimental values of elastic constants from Ref. 14, in 10^{11} dyn cm^{-2}. Raman frequency values in cm^{-1}.

which we have incorporated. Further, though four VFC's have been shown in the last column, it has to be remembered that in the Keating model there are only two independent constants.

In Table II, the experimental values of the elastic constants and the Raman frequency are compared to the theoretically calculated values. We have reevaluated the latter using the respective input data and have also listed a rms deviation for each set of calculations. Similar compilations have also been made for Si and Ge but have not been listed here to conserve space.

It can be seen from the tables that various sets of calculations yield essentially the same stretching force constant k_r but that the angle constants vary widely. The trend $k_r > k_\theta > k_{r\theta} > k_{rr}$ is generally obeyed. Judged by the fit to the long-wavelength data, the best fit to diamond is that of McMurry et al.[9] (and Solbrig[7] for Si). The calculations of Tubino et al.,[10] while being satisfactory for diamond, yield negative values of the elastic constant c_{12} for Si and Ge. In general, the $k'_{\theta\theta}$, $k''_{\theta\theta}$ constants are one order of magnitude lower than the smallest of the other constants, with $k''_{\theta\theta} > k'_{\theta\theta}$. However, putting these equal to zero substantially alters the fit to experiment, since their contribution to the TFC's is large.

The Martin-Keating[5] values of the VFC's give an excellent fit to the elastic constants. However, the Raman frequency is not so well described; the discrepancy with experiment being greatest for diamond and decreasing through Si and Ge. This might arise from the neglect of angle-angle interactions and/or the interrelations between the VFC's arising from the Keating model. Regarding the latter, Martin has already noted that the relations $k_{rr} = \frac{1}{8}k_\theta$ and $k_{r\theta} = k_\theta/2\sqrt{2}$ are not satisfied by the VFC's of McMurry et al.,[9] these holding only in the Keating model. However, the main Keating constants α and β given by

$$k_r = 3\alpha + \tfrac{1}{2}\beta, \qquad k_\theta = \tfrac{2}{3}\beta, \qquad (4)$$

show certain trends with ionicity,[5] which indicates that the variation of stretching and bending con-

stants on going through crystals of different ionicity are different.

IV. MODELS FOR THE DYNAMICS OF BeO

The dynamics of BeO (wurtzite structure, space group C_{6v}^4) have been worked out by Nusimovici,[15] using a VFF–rigid-ion model which had previously been applied to CdS by Nusimovici and Birman.[16] The VFF used differs from that defined in Sec. II; the common constants are k_r, $k_\theta^{(1)}$, and $k_\theta^{(2)}$.

We have used the constants given by Nusimovici to recalculate the long-wavelength data for BeO, using the equations of Ref. 16. This yields negative values for some of the optical frequencies, because of the negative values of the bending constants $k_\theta^{(1)}$ and $k_\theta^{(2)}$. Assuming that these are numerically the same but positive, results in frequencies which are about 50% more than the experimental values.

It was thought worthwhile, therefore, to study again the dynamics of this crystal. Essentially two types of models were chosen, their characteristics being dictated by the objectives of this work and by some tentative conclusions formed by the study of the data on the Group-IV crystals. The A-type models all had the VFC's of Eqs. (1) and (3), while the B-type models had only the VFC's of Eq. (1). Three variants of each type of model were examined, these arising from the kind of fitting procedure used in evaluating the parameters. Transference of force constants from diamond was made in models A_1 and A_2, starting from the VFC's of McMurry et $al.$[9] The effects of ionicity on the VFC's were incorporated by scaling the diamond constants by factors which were determined by fitting to the optical frequencies. In model A_1; k_r and k_θ were scaled by a factor λ_1 and all others by λ_1^2. In model A_2; k_r and k_θ were scaled by λ_2 and λ_3, respectively, the other interaction constants being scaled by λ_2^2, λ_3^2, and $\lambda_2\lambda_3$ for the (rr), $(\theta\theta)$, and $(r\theta)$ interactions. Fitting yielded $\lambda_1 = 0.308$, $\lambda_2 = 0.444$, and $\lambda_3 = 0.105$. In

TABLE III. VFC's for BeO (in 10^5 dyn cm^{-1}) for a general VFF (see text for explanation of models).

| VFC | Model | | |
	A_1	A_2	A_3
k_r	1.198	1.727	2.220
k_θ	0.110	0.038	0.164
k_{rr}	0.013	0.027	0.038
$k_{r\theta}$	0.019	0.009	0.149
$k_{\theta\theta}'$	−0.0008	−0.0001	0.001
$k_{\theta\theta}''$	0.0085	0.001	0.010

TABLE IV. Experimental and calculated values of long-wavelength data for BeO, with VFC's from Table III.

	Experimental[a]	A_1	A_2	A_3
c_{11}	46.0	23.5	13.0	44.6
c_{12}	12.7	6.4	21.0	13.2
c_{13}	8.8	5.2	14.6	7.3
c_{33}	49.0	27.3	21.1	54.7
c_{44}	14.8	9.1	−7.0	13.6
$\omega_{\Gamma(L)}$	1095	1106	1099	1095
$\omega_{\Gamma(T)}$	684	708	692	692
	1085	1092	1082	1082
$\omega_{\Gamma_6}^1$	725	730	720	713
$\omega_{\Gamma_5}^{(1)}$	680	601	654	696
$\omega_{\Gamma_5}^{(2)}$	340	390	336	440
Δ_{rms} (%)		30.65	⋯	11.24

[a]Elastic constant values (in 10^{11} dyn cm^{-2}) from Ref. 17 and optical frequencies (in cm^{-1}) from Ref. 18. Optical frequencies have been indexed by the irreducible representations of C_{6v}^4, following J. C. Slater, $Quantum$ $Theory$ of $Molecules$ and $Solids$ (McGraw-Hill, New York, 1965), Vol. II, p. 358.

model A_3 no transference was made and the VFC's were least-squares fitted to all the long-wavelength data. The B_1, B_2, and B_3 models differ from each other in that the VFC's were determined by least-squares fits to the optical data, elastic data, and all long-wavelength data, respectively. All Coulomb interactions were included on the basis of a rigid-ion model.

The results for the VFC's of the A-type models are given in Table III, and the calculated values of the long-wavelength parameters in Table IV. Tables V and VI list the corresponding information for the B-type models. The effective charge on the ions has been derived from the differences in the Γ_6 (Γ_1) and Σ_2(LO) [Σ_1(TO)] modes, and is $(1.04 \pm 0.03)e$, with Be assumed to be positively

TABLE V. VFC's for BeO (in 10^5 dyn cm^{-1}) for a restricted VFF (see text for explanation of models).

| VFC | Model | | |
	B_1	B_2	B_3
k_r	2.4877	1.9118	2.3005
k_θ	0.1972	0.0385	0.1722
k_{rr}	0.0217	0.0202	0.0354
$k_{r\theta}$	0.0439	0.0284	0.1249

TABLE VI. Comparison of experimental and calcula-
ted values of long-wavelength data for BeO, with VFC's
from Table V.

	Experimental[a]	B_1	B_2	B_3
c_{11}	46.0	13.2	47.0	44.0
c_{12}	12.7	23.0	13.0	14.5
c_{13}	8.8	15.8	8.6	6.8
c_{33}	49.0	22.0	52.0	52.0
c_{44}	14.8	−9.0	14.7	14.5
$\omega_{L(L)}$	1095	1092	1361	1155
$\omega_{L(T)}$	684	685	794	777
	1085	1086	1150	1138
$\omega_{\Gamma_6}^1$	725	726	1078	802
$\omega_{\Gamma_5}^{(1)}$	680	679	953	752
$\omega_{\Gamma_5}^{(2)}$	340	340	490	463
Δ_{rms} (%)	...		24.93	15.23

[a]See footnote to Table IV.

charged. We have neglected the small deviations
from the ideal wurtzite structure that exist in
BeO.

V. DISCUSSION

An inspection of Tables IV and VI shows that, of
the six models, only models A_3 and B_3 can be re-
garded as satisfactory. This clearly indicates
that transference of force constants from diamond,
in models A_1 and A_2, is not a valid step. That the
particular kind of scaling that we have chosen is
not responsible for the lack of agreement with
experiment can be seen by comparing the VFC's
of model A_3 with the VFC's for diamond in Table I,
from which no particular scaling combination can
be found. We have also examined the possibility
that the internal strain that occurs on going from
the cubic to the hexagonal structure may lead to a
change in the values of the VFC's, by calculating
the elastic constants of a hypothetical hexagonal
form of diamond with the VFC's of the cubic phase.
These values agree with the hexagonal constants
of diamond given by Martin,[19] bearing out his
statement that the internal strain contribution is
small in this case.

There is no major difference in the fit on going
from the four-parameter model B_3 to the six-pa-
rameter model A_3. That the latter shows an im-
provement can be ascribed to the fact that the $k'_{\theta\theta}$
and $k''_{\theta\theta}$ interactions not only increase the freedom
of the model by increasing the number of param-
eters but also give effective interactions up to the
fifth coordination sphere. A much better fit can

be obtained by including other angle-angle inter-
actions of the type discussed by Solbrig,[7] but have
not been tried out in detail for reasons discussed
later. At the stage of the A_3 model, we still re-
tain a VFF in which the VFC's have the same
physical significance as in the case of molecules
and follow similar trends, e.g., $k_r > k_\theta > k_{r\theta} > k_{rr}$
$> k'_{\theta\theta}, k''_{\theta\theta}$.

In passing we note that a four-parameter force
field (models B_1 and B_2) can be used to fit either
the elastic or the optical data very satisfactorily.

In models A_3 and B_3 it can be seen that the major
deviation from experiment is for the Γ_5 optical
modes. It is only in the expressions for these
frequencies that the constants $k_\theta^{(1)}$ and $k_\theta^{(2)}$, $k_{r\theta}^{(1)}$
and $k_{r\theta}^{(2)}$, etc., appear separately, and not in the
averaged combination. We have accordingly
tried varying $k_\theta^{(1)}$, $k_\theta^{(2)}$, etc., in order to fit the
Γ_5 modes, keeping the respective sums as con-
stants. It is found that improved fitting can be
obtained only when one of the constants becomes
negative, which we reject as being unphysical. An
examination of the Γ_5 modes suggests that in-
clusion of other angle-angle interactions can also
lead to an improved fit, as evidenced by the vast
improvement in the A_3 values for these modes as
compared to the B_3 values.

Dispersion curves, using the VFC's of model
A_3, have been calculated and are compared with
experiment in Fig. 1. The experimental curves
of Ostheller et al.[20] have been measured by neutron
scattering for some modes in the Δ and Σ direc-
tions. Dispersion curves have also been calculated
by Young,[21] Solbrig,[21] and Nusimovici.[15] The re-
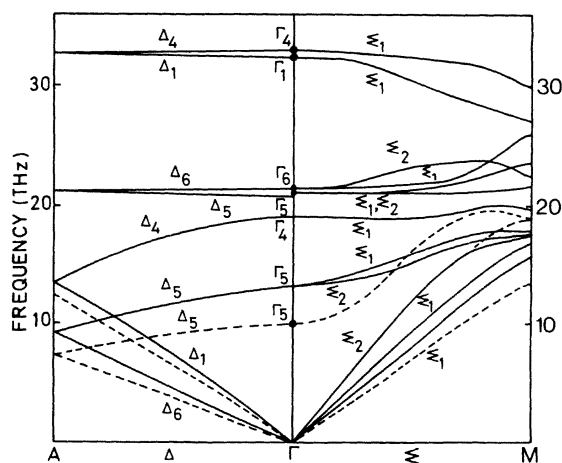sults of the former two workers have been pre-

FIG. 1. Dispersion curves for phonons in BeO in the
Γ-Δ-A and Γ-Σ-M directions. Full lines are the present
calculations; dashed lines are the measurements of
Ostheller et al. (Ref. 20); full circles at Γ are the mea-
surements of Loh (Ref. 18).

sented by Ostheller *et al.* and show poor agreement with experiment. A comparison with Solbrig's calculations would be of great interest in the context of the present work, since a VFF model has been used by him. Since the results quoted in Ref. 20 are of a preliminary nature and we have not come across further information, this is unfortunately not possible. The dispersion curves obtained by Nusimovici[15] agree fairly well with experiment, with the exception of the LA (Σ) mode. However, for reasons mentioned at the beginning of Sec. IV, we are unable to comment on the fit.

Figure 1 shows that the present work yields dispersion curves in fair agreement with experiment. The deviations arise essentially from the deviations in the fit to the long-wavelength data, i.e., the acoustic modes and the development of the Γ_5 mode. In the framework of the model, however, the agreement is satisfactory. Inclusion of polarizable ions may be considered to improve the fit. However, since there is no significant difference between rigid-ion and polarizable-ion models at $q = 0$, we expect that no substantial improvement would be attained by this method. In this context, it is to be noted that the piezoelectric constant d_{33} on the basis of the effective charge of $1.04e$ of this work turns out to be 1.8×10^{-12} C/N, which is to be compared with the experimental value[22] of 0.24×10^{-12} C/N. Since rigid-ion calculations of the piezoelectric constant are generally

in error by at least an order of magnitude, the comparison may be considered fair and may be taken to indicate that the polarizability effects are small. It is more likely that inclusion of further-angle interactions would reproduce good dispersion curves. In view of the large consequent increase in the number of VFC's, the uncertainty in the respective roles of $k_\delta^{(1)}$ and $k_\delta^{(2)}$, etc., and the comparative paucity of data, we have not attempted this refinement. Notwithstanding these comments, attempts are under progress to include the effects of ion polarizability.

VI. CONCLUSION

The dynamics of BeO have been studied using a rigid-ion with a valence-force-field model. It has been shown that transference of force constants from the Group-IV elements with the diamond structure cannot satisfactorily explain the long-wavelength data. Reasonable fits to these data can be obtained by using valence force fields with a restricted number of constants, determined by least-square fitting. Dispersion curves have been found to be in fair agreement with experiment. It has been argued that, in the context of the valence force field, long-range forces in the form of angle-angle interactions need to be considered in preference to polarizable ions to obtain better agreement with experiment.

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