Acta Cryst. (1983). A**39**, 411–415

Determination of the Diamagnetic Susceptibility and the Electron Static Polarizability of Crystals from X-ray Diffraction Data

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(*Received* 4 *October* 1982; *accepted* 18 *January* 1983)

Abstract

The relationships associating the structure amplitudes, measured in a diffraction experiment, with the diamagnetic susceptibility and the static electron polarizability of ions for crystals with the NaCl-type structure are obtained. The calculations, carried out for a number of alkali halides and alkaline-earth oxides, have shown a good coincidence with the results of magnetic and optical measurements. The accuracy of the obtained results is analyzed; it is shown that when using accurate diffraction data the diamagnetic susceptibility and the electron polarizability may be determined with an accuracy of about 1%.

Introduction

The study of the details of an electron distribution in molecules and crystals from accurate X-ray diffraction data has become possible in recent years owing to the progress achieved in experimental technology, in processing techniques and in methods of representation of results (Coppens & Stevens, 1977; Becker, 1980; Tsirel'son & Ozerov, 1981). At present, this experimental approach is a single direct source of information about the electron-charge distribution at any point in a crystal. The presence of high-quality information of such a type makes it possible not only to verify the traditional views on the nature of a chemical bond, but to pass to the direct investigation of material properties depending on the distribution of electron density, $\rho(\mathbf{r})$. For this purpose, calculation techniques are needed which would relate directly the diffraction data to the characteristics of these properties of crystals. Early attempts to develop such techniques were aimed at studying the features of the crystal field, forces and energy characteristics of crystals (Bentley, 1979; Stewart, 1974, 1977, 1979; Varnek, Tsirel'son & Ozerov, 1981). The purpose of this work is to develop a method which will relate the X-ray diffraction data with the diamagnetic susceptibility and the electron static polarizability of crystals.

In an early attempt to determine semi-qualitatively these characteristics from the diffraction of X-rays, the analytical approximations of the electron distribution by spherical Gauss functions (Sirota, 1962; Sirota & Scheleg, 1963) were used. The results of calculations were found to be close to experimental values. The possibility of estimating the diamagnetic susceptibility of inert gases from small-angle scattering of X-rays was also discussed (Weiss, 1966). In this work we shall present the general consideration of the problem and show that in the particular case of crystals with the NaCl-type structure the problem allows a simple analytic solution.

Calculation of the diamagnetic susceptibility

The calculation of the diamagnetic portion, χ_d, of the total magnetic susceptibility is based on the Langevin formula obtained for free atoms or ions (Van Vleck & Frank, 1929). For one mole of substance

$$\chi_d^z = -\frac{\mu_0 N e^2}{4m} \langle x^2 + y^2 \rangle. \qquad (1)$$

Here e and m are the electron charge and mass, μ_0 is the magnetic constant, N is the Avogadro number, $\langle x^2 \rangle$ and $\langle y^2 \rangle$ are the mean squares of projections of electron radius vectors on the appropriate coordinate axes. It is supposed that the magnetic field is directed along the z axis; the other components of the diamagnetic susceptibility may be obtained from (1) by means of a cyclic rearrangement of x, y, z.*

In order to apply (1) to multiatom systems, the system should be represented by a set of pseudoatomic fragments. Then, the diamagnetic susceptibility of the system, χ_d, will be equal to the sum of contributions from these fragments. Choosing the origin of a local coordinate system to be located at the center of gravity of the electron density of the jth fragment, one may write

$$\chi_d^j = -\frac{\mu_0 N e^2}{4m} \int_{\Omega_j} (x_j^2 + y_j^2)\, \rho(\mathbf{r})\, \mathrm{d}V. \qquad (2)$$

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* In the following we shall omit index z in χ_d^z without prejudice to understanding.

The integration is carried out over the volume of a fragment, Ω_j.

The electron-density function for a unit cell of a crystal, $\rho(\mathbf{r})$, may be represented by a Fourier series, the coefficients of which are represented by structure amplitudes, $F(hkl)$, measured experimentally (h, k, l are the Miller indexes). By substituting $\rho(\mathbf{r})$ into (2) the formula for determining the diamagnetic susceptibility of the jth fragment can be obtained:

$$\chi_d^j = -\frac{\mu_0 N e^2}{4mV}\sum_{hkl} F(hkl)\,J_j(hkl), \tag{3}$$

where V is the volume of a unit cell and

$$J_j(hkl) = \int_{\Omega_j} (x_j^2 + y_j^2)\exp[-2\pi i(hx + ky + lz)]\,\mathrm{d}V. \tag{4}$$

Thus, in order to determine the diamagnetic susceptibility of a crystal, the integral (4) should be calculated. The choice of the integration volume, Ω_j, is a part of the more general problem of dividing the charge of a system into pseudoatomic fragments. A simple approximate solution to this problem for an arbitrary system has been given recently by Hirshfeld (1977). We shall consider here another possibility of choosing the volume for ionic crystals with the NaCl-type structure by using the peculiarities of crystal and electron structures.

The analysis of the distribution of electron density in ionic crystals (Tsirel'son, Nozic & Urusov, 1983) permits the conclusion that ions in such compounds are fairly well separated in space. For example, the section of function $\rho(\mathbf{r})$ in a LiF crystal, constructed from the data of Killean, Lawrence & Sharma (1972) (Fig. 1), shows that the value of electron density in the interatomic space amounts to 0·05 e Å^{-3} approximately, whereas, at the centers of ions, the electron densities are at least 300 times as large. This gives the choice for the volume Ω_j for crystals with NaCl-type structure in the form of the Wigner–Seitz cell having the shape of a cube with the edge $a/2$, with an ion at the center (here a is the dimension of a cubic unit cell). The division of space of cubic crystals into similar fragments was used previously for determining the atomic charges (Galder, Cochran, Griffiths & Lowde, 1962). In the NaCl-type structure case, the choice of the Wigner–Seitz volume Ω_j allows the integration of (4) analytically and, taking into account the crystal symmetry, the following final formula for determining the mean diamagnetic susceptibility to be obtained from the diffraction data:

$$\chi_d = -\frac{\mu_0 N e^2 a^2}{4m}\left[\frac{n}{96} + \frac{1}{2\pi^2}\sum_{h=2,4,\ldots}(-1)^{h/2}\frac{F(h00)}{h^2}\right]. \tag{5}$$

Here n is the number of electrons in a unit cell; the summation is carried out over the even positive values of h. [The terms of the series in (5) with other values of h, k, l are mutually destroyed owing to the opposite sign of anion and cation contributions.]

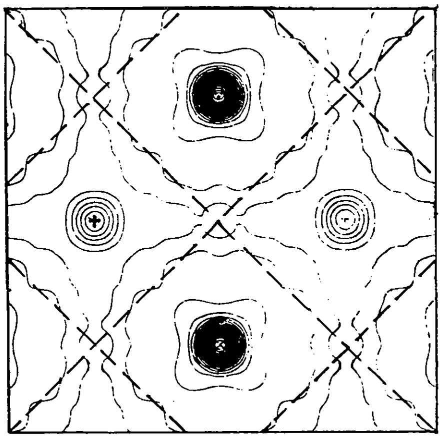

Fig. 1. Section of the full electron density of a LiF crystal in the (100) plane, plotted from the data of Killean *et al.* (1972). Broken lines are the Wigner–Seitz cell boundaries. Contour lines are drawn at intervals of 3·375 e Å^{-3}.

Diamagnetic susceptibility of some ionic crystals and estimation of the accuracy of the results

The diamagnetic susceptibilities for a number of alkali halides and alkaline-earth oxides were calculated by (5). The results of this calculation are given in Table 1. Let us consider here in more detail the determination of χ_d for the LiF crystal (the experimental data were taken from Killean *et al.*, 1972). Since the diffraction

Table 1. *The results of calculations of diamagnetic susceptibility, χ_d, Van Vleck part susceptibility, χ_p (in* mm^3 mol^{-1} × 10^{-1}) *and electron polarizability,* α *(in* 10^{-30} m^3) *determined by the authors from the diffraction data, absolute values of errors are in parentheses, as compared with χ_d^*, χ_p^* and* α* *values determined by other methods (Dorfman,* 1961, *except for* ** *value which is taken from Tables of Physics Values,* 1976)

	$-\chi_d$	$-\chi_d^*$	χ_p	χ_p^*	α	α*
MgO[a]	2·10	2·31	0·82	1·03	18·4	22·6
CaO[b]	3·67 (12)	3·56	1·79 (12)	1·68	49 (3)	37·2
SrO[b]	4·54 (22)	4·96	0·14 (22)	0·56	38 (4)	44·0
BaO[b]	7·6 (5)	7·16	3·9 (5)	3·4	75 (11)	66·6
LiF[c]	1·35 (1)	1·31	0·09 (1)	0·05	12·8 (2)	11·7
NaF[d]	2·38 (2)	1·93** 2·44	0·42 (2)	0	23·7 (3)	14·9** 23·8
NaCl[e]	4·2 (7)	3·82	0·4 (7)	0·01	54 (18)	44
NcCl[f]	4·45 (17)	3·82	0·64 (17)	0·01	59 (5)	44
KBr[g]	6·65 (23)	6·82	0·47 (23)	0·64	68 (5)	69·1

References: (*a*) Sanger (1969). (*b*) Vidal-Valat, Vidal & Kurki-Suonio (1978); (*c*) Killean *et al.* (1972); (*d*) Howard & Jones (1977); (*e*) Schoknecht (1957); (*f*) Göttlicher (1968); (*g*) Meisalo & Inkinen (1967).

experiment allows only a limited number of reflections to be measured, one should elucidate first of all how the series-termination effect influences the final result. Fig. 2 gives the dependence of χ_d on the number of terms of a series used in the calculation according to (5) for LiF. It is seen that the first five points on a plot, which correspond to experimentally measured structure amplitudes $F(h00)$, converged well to the value $\chi_d = -0{\cdot}135$ mm^3 mol^{-1}. The inclusion into the sum of three more values of structure amplitudes, calculated analytically with the f curves taken from *International Tables for X-ray Crystallography* (1974), confirms this conclusion once again.

The main information on the diamagnetic susceptibility of a crystal is contained in the reflections determined by valence electrons from the inner region of the reciprocal space. If the number of measured reflections in this region is small, then the analytically calculated structure amplitudes for reflections with larger values of $\sin\theta/\lambda$ can be included in the summation (5). The presence of the weight coefficients, $1/h^2$, in (5) minimizes the error introduced in this case.

The influence of the experimental uncertainty on the calculation results can be estimated by the expression

$$\sigma(\chi_d) = \frac{\mu_0 N e^2 a^2}{8\pi^2 m}\left(\sum_{h=2,4,\ldots} \frac{\sigma^2[F(h00)]}{h^4}\right)^{1/2}, \qquad (6)$$

where $\sigma^2[F(h00)]$ is the structure-amplitude variance. This value is usually determined in diffraction measurements; when the experimental structure amplitudes are replaced by calculated ones, this value may be estimated by the relation

$$\sigma^2[F(h00)] = \sum_j \left\{\frac{\sigma^2(f_j)}{f_j^2} + \left(\frac{\sin\theta}{\lambda}\right)^4 \sigma^2(B_j)\right\} \times f_j^2\, T_j^2 \cos^2[2\pi(hx + ky + lz)], \qquad (7)$$

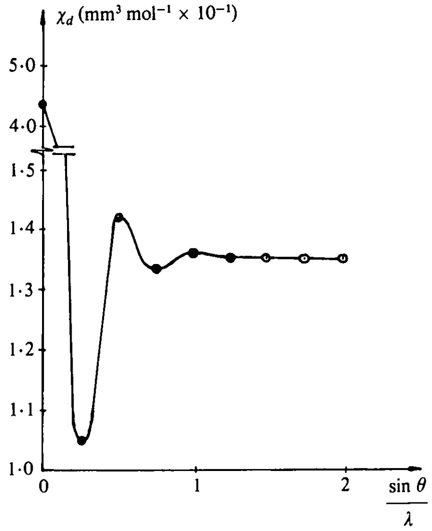

Fig. 2. χ_d values calculated from equation (5) for LiF.

i.e. it may be expressed in terms of uncertainties in atomic amplitudes, $\sigma(f_j)$, and in thermal parameters, $\sigma(B_j)$; T_j are thermal factors. The value $\sigma(f_j)/f_j$ is equal to 0·002–0·005 approximately (Tsirel'son *et al.*, 1983), the value $\sigma(B_j)$ is determined when refining the parameters of a structure by the least-squares method.

Another source of errors is related to the termination of a series in (5). This inaccuracy may be estimated by using plots similar to that in Fig. 2: the corresponding error will not exceed the half value of the last term in (5).

For LiF the error in χ_d due to the series termination can be estimated as 0·02%, whereas the error caused by uncertainties in structure amplitudes is 0·65%. The final result for LiF is $\chi_d = -0{\cdot}135 \pm 0{\cdot}001$ mm^3 mol^{-1}. Note that this estimation does not include the uncertainty related to the choice of the integration volume. Apparently, for the scope of objects under consideration, the latter uncertainty is small.

In a similar way, (5), (6), (7) were used for calculation of the diamagnetic susceptibility and the total error in the diamagnetic susceptibility (see Table 1).

Discussion of the results

First of all, it should be pointed out that all the diamagnetic susceptibilities, calculated from the diffraction data, are close to values determined from the other experiments. It can be seen from Table 1 that for four compounds, CaO, LiF, NaF and KBr, the minimum inaccuracy is not more than 3·4%. Our results coincide with the magnetic measurement data most reliable for these four compounds. Thus, one may conclude that the diamagnetic susceptibility of these objects has been determined experimentally with the best precision. For the other compounds the value of χ_d was determined less accurately because less-accurate diffraction data had been used.

The achieved coincidence of the calculated values of χ_d with the experimental ones allows the conclusion to be made that for ionic crystals the choice of pseudo-atomic fragments in the form of the Wigner–Seitz cells is a satisfactory approximation. As seen from Fig. 1, the boundary between two cells lies in the region of the interatomic space with the minimum and near-constant electron density. The calculation of the number of electrons, located in the cells, for a positive and a negative ion in LiF gives the values 2·29 ± 0·05e for Li$^+$ and 9·71 ± 0·05e for F$^-$. The integration over a sphere, restricted by a radius of the best separation of the electron density, carried out by Kurki-Suonio & Salmo (1971) with the LiF data of Merisalo & Inkinen (1966), yielded for these ions the values 2·05 ± 0·05e and 9·7 ± 0·09e, respectively. Therefore, the integration in (4) over the volume of the Wigner–Seitz cell is well founded, and the error, introduced by this integration into the results of calculation of χ_d, is insignificant and, apparently, lies within the limits of the experimental data uncertainty.

The choice of pseudoatomic fragments within the framework of the Hirshfeld (1977) model may become the next step in applying the above approach to the determination of the diamagnetic susceptibility of crystals with the arbitrary distribution of electron density. One cannot exclude the possibility that this step will allow direct and accurate enough determination of the diamagnetic susceptibility for any crystal. The usual procedure of separating the diamagnetic component from the experimentally measured total magnetic susceptibility is related to the preliminary calculation of the paramagnetic Van Vleck part of the susceptibility (Van Vleck & Frank, 1929). Such an approach meets both calculational and experimental difficulties (Dorfman, 1961), its accuracy is limited and does not lend itself to estimation. In the case of the diffraction data, as shown above, the accuracy may be controlled without any difficulty at any stage of calculation.

An obvious consequence of the direct determination of the diamagnetic susceptibility is a possibility of separating the paramagnetic component, $\chi_p = \chi - \chi_d$, where χ is the experimentally measured total magnetic susceptibility. The values χ_p for some crystals, calculated in such a way and estimated by other methods, are given in Table 1. The crystals with higher values of χ_p are chosen here since they have a lower relative determination error. It is seen that in the series of compounds MgO, CaO, BaO the value χ_p gradually increases, which indicates the growth of a mutual deformation of ions (χ_p for SrO breaks down this dependence: see discussion by Dorfman, 1961). The inaccuracy of determination of χ_p is higher than that for χ_d; however, similar estimations are simply absent for other approaches.

It is worth noting that, in the case of NaF, where different methods of determination of the magnetic susceptibility give different values (see Table 1), the result given in *Tables of Physics Values* (1976), where the value $\chi_d = -0{\cdot}244$ mm^3 mol^{-1} was obtained, is preferable because it only slightly differs from that obtained in our calculation, that is, $\chi_d = -0{\cdot}238$ mm^3 mol^{-1}.

The calculation of the electron static polarizability

The electron static polarizability, α, can be calculated from the diffraction data within the framework of the Kirkwood (1932) model, which gives for many-atomic systems, consisting of relatively symmetrical fragments, the following relation:

$$\alpha = \frac{16\pi}{9ka_0}(\langle r^2\rangle)^2, \tag{8}$$

where k is the number of electrons in a molecular unit; a_0 is the Bohr radius; $\langle r^2\rangle$ is the mean square of the electron radius vector, the origin of the coordinate system being located at the center of gravity of a fragment. For such systems $\langle r^2\rangle = \frac{3}{2}\langle x^2 + y^2\rangle$. Using (1) to (5) and (8), we obtain, for the NaCl-type structure,

$$\alpha = \frac{16\pi a^4}{a_0 n}\left(\frac{n}{96} + \frac{1}{2\pi^2}\sum_{h=2,4,\ldots}(-1)^{h/2}\frac{F(h00)}{h^2}\right)^2. \tag{9}$$

Here a is the dimension of a unit cell; n is the number of electrons in it. The values of α, calculated by (9) and determined from the experiment, and errors $\sigma(\alpha)$, computed by formula analogous to (6), are presented in Table 1. It can be seen that the approach, described above, is satisfactory for determining this value as well. Previously, the experimental values of α have been used for the recalculation of χ_d (Dorfman, 1961). Our technique allows both values to be calculated independently. The above remarks relative to the choice of volume Ω_j for arbitrary systems, as well as the remarks relative to the accuracy of the results, which were related to χ_d, are applicable to α as well.

Summary

The calculations carried out in this work have shown that the diffraction data allow the determination, with a good accuracy, of the diamagnetic susceptibility and the static polarizability of crystals. The reproducibility of the observed characteristics is an encouraging argument favoring the fact that the valence-electron distribution, determined from an experiment, is known reliably enough. In this case the interpretation of the details of this distribution from the viewpoint of studying the peculiarities of the chemical bond becomes well founded.

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Acta Cryst. (1983). A**39**, 415–421

Geometric Units in Tetragonal Crystal Structures

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(*Received* 20 *July* 1982; *accepted* 21 *December* 1982)

Abstract

Tetragonal space groups are classified from the geometric-unit view point by considering crystal structures as a result of combinations and permutations of some basic polyhedral units. There are nine patterns among two categories represented by four units packed on the $(1\bar{1}0)$ and (100) planes. Category (I) consists of five types with four units packed on the $(1\bar{1}0)$ plane. The centers of these units are $0,0,0$; $0,0,\frac{1}{2}$; $\frac{1}{2},\frac{1}{2},0$ and $\frac{1}{2},\frac{1}{2},\frac{1}{2}$. In that order, the patterns can be represented by $ABCD$, $AA'BB'$, $ABA'B'$, $ABB'A'$ and $AA'A''A''$. Each letter here represents an independent unit: primes are used to indicate one of the following orientation relationships: identity, fourfold rotation, mirror plane parallel to (110), and mirror plane parallel to (100). These units have the shape of tetragonal prisms and they stack in the same way as the crystallographic unit cells. Category (II) has four types packed on the (100) plane and the centers of these units are at $0,0,0$; $0,\frac{1}{2},\frac{1}{4}$; $0,0,\frac{1}{2}$ and $0,\frac{1}{2},\frac{3}{4}$. In that order, the patterns can be represented by $ACBD$, $ABA'B'$, $AA'BB'$ and $AA'A''A''$. The ideal polyhedra for category (II) are truncated tetragonal prisms or flattened truncated octahedra depending on the axial ratio c/a. For simplicity, these polyhedra are transformed into tetragonal prisms so that all geometric units have the same shape. Units in category (II) stack in an interlocking fashion, like the work of a bricklayer. The overlap displacements for the interlocking are in the (001) direction. The symmetries of the geometric units in some space groups depend on the choice of origin, but a shift to equivalent origins changes neither the packing patterns nor the symmetries of the geometric units.

Introduction

Plato's hypothesis about the structure of matter is that all matter is the result of combinations and permutations of a few basic polyhedral units. From a geometric view point, these polyhedral units are made up of atoms, ions, or molecules. Furthermore, a polyhedral unit may contain a group of nested polyhedra whose vertices are marked by positions of symmetry-related atoms. This paper reports the exploration along this idea of combinations and permutations of some basic units for the tetragonal system.

The problem of space filling with polyhedra has fascinated many mathematicians and crystallographers alike for more than two thousand years (Senechal, 1981). For example, Dirichlet (1850) and Wigner & Seitz (1933) introduced methods for finding the polyhedra enclosing each of the lattice points. These polyhedra are called Dirichlet regions (or domains) or Wigner–Seitz cells.

For the cubic crystal system, it has been demonstrated that all geometric units have the shape of an Archimedean truncated octahedron (Chieh, 1979). The

0567-7394/83/030415-07$01.50