

optimum effective source size in the diffraction plane of $\sim 25 \mu\text{m}$.

The data presented in this paper, for the $\bar{1}\bar{1}2$ reflection of CuInSe_2 , were collected using a take-off angle of 4° or approximately 1 in 14. Reflectivity curves for the $\bar{1}\bar{1}2$ reflection have also been derived from data collected with a take-off angle of 2° or approximately 1 in 30, using $\text{Mo } K\beta$, $\text{Mo } K\alpha$ and $\text{Cu } K\alpha$ unfiltered radiations. These r^*/μ^* distributions are very similar in shape to that in Fig. 3(c), the lowest FWHH being $\sim 1.6'$.

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Transferability of Nonbonded $\text{Cl}\cdots\text{Cl}$ Potential Energy Function to Crystalline Chlorine

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Abstract

The crystal structure of molecular chlorine could not be accurately predicted using a transferred nonbonded $\text{Cl}\cdots\text{Cl}$ potential function that was found satisfactory for prediction of perchlorohydrocarbon crystal structures. Additional consideration of quadrupole-quadrupole interaction did not resolve this problem. One possible solution, which has been explored in the literature, was to define a new, nontransferable, $\text{Cl}\cdots\text{Cl}$ potential function specifically tailored to molecular chlorine. Such a specialized $\text{Cl}\cdots\text{Cl}$ function required additional adjustable parameters that defined an anisotropic nonbonded energy function for chlorine. A second possible approach, explored here, transferred the perchlorohydrocarbon $\text{Cl}\cdots\text{Cl}$ potential function to molecular chlorine. This simple isotropic nonbonded energy function was then supplemented by a partial intermolecular bonding force constant, which was applied to the short contacts present in this structure type. The resulting empirical model described the crystal structure of molecular chlorine within threshold accuracy.

Introduction

The heavier halogens Cl_2 , Br_2 and I_2 have similar crystal structures with space-group symmetry $Cmca$. A summary of the crystal data is given in Table 1, and the structure type is illustrated in Fig. 1. Table 2 gives a summary of the observed lattice energies, and also the intramolecular bond distances and energies of the isolated molecules. The fact that these structures are layered, with all atoms in planes parallel to (100), immediately suggests that these are not simple van der Waals type structures. This is true because a normal van der Waals interaction would lead to a nonplanar type of molecular packing where the ends of the molecules in one layer are placed in staggered positions between the ends of molecules in the adjacent layer.

English & Venables (1974) have presented a general discussion of the crystal packing of diatomic molecules. They made a systematic study of several possible space groups for the packing of H_2 , N_2 , O_2 , F_2 , Cl_2 , Br_2 and I_2 molecules in the crystal. One of their conclusions was that intermolecular bonding

Table 1. Crystal structure data for chlorine, bromine and iodine

θ is the angle between the molecular axis and the c axis in the bc plane. r_s is the shortest intermolecular distance. r_{vdw} is the van der Waals diameter. The units are Å and °; e.s.d.'s are given in parentheses. An * indicates that the e.s.d. is unstated.

Parameter	Cl ₂	Br ₂	I ₂
a	6.207 (2)	6.67 (*)	7.136 (10)
a	4.441 (3)	4.48 (*)	4.686 (7)
b	8.117 (2)	8.72 (*)	9.784 (15)
θ	33.2 (*)	32.2 (*)	32.2 (*)
r_s	3.271 (*)	3.31 (*)	3.50 (*)
r_{vdw}	3.60	3.96	4.30
Reference	(a)	(b)	(c)

References: (a) Stevens (1979); (b) Vonnegut & Warren (1936); (c) Van Bolhuis, Koster & Migchelsen (1967).

Table 2. Observed intramolecular bond distances and bond energies of the isolated molecules, and the observed lattice energies

The original references should be consulted for error estimates.

Molecule	r_e (Å)	E_d (kJ mol ⁻¹)	v_{obs} (kJ mol ⁻¹)
Cl ₂	1.988 ^{a,b}	239.325 ^f	-31.9 ⁱ
Br ₂	2.280 ^{c,d}	192.882 ^{g,h}	-50.1 ⁱ
I ₂	2.666 ^e	151.042 ^{g,h}	-63.5 ⁱ

References: (a) Douglas, Moller & Stoicheff (1963); (b) Clyne & Coxon (1970); (c) Horsley & Barrow (1967); (d) LeRoy & Burns (1968); (e) Rank & Rao (1964); (f) LeRoy & Bernstein (1971); (g) National Bureau of Standards (1968); (h) *Codata Bulletin* (1970); (i) English & Venables (1974).

exists in the crystal structures of the orthorhombic halogens. It is interesting to note that the fluorine crystal structure is different (Meyer, Barrett & Greer, 1968; Pauling, Keaveny & Robinson, 1970). The fluorine crystal structure is monoclinic, and the ends of the molecules are staggered, rather than being in the same plane as in the heavier halogens.

According to the concepts of the atom-atom potential method (Kitaigorodsky, 1973) there exists a normal nonbonded potential energy function for each type of atom, which is transferable between different bonding environments. Cox, Hsu & Williams (1981) found that the same nonbonded potential function that described the crystal structure of molecular oxygen was also satisfactory for the crystal structures of

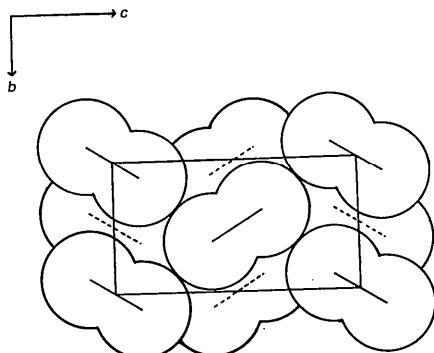


Fig. 1. The molecular packing in the crystal structures of chlorine, bromine and iodine.

oxohydrocarbons. Further, Williams & Cox (1984) found that the same nonbonded potential function that described the crystal structure of molecular nitrogen was also satisfactory for the crystal structures of azahydrocarbons, except for azabenzene where additional lone-pair electron sites were needed (Williams & Weller, 1983). Hsu & Williams (1979) determined that the Cl...Cl nonbonded potential function derived from the crystal structures of perchlorohydrocarbons was not transferable to the crystal structure of molecular chlorine. The addition of a molecular quadrupole-quadrupole interaction did not solve this transferability problem.

There have been several studies in which the existence of a weak intermolecular bond was postulated for the heavier halogens. Yamasaki (1962) used a (12-6) nonbonded potential function plus a quadrupole interaction in an attempt to describe the crystal structure of chlorine. This model was insufficient, and to stabilize the model at the observed structure a weak partial bond was postulated to exist in the structure. This partial bond corresponded to the short Cl...Cl contacts between different molecules of 3.271 Å. The next-shortest distance of 3.697 Å is considerably longer and was believed to be a normal van der Waals type. The situation is similar in bromine and iodine. For bromine, the anomalous short distance is 3.31 Å, and the next shortest distance is 3.79 Å. For iodine, the anomalous short distance is 3.50 Å, while the next shortest distance is 3.97 Å. If one compares the shortest distances with expected van der Waals diameters, the partial bonding becomes stronger as we proceed from chlorine to iodine, since the apparent compression of the van der Waals diameter increases along the series. There is a large body of chemical data that indicates that iodine readily forms weak bonds or complexes; bromine also is known to form additional weak bonds. For chlorine, the tendency to form such weak bonds is not so obvious, from purely chemical information. If the fluorine structure is typical for a halogen that does not show intermolecular bonding, then the fact that chlorine switches to the iodine-type structure is evidence for the presence of intermolecular bonding.

It should be noted that the short intermolecular distances and the large differences between the nearest and next-nearest intermolecular distances suggest a specific chemical interaction involving only these nearest neighbors. Thus, partial bonding might be expected to apply only to these specific nearest contacts, and not to the longer nonbonded contacts. Since the nearest-neighbor contacts are in specific directions (see Fig. 1), the inclusion of a special partial bonding force constant for short contacts is anisotropic in its effect on the crystal structure.

The arguments in favor of partial bonding in the crystal are stronger for bromine and iodine than for chlorine. Several types of experimental evidence can

be cited. For iodine the bond distance in the molecule increases from 2.662 Å in the gas to 2.715 Å in the crystal (Van Bolhuis, Koster & Migchelsen, 1967). For bromine there appears to be no change, although the accuracy of the measurement in the crystal is not good (Vonnegut & Warren, 1936). A recent very accurate determination for the bond length in the chlorine crystal (Stevens, 1979) also indicates no change from the gas value. It is significant that in iodine, where the partial bonding effect is expected to be strongest, there is an increase in the bond length in going from the gas to the crystal. The partial bonding in bromine and chlorine is expected to be weaker, so that any such bond lengthening, if present, could be inside experimental error.

Another line of evidence favoring a partial bonding model is the changes in the molecular vibrational frequencies in going from the gas to the crystal. Since even normal van der Waals interactions can cause some small shifts in the intramolecular vibrational frequencies, we look for somewhat larger shifts that might be caused by a partial bonding effect. Table 3 summarizes the available experimental vibrational frequencies for the halogens. Only fluorine shows a negligible shift; chlorine, bromine and iodine all show significant shifts toward lower frequency in the crystal. These shifts are compatible with a partially bonded model for the crystals of the heavier halogens.

According to simple selection rules, the infrared vibrational frequencies should not be active for the halogens. As can be seen from Table 3, infrared vibrational frequencies are observed in both bromine and iodine crystals, and also in liquid bromine. The available experimental infrared data for crystalline chlorine in the region of the stretching frequency are not good because of a poor intensity-to-background ratio (Wong & Whalley, 1972). These authors were primarily interested in the intermolecular frequencies, where their experimental background intensity was lower. They did calculate the theoretical intensities of the translational lattice vibrations. The observed intensity of absorption was about 35 times the calculated value. The authors state that this provided strong evidence for the presence of intermolecular bonding between chlorine molecules. Starr & Williams (1977) found that use of lattice vibrational frequency data for hydrocarbon crystals, in addition to crystal structure data, did not significantly change values of nonbonded potential parameters derived from crystal-structure data alone. In contrast to the crystal structure, lattice vibrations have a strong temperature dependence and therefore their accurate treatment requires more elaborate models.

The presence of partial bonding in the solid halogens is supported by nuclear quadrupole resonance measurements. The asymmetry of the electric field gradient has been measured for solid chlorine by Gibson, Brookeman & Scott (1974), and the results

Table 3. *Raman and infrared observed vibrational frequencies for the halogens (cm⁻¹)*

The original references should be consulted for error estimates.

Halogen	Gas		Liquid		Solid	
	Raman		Raman	Infrared	Raman	Infrared
F ₂	891.85 ^a		888 ^a	897.5 ^a	895 ^c	
	891.4-892.8 ^b		891.5 ^c		895.2 ^f	
Cl ₂	557 ^a		548 ^a		538 ^a	
	559.72 ^g					
	565 ^h					
	554 ⁱ					
Br ₂	322 ^a		306.1 ^a	307 ^a	297 ⁱ	298 ^h
	324.24 ^g					
	323 ^h					
	318 ⁱ					
	306.1 ^a					
I ₂	214.52 ^g				180-188 ⁱ	211 ^h
	215 ^h				180.6-	
					189.3 ⁱ	
			213 ⁱ			

References: (a) Jacob (1970); (b) Andrychuk (1950); (c) Barral (1972); (d) Barral (1974); (e) Niemczyk (1973); (f) Barral (1973); (g) Downs & Adams (1975); (h) Walmsley & Anderson (1964); (i) Anderson (1970); (j) Smith, Nielsen & Clark (1975).

imply that there is substantial intermolecular bonding in the solid. NQR studies on solid bromine and iodine by Robinson, Dehmelt & Gordy (1954) led to a similar conclusion. However, Weber, Gubanov & Gibson (1975) did not predict any significant asymmetry of the EFG of solid chlorine or bromine with CNDO- or INDO-type molecular orbital calculations. They suggest that an accurate *ab initio* SCF calculation would be helpful to clarify the theoretical prediction of the EFG asymmetry parameter. Coker, Lee & Das (1977) used a self-consistent-charge extended Hueckel procedure to study successfully the intermolecular bonding and explained the experimental asymmetry parameter. They found good agreement for bromine and iodine; for chlorine their theoretical result lies between the two reported experimental observations of near zero and evidence for a substantially larger value.

Nyburg & Wong-Ng (1979) derived a complex anisotropic shape for the Cl...Cl nonbonded potential, which flattened the chlorine atoms on their ends and sides. Their model has, in our opinion, an unjustifiably larger number of adjustable parameters. The model was custom tailored for crystalline molecular chlorine and was not checked for transferability to chlorine in other bonding situations. It also should be noted that Nyburg & Wong-Ng did not check if their potential correctly reproduced the molecular tilt angle in the chlorine structure. Thus, it is not known whether their model is force free with respect to molecular rotation.

Other workers have developed customized nonbonded potentials for molecular chlorine. Toukan & Chen (1982) used an interatomic potential for chlorine that had ten adjustable parameters. Burgos, Murthy & Righini (1982) used an anisotropic potential model

that has five adjustable potential parameters. Price & Stone (1982) also tailored their potential to molecular chlorine with the use of a large number of adjustable potential parameters. The net effect of these models was to account for the chlorine structure by defining a new Cl...Cl nonbonded potential specifically for the crystal structure of molecular chlorine.

It is clear that one could account for the short distances in the orthorhombic halogen crystals by postulating a reduced repulsion in the direction of the shortest nonbonded contacts. Alternatively, one could transfer Cl...Cl nonbonded potentials from other structures and treat the chlorine structure as having a partial intermolecular bond. The first alternative will decrease the repulsion for the short contacts, while the second alternative will increase the attraction.

Thus it is difficult to distinguish physically between the two types of models, since the models differ only in their internal partitioning of energy types. The partial bond model is simpler, requiring only one adjustable parameter in addition to an estimate of the molecular electric quadrupole, and is more suitable for use with generally available molecular-packing-analysis programs (Busing, 1981; Williams, 1984). Since empirical models in general often do not yield theoretical insight, choice among such models is usually based on simplicity and transferability considerations. Future theoretical studies, which are beyond the scope of this paper, might show a preference for a certain empirical model.

Potential-energy model

The potential energy of the chlorine crystal was assumed to be a pairwise sum of (exp-6) atom-atom terms according to the usual methods of molecular-packing analysis (Williams, 1972). The energy contributed by each term for a nonbonded atom-atom distance r_{ij} (including the short distances) was taken as the sum of an attractive dispersion energy term and a repulsive exponential energy term:

$$V_{NB}(r_{ij}) = -Ar_{ij}^{-6} + B \exp(-Cr_{ij}).$$

Values for A , B and C were transferred from results obtained from perchlorohydrocarbon crystal structures (Hsu & Williams, 1980). These values were $A = 7939$, $B = 950\,430$ and $C = 3.51$ in units of kJ mol^{-1} and \AA , and they were used unchanged throughout this study.

A distributed molecular quadrupole was taken into consideration by placing net charges q on the chlorine atoms and a charge $-2q$ at the molecular center. The quadrupole-quadrupole energy was then evaluated by using Coulomb's law between point charges:

$$V_Q(r_{ij}) = q_i q_j r_{ij}^{-1}.$$

The quadrupolar charge q was taken as an adjustable

parameter to be determined from the observed crystal structure. As has been noted previously (Hsu & Williams, 1979; Williams, 1981), the use of quadrupole-quadrupole interactions, along with (exp-6) nonbonded potentials, are insufficient to explain the chlorine crystal structure. The predicted structure is not very sensitive to the quadrupolar charge, in contrast to its sensitivity to the partial bonding force.

The pair potentials were summed over the crystal lattice, using computer program *PCK83* (Williams, 1984). In the lattice summation the convergence acceleration method (Williams, 1971) was used and the treated lattice sum was truncated at 12 \AA . The estimated truncation error of the lattice sum was less than 0.1%. The derivatives of the crystal potential energy were evaluated analytically rather than numerically.

In agreement with work discussed in the *Introduction*, preliminary calculations of the chlorine crystal structure using only V_{NB} and V_Q gave very poor agreement with the observed values of the lattice constants a , b , c and the molecular tilt, θ . It was very clear that this model needed augmentation to permit the very short Cl...Cl contact distances of 3.271 \AA to occur.

A partial bonding force, F , was assumed to be present in the chlorine crystal, only for the two short distances. This intermolecular force operated only between these two atom pair types. The components of this intermolecular bonding force were added to the normally obtained structural forces (the negatives of the first derivatives of the lattice energy). The pertinent components of F are F_b , F_c and F_θ in the chlorine structure, the other forces being zero by symmetry. Only the magnitude of F is adjustable, since the components are determined from the structural geometry. The introduction of the partial bonding force constant does not affect lattice constant a because the partial bonds are in the bc plane and thus there is no partial bonding component in the a direction. In the actual calculations an attractive exponential function was used for the short Cl...Cl distance. The force, F , is the negative of the derivative of this function with respect to distance. The energy obtained from this function was simply set to zero, while the force was added into the lattice sums in the normal way. Our empirical model thus contained two adjustable parameters, q and F , which were optimized to give the best prediction of the crystal structure. The optimum values found were $q = 0.094e$ and $F = -0.236 \text{ \mu N}$. In the context of this model q was not well defined, but in contrast F was rather sharply defined.

With these parameters the crystal energy of the observed structure was calculated as $-17.2 \text{ kJ mol}^{-1}$. The quadrupole-quadrupole component was very small, -0.1 kJ mol^{-1} . When the crystal energy was minimized subject to the partial bonding force con-

straint, a value of $-17.1 \text{ kJ mol}^{-1}$ was obtained. The predicted lattice constants were $a = 6.260$, $b = 4.469$ and $c = 8.110 \text{ \AA}$. The molecular tilt angle was predicted as 32.3° .

Discussion

Experience with atom-atom molecular packing analysis has led to the selection of expected threshold accuracy values (Hsu & Williams, 1980). The relevant values here were 1% in the lattice constants and 2° in the molecular tilt. The concept of threshold accuracy was that predictions more accurate than threshold values were not usually expected because of the presence of known approximations in the empirical model. The first of these approximations was implied by the transferability idea itself. As a given type of atom is involved in different bonding situations, it was expected that nonbonded potential variations could cause threshold-size errors for predictions. Another approximation was the lack of provision for the effects of thermal motion in the model. Again, this feature could have caused threshold-size errors, e.g. thermal expansion could not be predicted with the model. Finally, of specific interest for the chlorine structure were the assumptions that the nonbonded interaction potential was isotropic and that no intermolecular bonding was present.

As was mentioned in the *Introduction*, an isotropic nonbonded potential model used alone did not successfully predict the chlorine structure. Since in any crystal structure there is a balance between attraction and repulsion, there was the choice of modifying the model by introducing anisotropy either into the attractive energy or into the repulsive energy function. This anisotropy would allow the short distances in the chlorine crystal structure to be modelled. There are several problems with defining an anisotropic repulsion energy. Such an energy function is not generally suitable for large molecules because of the complexity and time required for evaluation of the anisotropic function for a complicated crystal structure. Closely related to this is the situation that a rather large number of adjustable empirical parameters may be necessary to define the anisotropic function. Finally, a potential function for a given type of atom that is specifically tailored to only one crystal structure is not likely to have good transferability properties to other structures.

By comparison, the modification of the nonbonded potential energy to include a specific force operating between two chlorine atoms in close contact was easier and only required one adjustable parameter, if normal nonbonded functions were transferred from perchlorohydrocarbons. Readily available molecular-packing-analysis computer programs (Busing, 1981; Williams, 1984) could quickly find the predicted crystal structure using the modified potential.

For the chlorine structure, our modified nonbonded potential treatment predicted the crystal structure within threshold accuracy. The percentage change in the lattice constants a , b and c were 0.9, 0.6 and -0.1% , respectively, and the change in the molecular tilt angle was -0.9° . We note that the good agreement for the a lattice constant was achieved even though the partial bonding force constant has no component in this direction. This was consistent with a good transferability property for the normal Cl...Cl nonbonded potential function. The use of transferred Cl...Cl nonbonded potential parameters means that our empirical model is not entirely customized for this single structure; only the partial bonding force was customized to (or derived from) the chlorine crystal structure.

At the present time similar models for bromine and iodine crystals cannot be obtained. This is because normal Br...Br and I...I nonbonded potential functions must be developed before this model can be used.

The observed lattice energy of chlorine is $-31.9 \text{ kJ mol}^{-1}$ (English & Venables, 1974). Our empirical force model included no partial bonding energy and yielded a lattice energy of $-17.2 \text{ kJ mol}^{-1}$. The difference between these two figures provided an empirical estimate of the partial bonding energy in the chlorine crystal: $-14.7 \text{ kJ mol}^{-1}$. This amount of energy was obviously quite significant relative to the total lattice energy: 46%. However, the two partial bonds are quite weak relative to the normal Cl-Cl bond energy (Leroy & Bernstein, 1971) of $239.325 \text{ kJ mol}^{-1}$ in the gaseous monomer. Each partial intermolecular bond has only 3% of the energy of the normal intramolecular bond.

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Relativistic Corrections to the Kinematic X-ray Scattering in the Pauli Approximation

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Abstract

Expressions for the kinematic scattering of X-rays by electrons are obtained from the Pauli Hamiltonian. In addition to the modified electron density, relativity is shown to contribute with an additional term, the kinetic form factor. A formula for this term is given for one-electron atoms.

1. Introduction

Relativistic quantum mechanics leads in some cases to a considerable modification of the electron distribution in atoms, molecules and solids as compared to non-relativistic results, and the use of relativistic electron densities in the calculation of atomic form factors for X-ray crystallography has become standard (Cromer & Waber, 1974; see also Hubbell & Øverbø, 1979). In the present paper, we study the impact of relativistic theory on the equations for the scattering amplitude. Our study is based on the Pauli equation, which represents the conceptually simplest

approach, where comparison with the non-relativistic expressions is most straightforward. In addition, this approach has the advantage of being independent of the choice of relativistic N -particle theory, which is still a problem containing many unsettled questions (Grelland, 1981; Mittleman, 1981; Sucher, 1980; Buchmüller & Dietz, 1980). All theoretical approaches to this problem lead to the Pauli equation in the first approximation. The calculation results presented in § 4 show that the Pauli approximation is adequate for the present purpose. With this method it becomes possible to relate the relativistic corrections due to relativistic scattering theory directly to the form of the non-relativistic wave function. Thus a transparent picture of the form and size of the correction is provided, which can be used in relativistic electron density studies based on X-ray crystallographic measurements.

The present theory is restricted to the first Born approximation, and higher-order effects (anomalous scattering) must be added by a separate calculation. Thus, the method cannot be directly compared to