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A Simple Model For the Intermolecular Interactions in Halogene Crystals

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A simple effective atom-atom intermolecular potential for halogene solids (F_2, Cl_2, Br_2 and I_2) is proposed. The centers of interaction of the effective potential (6-exp type) are shifted from the atomic sites in order to reduce anisotropy of the intermolecular distances.

The calculated results of the static properties for fluorine and chlorine are in good agreement with the experimental results. The calculated results for bromine and iodine crystals are less satisfactory.

The limitations of the atom-atom model for description of the dynamical properties of halogene solids are also briefly discussed.

INTRODUCTION

The physical properties of halogene solids (fluorine, chlorine, bromine and iodine) have been the subject of extensive experimental and numerical studies.[1–10] Many of their physical properties are unusual for a typical molecular crystal.

All the halogene molecules crystallize in orthorhombic system (space group *Cmca*) except fluorine which is a monoclinic crystal, space group *C*2/*c* or *C*2/*m*. Bromine, chlorine and iodine molecules pack in layered structure (Figure 1)[13–15] with intermolecular distances in the bc plane significantly shorter that the distances between molecules in adjacent planes (which are of the order of the van der Waals radii).

There are a number of proposed semiempirical potential models for description of the static and dynamic properties of halogene crystals, with various degrees of success.[1–7] The reproducibility of the solid properties depends on a number of adjustable parameters describing the intermolecular potential (usually 5 to 10 or more). Previous studies have shown that the simple isotropic atom-atom potential model cannot give a satisfactory agreement between the observed and the calculated properties of halogene solids. These difficulties can be understood as a consequence of the electron distribution around the halogene molecules in the crystal. The electron distribution around atomic sites (the shape of the atom) is not spherical but approximately elliptical. The departure from sphericity is almost negligible for the fluorine but very significant for the iodine atom.[8] The crystal

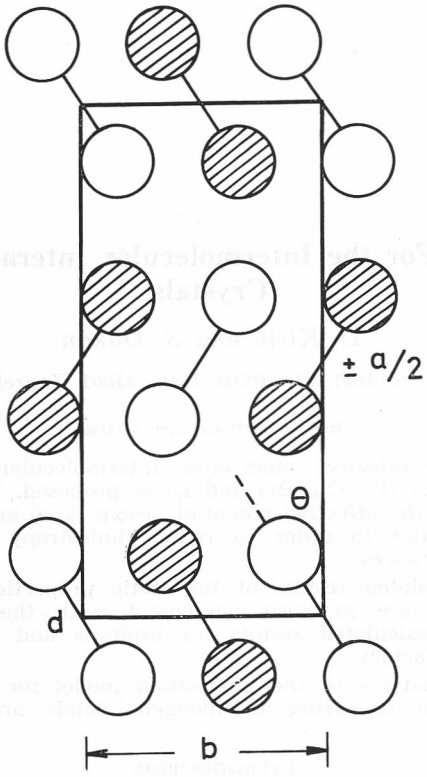

Figure 1. The crystal structure of halogene solids (Cl_2, Br_2 and I_2). The molecules are in the *bc* plane (the shaded molecules are at $\pm a/2$).

structure of halogene solids is very anisotropic with the shortest distances between atoms in the *bc* plane. It is unlikely that the simple isotropic atom-atom potential model will describe the intermolecular interactions in halogene crystals very accurately.

There have been many attempts to develop anisotropic potential models (for review see ref. 5) in order to take into account the actual charge distribution around the halogene atoms. Most of them are the angular dependent potentials with a number of adjustable parameters which are fitted to the observed lattice structure, cohesion energy, and phonon spectra of halogene solids. Many of the model calculations found in the literature have a large number of free parameters in contrast to the few physical properties they describe. Besides, they cannot be easily transfered to the similar structures containing halogene atoms because they depend on a given configuration, more precisely on the specific mutual orientations of the molecules in the unit cell.

DESCRIPTION OF THE MODEL

In the present paper a simple potential model for the intermolecular interactions in halogene solids is developed. It partly takes into account the anisotropy of intermolecular interactions. The centers of interaction

were shifted from the atomic positions toward the center of the molecule. The real molecule (longer and nonspherical) is replaced with the shorter »effective« molecule. In this way, we made the crystal structure more isotropic with respect to the interatomic distances in the *bc* plane. Shortening the molecular length we made these in-plane distances longer and comparable in size to the distances between the adjacent *bc* planes. On the other hand, the distances between the planes are almost unaffected. Shifting the interaction sites we can take into account the angular dependence of the interaction, of course, only on an average level. It is by no means obvious where to put the new interaction site and, therefore, we treated it as an additional free parameter in our model.

The Buckingham (6-exp) type of interaction between the shifted sites is chosen (specified with 3 parameters A, B and α). Including the shifting parameter $SH = d'/d$ (d' — the distance between the intramolecular sites, d — the observed length of the molecule) there are 4 parameters for the dispersion-overlapping part of the atom-atom interaction.

The electrostatic interaction in halogene solids plays a very important role and must be included in order to reproduce the orientation of the molecules in the unit cell. The point charge $2q$ is put in the center of the molecule and the charges $-q$ at the corresponding sites along the bond in order to represent the zero dipol and nonzero quadrupole moment of the molecule. The magnitude of the charges may be calculated from the reported experimental values of the quadrupole moments but the data for halogene molecules are scarce and not very accurate. Because of that we included the quadrupole moment as an additional parameter in the model.

The lattice energy in our model is given as:

$$U_{\text{latt}} = \sum_{ij} \left(-\frac{A}{R_{ij}^{6}} + B e^{-\alpha R_{ij}}\right) + U_{qq} \qquad (1)$$

where U_{qq} is the quadrupole-quadrupole interaction energy represented by the sum of the Coulombic energies between the point charges. R_{ij} are the distances between the shifted interaction sites. For the crystal structure at equilibrium the lattice energy must be minimal (at zero temperature and zero pressure). We minimize (1) by small variation of the lattice parameters and the orientation of the molecule in the unit cell and compare the obtained equilibrium structure with the observed one. Besides, all the calculated frequences in the phonon spectra for every point in the Brillouine zone must be real (condition for the stable lattice). This is an additional test of the model.

RESULTS

A number of potential parameters were tested in order to obtain the best agreement between the calculated and the experimental crystal structure. The parameters which give a reasonably good agreement are listed in Table I.

The experimental value of the unit cell parameters and its volume, the angle which defines the orientation of the molecule in the *bc* plane, the crystal energy and the length of the molecule for fluorine, chlorine, bro-

TABLE I

The values of parameters A, B, *a*, SH *and* Q *in the intermolecular potential for halogene solids*

	F_2*	Cl_2	Br_2	I_2
A(kcal Å^6/mol)	260	2371	4767	11559
B(kcal/mol)	39922	38329	90534	48405
a (Å^{-1})	3.95	3.00	3.00	2.50
SH	0.92	0.92	0.85	0.85
Q(esucm^2 10^{-26})	0.65	0.96	1.29	2.90

* From ref. 4.

TABLE II

The experimental values of the structural parameters for halogene crystals

	F_2	Cl_2	Br_2	I_2
a(Å)	5.500	6.145	6.567	7.136
b(Å)	3.180	4.395	4.468	4.686
c(Å)	7.280	8.154	8.639	9.784
V(Å)	131.33	220.24	255.08	327.17
Θ(deg)	18.0	33.2	32.7	32.2
E(kcal/mol)	—2.19	—7.28	—11.99	—16.25
d(Å)	1.42	1.99	2.30	2.72
Ref.	13	14	14	15

TABLE III

The calculated values of the structural parameters for halogene solids

	F_2	Cl_2	Br_2	I_2
a(Å)	5.38	5.941	6.170	6.711
b(Å)	3.40	4.466	4.568	5.668
c(Å)	7.20	8.198	8.732	8.339
V(Å)	131.70	216.03	246.11	317.21
Θ(deg)	25.0	35.4	341.	47.8
E(kcal/mol)	—2.18	—7.33	—12.30	—16.38
d'(Å)	1.30	1.83	1.96	2.31

mine and iodine crystals are given in Table II. The calculated values are represented in Table III.

DISCUSSION

The results of our calculations for the static properties of halogene solids are presented in Table III. In spite of the very simple model we used, the calculated results are in reasonable agreement with the observed ones.

The results for static properties of fluorine crystal (taken from our previous calculations[4]) show a very good agreement with the observed data. In that respect, fluorine is similar to other diatomic molecular solids (nitrogen and oxygen) with the quadrupole moment between those of oxygen and nitrogen.[9] In oxygen the small quadrupole moment has very little effect on the molecular orientation while in nitrogen the large quadrupole moment determines the orientation and structure ($Pa3$).

On the other hand, the remaining halogene solids show a gradual departure from the typical molecular solids. It can be seen from Table III that our simple model is able to reproduce the static properties of chlorine crystal reasonably well. For bromine crystal and especially for iodine (Table III) the agreement is less satisfactory. This can be explained by the large departure from sphericity of halogene atoms in those crystals[8] and our simple model[10] is not able to reproduce the observed properties. It is questionable if it is possible to tailor the effective atom-atom potential for a system like iodine because of the large nonspherical electronic charge distribution. It is particularly questionable if the dynamic properties of these systems (vibrational spectra and phonon dispersion curves) can be reasonably well explained on the basis of the unpolarized rigid molecule. Our preliminary calculations of the lattice vibrations are not in very good agreement with the observed Raman and IR frequencies. This means that our simple model is not able to describe the actual anisotropy of the intermolecular interaction. Even more complex models with a larger number of potential parameters do not give a very good agreement for vibrational frequencies of halogene solids. It seems that a complete description of the physical properties of halogene solids requires a more realistic model which takes into account the electronic degrees of freedom, like the shell model[11] or the Car-Parinello unified approach for treating electronic and nuclear degrees of freedom simultaneously.[12]

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SAŽETAK

Jednostavan model za opis međumolekulskih interakcija u kristalima halogena

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Prikazan je jednostavan model za opis međumolekulskih interakcija u kristalima halogena (F_2, Cl_2, Br_2 i I_2).

Model se zasniva na efektivnom potencijalu (tipa 6-exp) s centrima interakcije pomaknutim s atoma prema središtu molekule. Na taj je način reducirana anizotropija u međumolekulskim udaljenostima.

Izračunana statička svojstva za fluor i klor dobro se slažu s eksperimentalnim podacima, dok je slaganje za kristale broma i joda slabije.

Ukratko se raspravlja o ograničenjima ovako jednostavnog modela, posebno za opis dinamičkih svojstava (fononske frekvencije).