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Anisotropy of effective charges in NaNO_2 , NaNO_3 , KNO_3 and CaCO_3

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Abstract. Effective charges of the constituents of NaNO_2 , NaNO_3 , KNO_3 and CaCO_3 are calculated from the splitting of polar optical modes into transverse and longitudinal components, obtained from the simulation of the infrared reflectivity spectra polarised along the different crystallographic directions. Effective charges within planar molecular ions are found to be highly anisotropic, whereas the effective charge of external cations depends little on polarisation. The temperature dependence of the effective charges is reported in NaNO_2 , NaNO_3 and KNO_3 . The dependences are discussed in terms of correlation of the cation–anion distance with the ionic-covalent character of the bond, in particular near structural phase transitions where the cation–anion distances may change.

1. Introduction

The concept of infrared spectroscopy is based upon the coupling of an instantaneous dipole moment with the electric field of infrared electromagnetic radiation. The instantaneous dipole moment is created by the relative motion of charges—with opposite signs—that are carried by the atoms. All ionic solids consistently absorb infrared radiation. But even covalent solids, *if they are heteropolar*, also absorb infrared radiation with, however, lower absorption coefficients than ionic solids. This means that the existence of stretching vibrational modes of heteropolar covalent solids implies some instantaneous dipole moment, which itself implies some *effective charge* carried by each atomic site, even if the chemical bonding is dominantly covalent. Thus, starting from the basic concept of infrared spectroscopy, it appears feasible to measure accurately the effective charges carried by atoms.

Within the context of a general description of the chemical bonding, the measured effective charge divided by the nominal valence gives some indication about the degree of ionicity. The ratio should be unity for a purely ionic bond and zero for a purely covalent bond. As a result, covalent homopolar crystals, such as diamond, do not absorb infrared radiation (at least to the first order of dielectric susceptibility). The measurement of effective charge has been proved to be especially useful in oxides, for example, a family of materials which cannot be safely classified as purely ionic or covalent (Scott 1971, Gervais 1976, Gervais and Arend 1983). In addition, the method is

applicable to measurements in polarised light, and a correlation between bond strength and bond length has been verified in all cases investigated.

One significant example in an important class of physical phenomena concerns ferroelectrics, in which *any displacive paraelectric-ferroelectric phase transition* experimentally manifests itself by a *decrease* of the effective charge *measured* in the direction of the ferroelectric axis, irrespective of the order of the phase transition. The reason is easily understood. Ferroelectricity is due to the appearance of a spontaneous electric dipole moment below a certain temperature. This implies that whereas the centres of gravity of positively and negatively charged ions coincide in the upper paraelectric phase, they no longer coincide in the low-temperature ferroelectric phase because some cation-anion distances have been shortened at temperatures below T_c . Now if we bring together one cation and one anion, we may expect that bond overlap—and therefore increased covalency—will take place progressively as the cation-anion distance is reduced. This is just what has been observed experimentally for oxide perovskites, ilmenites, KDP-family or SbSI ferroelectrics. In all cases the formation of the cation-anion pair that is the origin of the spontaneous polarisation in the ferroelectric phase manifests itself by a significant decrease of the effective charge measured along the direction of cation-anion pairing with respect to the perpendicular direction.

It is known from half a century ago that the infrared absorption coefficient is related to the square of the effective charge of the atoms involved in the vibrational motion under consideration. For a cubic diatomic crystal the effect may be visualised in the form (see e.g. Scott 1971, Gervais 1976)

$$(Ze)^2/\mu\varepsilon_v V = \Omega_{LO}^2 - \Omega_{TO}^2 \quad (1)$$

where Ω_{LO} and Ω_{TO} stand for the longitudinal and transverse optical frequency components of the polar vibration, Ze is the effective charge carried by the ions, μ their reduced mass and ε_v the dielectric constant of vacuum. The method discussed here assumes that TO-LO splittings of all polar vibrational modes are known from the analysis of infrared reflection spectra in polarised light. It is based on a generalisation of the equation above to several modes and types of atoms in the form

$$\sum_k \frac{(Ze)_{k\alpha}^2}{m_k} = \varepsilon_v V \sum_j (\Omega_{jLO}^2 - \Omega_{jTO}^2)_\alpha \quad (2)$$

derived by Scott (1971) and discussed in detail by Gervais and Arend (1983). The summation in the left-hand side is taken over all ions k with mass m_k located in the elementary volume V , whereas the summation in the right-hand side is over all polar modes polarised along the direction α . There are several possible definitions of the effective charge. Ze in equation (2) is nothing but the effective charge that enters a rigid ion model of lattice dynamics. The electric neutrality of the unit cell

$$\sum_k (Ze)_k = 0 \quad (3)$$

provides a second equation for solving (2).

The infrared reflectivity spectra recorded with polarised light in the range 10–4000 cm^{-1} , cover all the vibrational optical modes of the compounds studied. The simulation of the infrared reflectivity spectra, using the factorised form of the dielectric function, provides all Ω_{jTO} and Ω_{jLO} frequencies accurately (Gervais 1983).

The aim of the present paper is to calculate the effective charge carried by the ions of four compounds: sodium nitrite (NaNO_2), sodium nitrate (NaNO_3), potassium nitrate

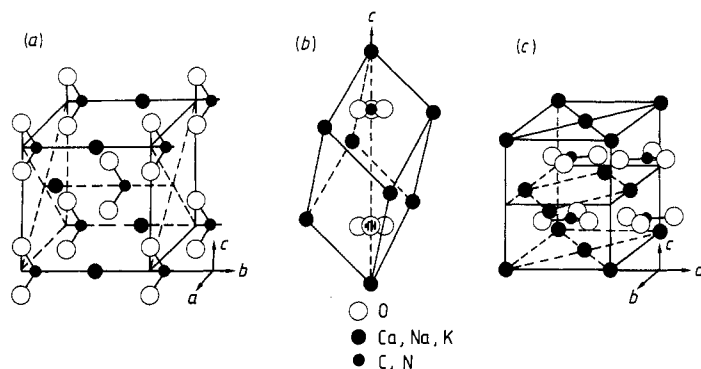


Figure 1. Crystal structure of: (a) NaNO_2 ; (b) CaCO_3 , NaNO_3 ; (c) KNO_3 .

(KNO_3) and calcium carbonate (CaCO_3), using the analysis of the infrared reflectivity spectra (Bréhat and Wyncke 1985a, b, 1988, Onomichi *et al* 1971), to compare them and to study the dependence of each charge on temperature. More important is to check the expected anisotropy of the effective charge within planar molecular ions.

2. Structure

We consider four ternary compounds, which possess a planar anion: NO_2^- , NO_3^- or CO_3^{2-} . Two of them are uniaxial, NaNO_3 and CaCO_3 ; the other two are biaxial in their low temperature phase, NaNO_2 and KNO_3 .

At room temperature, NaNO_3 and CaCO_3 crystallise in the rhombohedral calcite structure (D_{3d}^6 , R_{3c}) (figure 1b). The crystal structure consists of alternate layers of cations (Na^+ or Ca^{2+}) and planar anions (NO_3^- or CO_3^{2-}), perpendicular to the c axis (see Bréhat and Wyncke 1985b). Above 549 K, NaNO_3 has a completely disordered structure that is not considered in this work.

KNO_3 crystallises in the orthorhombic aragonite structure (D_{2h}^{16} , Pmcn) (figure 1(c)). The crystal structure shows the alternate layers of K^+ and planar NO_3^- ions, perpendicular to the c axis. The NO_3^- layers do not lie exactly midway between two adjacent K^+ layers, but are slightly shifted in the c direction, giving rise to an ordered antiferroelectric structure (Nimmo and Lucas 1973). When temperature is increased above 370 K, the planes of K^+ ions shift slightly along the $[001]$ direction, in such a way that, at 401 K, KNO_3 undergoes a structural phase transition to a rhombohedral paraelectric phase, which has a structure closely related to calcite structure (figure 1(b)) in which K^+ and NO_3^- ions are aligned along the c axis (see Bréhat and Wyncke 1988).

NaNO_2 has a body-centred orthorhombic structure below 437 K (C_{2v}^{20} , $\text{Im}2m$) (figure 1(a)). In this phase the crystal is ferroelectric, the spontaneous polarisation being parallel to the b axis. The planar NO_2^- ions lie in the (b, c) plane; the two oxygen atoms are on a line parallel to the c axis. The Na^+ and NO_2^- ions are aligned along the b axis, Na^+ having an asymmetric position between two NO_2^- ions (figure 1(a)). At 437 K, NaNO_2 undergoes a structural phase transition to an orthorhombic orientationally disordered paraelectric phase (D_{2h}^{25} , Immm) due to the random orientation of the NO_2^- ions along either $+$ or $-b$ (see Bréhat and Wyncke 1985a). An incommensurately-modulated

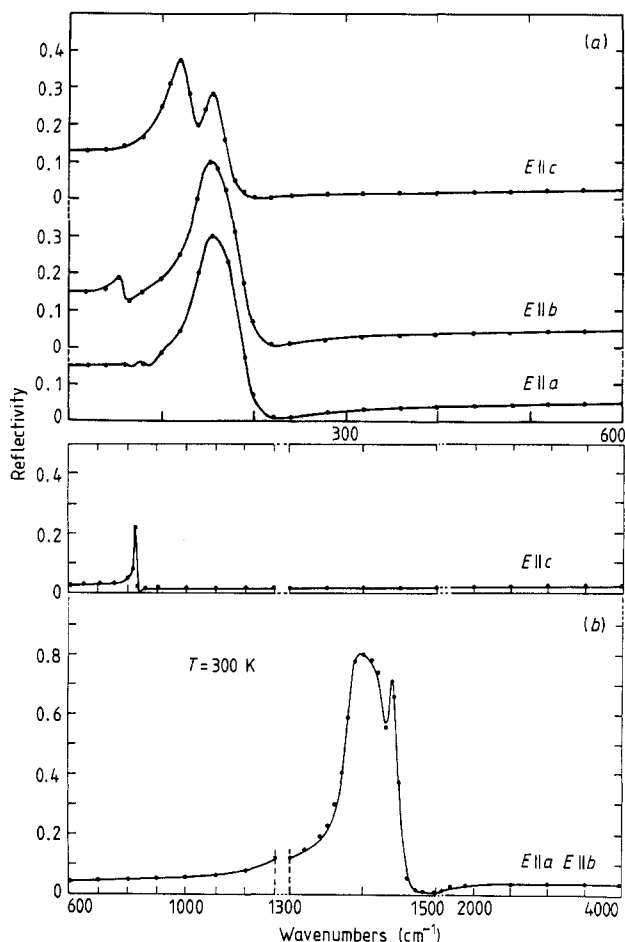


Figure 2. Far IR reflectivity spectra of KNO_3 at room temperature, along the three crystallographic directions. Full curves correspond to the best fit of the factorised form of the dielectric function model to the experimental data (dots): (a) lattice modes; (b) internal modes.

structure takes place over two degrees between the commensurate paraelectric and ferroelectric phases.

3. Vibrational optical modes

The infrared reflectivity spectra are known between 10 and 4000 cm^{-1} for the four compounds. We have recently studied the temperature dependence of the polarised infrared reflectivity spectra in NaNO_2 (Bréhat and Wyncke 1985a), NaNO_3 (Bréhat and Wyncke 1985b) and KNO_3 (Bréhat and Wyncke 1988) between 10 and 500 K in the frequency range 10–600 cm^{-1} , and extended the measurements from 600 up to 4000 cm^{-1} at room temperature. Figure 2 gives an example of the infrared reflectivity spectra in the case of KNO_3 at 300 K. The infrared reflectivity spectra of CaCO_3 at 300 K between 10 and 4000 cm^{-1} are taken from Onomichi *et al* (1971). Experimental results

show that in each crystal the external lattice modes are well separated from the internal modes, and no coupling between both types of modes is observed (Bréhat and Wyncke 1988) since the dispersion between 300 and 700 cm^{-1} is negligible. These spectroscopic results indicate that the anions form rigid molecular complexes, with nearly the same structure as the free anions.

A computer simulation of the experimental spectra was achieved with the aid of the factorised form of the dielectric function (Gervais 1983).

$$\varepsilon(\omega) = \varepsilon_{\infty} \prod_j \frac{\Omega_{j\text{LO}}^2 - \omega^2 + i\omega\gamma_{j\text{LO}}}{\Omega_{j\text{TO}}^2 - \omega^2 + i\omega\gamma_{j\text{TO}}} \quad (4)$$

where the Ω_j and γ_j represent the frequencies and dampings of the TO and LO optical modes and ε_{∞} is the high frequency dielectric constant. The lattice mode parameters that give rise to the best fit to experimental reflectivity spectra are given in (Bréhat and Wyncke 1985a, b, and 1988).

4. Effective charges

Since the TO–LO splitting of all polar modes are known experimentally for each polarisation with the data reduction described in the preceding paragraph, the effective charges of any binary system may be evaluated without any assumption or approximation. In a ternary compound, there are three unknowns but only two equations. However, in systems like the four studied here, where there is no measurable dispersion between the spectral range of modes internal to the molecular anions and that of external modes, i.e. in cases where internal modes are uncoupled to external modes, the evaluation of effective charges may be performed in two steps as is detailed below.

As a first step we consider the external modes, i.e. the vibrations of the cations against the molecular anions, and sum over the external modes only, so that equation (2) is rewritten

$$\frac{(Ze)_{\text{C}\alpha}^2}{m_{\text{C}}} + \frac{(Ze)_{\text{A}\alpha}^2}{m_{\text{A}}} = \varepsilon_v V \sum_j (\Omega_{j\text{LO}}^2 - \Omega_{j\text{TO}}^2)_{\alpha} \quad (5)$$

where $\text{C} = \text{Na}^+$, K^+ or Ca^{++} and $\text{A} = \text{NO}_2^-$, NO_3^- or CO_3^{--} . One has to consider in this case, only the effective charge of cation (C) and of the anion (A). Combined with the electric neutrality of the system, (5) provides the effective charge of cation C for each polarisation. As a next step we apply equation (2) to all ions and all polar modes of the system and the evaluations are straightforward since the effective charge of cation C is already known.

Table 1 lists the values of the reduced effective charge of the ions of the four studied compounds at 300 K, along the different crystallographic directions. For the two uniaxial crystals, \parallel means the polarisation along the c axis, and \perp the polarisation normal to the c axis. For KNO_3 , \parallel means along the c axis, \perp_1 along the a axis, \perp_2 along the b axis. For NaNO_2 , \parallel means along the a axis, \perp_1 along the ferroelectric b axis and \perp_2 along the c axis.

The effective charges measured in NaNO_3 and KNO_3 are found to depend little on temperature with a tendency at larger evolution in the vicinity of the phase transitions. The situation is the more marked for NaNO_2 . Results are shown in figure 3. In this order–disorder ferroelectric, the situation does not appear as easily interpretable as

Table 1. The reduced effective charges Z/Z_0 at 300 K along the different crystallographic directions (Z is the effective charge and Z_0 is the nominal valence of the ion); and the ratio of the effective charge normal to the molecular anion plane (Z_{\perp}) to the effective charge in the molecular anion plane (Z_{\parallel}) (for key see text).

		$ Z/Z_0 _{\parallel}$	$ Z/Z_0 _{\perp 1}$	$Z_{\parallel}/Z_{\perp 1}$	$ Z/Z_0 _{\perp 2}$	$Z_{\parallel}/Z_{\perp 2}$
Cation	NaNO ₂	0.77	0.76		0.73	
	NaNO ₃	0.78	0.77			
	KNO ₃	0.79	0.82		0.82	
	CaCO ₃	0.70	0.70			
N or C ion	NaNO ₂	0.01	0.09	0.11	0.54	0.02
	NaNO ₃	0.06	0.33	0.18		
	KNO ₃	0.05	0.33	0.15	0.33	0.15
	CaCO ₃	0.07	0.50	0.15		
O ion	NaNO ₂	-0.20	-0.26	0.78	-0.59	0.34
	NaNO ₃	-0.18	-0.40	0.45		
	KNO ₃	-0.18	-0.41	0.45	-0.41	0.45
	CaCO ₃	-0.30	-0.55	0.55		

near-displacive ferroelectric phase transition. An interesting fact is that the behaviour observed along the ferroelectric b axis is opposite to what is found in both perpendicular directions.

5. Discussion

5.1. Comparison with calculations

The measurements reported here may be compared to evaluations by other methods and authors.

For NaNO₃, Yamamoto *et al* (1976), using the polarisable-ion model, obtained $Z_{\text{Na}} = 0.77$, $Z_{\text{N}} = 0.15$ and $Z_{\text{O}} = -0.31$; and $Z_{\text{Na}} = 0.87$, $Z_{\text{N}} = 0.17$ and $Z_{\text{O}} = -0.35$ using the rigid ion model (Yamamoto *et al* 1974). Those calculations yield results not very different from the experimental data along the c axis reported here.

For CaCO₃, using the rigid-ion model, these authors obtained: $Z_{\text{Ca}} = 1.21$, $Z_{\text{C}} = 0.20$ and $Z_{\text{O}} = -0.47$ (Yamamoto *et al* 1975). Again, calculations compare well with present experimental data for the polarisation along the c axis.

Goddard *et al* (1983) have examined the charge distributions in anion and cation of NaNO₂ in terms of the Mulliken net charges on the atomic centres, they obtained: $Z_{\text{Na}} = 0.948$, $Z_{\text{N}} = 0.31$ and $Z_{\text{O}} = -0.629$. Those values are similar to what is found in this paper for the polarisation $E \parallel b$, where b is the ferroelectric axis.

5.2. Characterisation of the bonds

The main result to emerge from the present study is that the effective charges of planar molecular ions depend strongly upon polarisation, whereas the effective charges of external cations are nearly isotropic. In all cases, the effective charge found for the atomic constituents of planar molecular ions is several times higher within the plane than perpendicular to it, as summarised in table 1. Perpendicular to the planes, and only

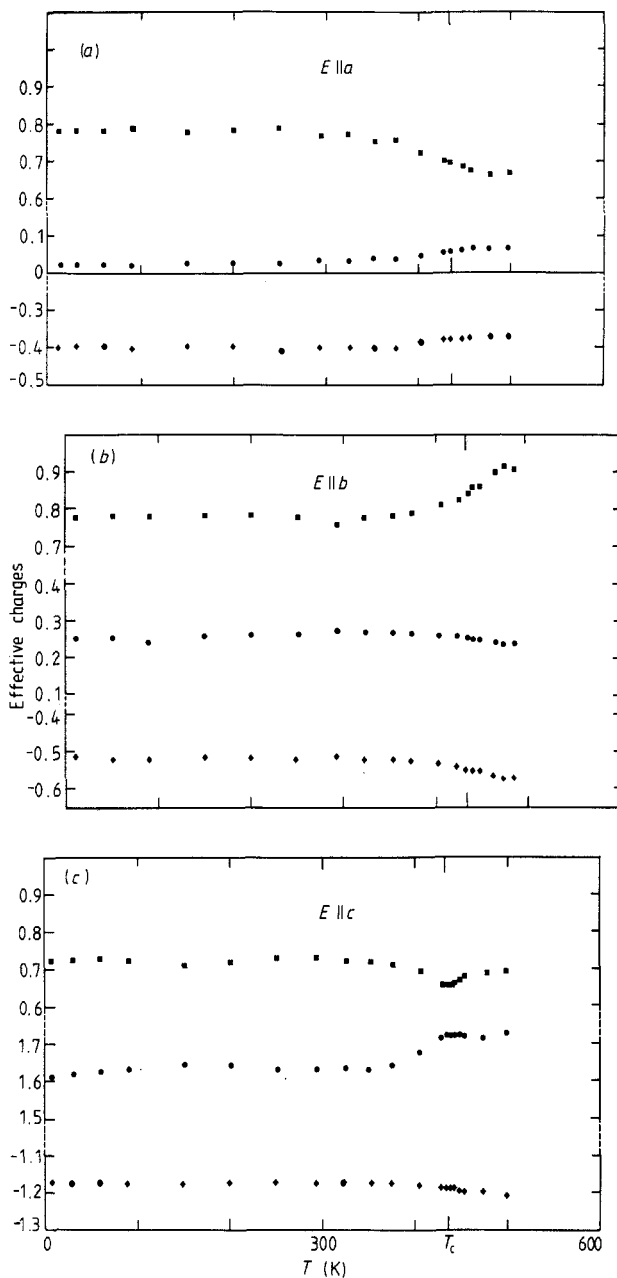


Figure 3. Temperature dependence of the effective charges in electron units carried by the ions (■ cations, ● nitrogen and ◆ for oxygen) measured along the crystallographic directions for NaNO_2 .

in that case, the values compare well with calculations based on point charge models. Vibrational motions in the direction perpendicular to the plane of the molecular anions leave invariant the C–O (or N–O) bond distance. We obtain therefore the experimental ‘static’ effective charge, which gives information about the residual ionicity of the bonds.

Conversely, vibrational motions within the plane of the molecular ions change the carbon (or nitrogen)–oxygen bond lengths as a function of time at a frequency of $\approx 4 \cdot 10^{13}$ Hz. In addition, the polarisability of the electron cloud of oxygen may give rise to some retardation in the motion of the cloud with respect to the hard core of the anion. The oxygen shell also carries a charge and contributes, therefore, to the instantaneous dipole moment. The anisotropy of the effective charge may be compared to the anisotropy of the chemical shift of ^{13}C measured by NMR in calcite (Lauterbur 1958) for example. The method presented here based on infrared measurements, however, implies a simpler concept than the chemical shift, in that the dipole moment probed by infrared radiation is nothing but the electric charge localised at the ionic site times a relative displacement. As soon as the chemical bond involves non-rigid ions, the effective charge becomes a tensorial quantity owing to the appearance of directional electron clouds (bonding orbitals). As a result, external cations Na, K or Ca carry an effective charge that is found experimentally to be (i) not very different from the nominal charge, (ii) isotropic within experimental error. Conversely, large anisotropies are consistently found for planar oxyanions. The values measured perpendicular to the oxyanion planes involve the effective charges localised at the atomic sites only, and constitute a measurement that is relevant for the evaluation of the residual ionicity.

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