Acta Cryst. (1979). A**35**, 236–240

Derivation of Selenium–Selenium Non-Bonded Potential Parameters for Molecular Crystals

By H. A. J. Govers

General Chemistry Laboratory, Chemical Thermodynamics Group, Rijksuniversiteit Utrecht, Padualaan 8, *Utrecht* 2506, *The Netherlands*

(*Received* 10 *July* 1978; *accepted* 4 *September* 1978)

Abstract

Potential-function parameters for Se–Se non-bonded atom–atom pair interactions have been derived from the room-temperature heat of sublimation of a mixture of monoclinic α- and β-Se_8 and from the crystal structures of these two modifications. The first procedure applied was that of Nauchitel' & Mirskaya [*Sov. Phys. Crystallogr.* (1972), **16**, 891–892]; the second was that of Williams [*J. Chem. Phys.* (1967), **47**, 4680–4684]. In the latter procedure, the exponential parameter for the Se–Se repulsive term from the previous procedure was used and the coefficients of the attractive and repulsive terms were fitted to 22 observational equations by a weighted least-squares calculation. The second procedure proved to be more reliable than the first. Unlike the first procedure it yielded parameters with which a heat of sublimation of α-Se_8 could be calculated that was 0·8 kcal mol^{-1} higher than that of β-Se_8. At the same time, the calculated heats of sublimation of both modifications deviate by less than 2% from the experimental value of the monoclinic mixture. A low average value of 2·7% for the standard deviation of the parameters derived was obtained.

Introduction

The atom–atom approximation has proved to be a valuable tool for calculating the lattice energies of molecular crystals (Kitaigorodskii, 1973; Williams, 1974). Recently we have been able to show that this approximation can be used for organic crystals such as 2,2′-bis-1,3-dithiole (TTF), 7,7,8,8-tetracyanoquinodimethane (TCNQ) and their 1:1 complex (TTF–TCNQ) (Govers, 1978*a*). The latter compound is an organic metal. As several organic metals contain the Se analogue of TTF (*e.g.* Engler, Scott, Etemad, Penney & Patel, 1977) and as Se–Se non-bonded atom–atom parameters have not been derived before, we performed this derivation.

The parameters derived have to be used in combination with parameters for atom–atom interactions involving C, H, N and S atoms (Govers, 1975, 1978*b*). Therefore, we used the procedures of Williams (1967) and Nauchitel' & Mirskaya (1972). Both procedures require the experimental values of the heats of sublimation and of the structural parameters of molecular crystals which contain a considerable number of Se atoms in the absence of intermolecular interactions other than van der Waals and/or electrostatic. For our purposes we chose monoclinic selenium crystals belonging to the rare selenium compounds which more or less fulfil these requirements.

Method

In both procedures the general form of the atomic interaction E_{kij} between atom i of a central molecule and atom j of a surrounding molecule k is considered to be:

$$E_{kij} = -Ar_{kij}^{-6} + B\exp(-Cr_{kij}). \qquad (1)$$

In this Buckingham expression A, B and C are the Se–Se potential parameters. Electrostatic (Coulombic) interactions are not treated explicitly. Another parameter Sl represents the summation limit beyond which the lattice summation is cut off. In the procedure of Nauchitel' & Mirskaya (1972) (hereafter called NM) the summation limit is 15 Å, which yields 100% of the lattice energy. In the procedure of Williams (1967) and Govers (1975) (hereafter called WG) the summation limit is 6 Å, yielding 80% of the lattice energy.

The distance r_{kij} between the interacting atoms is calculated from

$$r_{kij} = \mathbf{D}\mathbf{s}_k\,\mathbf{D}^{-1}(\tilde{\mathbf{R}}\mathbf{K}_{jo} + \mathbf{T}) + \mathbf{D}\mathbf{t}_k - (\tilde{\mathbf{R}}\mathbf{K}_{io} + \mathbf{T}). \qquad (2)$$

In this expression, which is identical to expression (2) of Govers (1975), the elements of matrix $\mathbf{D}$ are a function of the monoclinic cell parameters a, b, c and β of crystalline selenium. The elements of matrix $\tilde{\mathbf{R}}$ are written as a function of the Eulerian angles φ,θ,ψ, which define the orientation of the Se_8 molecule with respect to a unit-cell-fixed orthogonal system. The elements of vector $\mathbf{T}$ define the position of the centre of gravity of the molecule. $\mathbf{K}_{io}$ are atomic coordinates. $\mathbf{R}$ (φ,θ,ψ), $\mathbf{K}_{io}$, $\mathbf{D}$ (a,b,c,β) and $\mathbf{T}$ $(T1,T2,T3)$ can be calculated directly from the experimental crystal

0567-7394/79/010236-05$01.00 © 1979 International Union of Crystallography

structure determination. $\mathbf{s}_k$ and $\mathbf{t}_k$ are given by the space-group symmetry and by the summation limits defining the surrounding molecules to be included.

The heat of sublimation, ΔH^{subl}, or lattice energy is calculated with the expressions (3) and (4) in the NM and WG procedures respectively:

$$\Delta H^{\text{subl}} = -\tfrac{1}{2} N \sum_{k}^{z} \sum_{i}^{n} \sum_{j}^{n} E_{kij}(r_{kij}) - 2RT, \qquad (3)$$

$$\Delta H^{\text{subl}} = -\tfrac{1}{2}.\, 1{\cdot}25 N \sum_{k}^{z} \sum_{i}^{n} \sum_{j}^{n} E_{kij}(r_{kij}). \qquad (4)$$

In these expressions, N is the number of molecules in the lattice, z the number of molecules surrounding a central molecule and lying within the summation limits, and n is the number of atoms per molecule. The factor 1·25 is introduced into (4), as the summation limit in the WG procedure yields only 80% of the lattice energy. The factor $\frac{1}{2}$ corrects for double counting of interactions. The term $-2RT$ in (3), in which R is the gas constant and T the absolute temperature, stands for a crude estimation of lattice and gaseous dynamical contributions (Govers, 1974), which are not treated explicitly in the WG procedure. At 298 K, $2RT$ is 1·2 kcal mol^{-1}.

In the NM procedure the exponential parameter C of the repulsive contribution in (1) is found by minimization of $\Delta H^{\text{subl}} + 2RT$ in (3) with respect to an auxiliary parameter $r_0 = 13{\cdot}6/C$ Å. In this step the parameter $A = 0{\cdot}119\ r_0^6$ Å^6 kcal mol^{-1} and $B = 42\,000$ kcal mol^{-1}.* In this way a minimal value of $\Delta H^{\text{subl}}(r_0) + 2RT$ is found, which has to be multiplied by a factor K in order to obtain the experimental value of $\Delta H^{\text{subl}} + 2RT$. The value of K found is used to obtain the final values of the parameters $A = K\, 0{\cdot}199\ r_0^6$ Å^6 kcal mol^{-1} and $B = K\ 42\,000$ kcal mol^{-1}.

In the WG procedure a set of linear observational equations of types (5) and (6) is constructed from the expressions (1) + (4) and from an equilibrium condition which states that the derivative of the heat of sublimation with respect to the structural parameter p (cell parameters, Eulerian angles, coordinates of the centre of gravity) has to be zero:

$$-A \textstyle\sum_s U_{\text{attr}} + B \sum_s U_{\text{rep}} = \Delta H_s^{\text{subl}}, \qquad (5)$$

$$-A \textstyle\sum_s \Delta_p U_{\text{attr}} + B \sum_s \Delta_p U_{\text{rep}} = 0. \qquad (6)$$

$\sum_s U_{\text{attr}}$ is a summation of attractive contributions of type r_{kij}^{-6} and $\sum_s \Delta_p U_{\text{attr}}$ a summation of type $\delta r_{kij}^{-6}/\delta p$. Both summations are performed for each of the compounds s of which the heat of sublimation and crystal structure have been determined experimentally. In the repulsive contributions $\sum_s U_{\text{rep}}$ and $\sum_s \Delta_p U_{\text{rep}}$ an analogous summation takes place for $\exp(-Cr_{kij})$ and $\delta[\exp(-Cr_{kij})]/\delta p$ respectively. Furthermore, each of the observational equations must be weighted adequately. A simple least-squares procedure is then used in order to solve the over-determined linear system. The calculated standard deviations in the calculated parameters A and B as well as the deviations of the calculated heats of sublimation from the experimental ones are regarded as criteria for the success of the derivation.

The parameter C, which has to be known in this procedure, might have been found by external variation of C. However, we prefer a fixed value for C as obtained by the NM procedure, which well satisfies the experimental structural requirements.

Experimental data

As mentioned above, crystalline selenium is one of the rare systems which has been studied extensively enough to be suitable for the derivation of Se–Se potential parameters. In the solid phase selenium exists in several modifications, of which only the α and β monoclinic ones can be considered as molecular crystals consisting of Se$_8$ molecules (Cherin & Unger, 1972; Marsh, Pauling & McCullough, 1953). However, the metallic trigonal modification is the more stable in normal conditions. This difficulty is not too serious as the minimum of the lattice energy with respect to r_0 or to the 10 structural parameters will be quite distinct even when it is not an absolute minimum (Kitaigorodskii, 1973). Furthermore, there are several very short intermolecular distances of about 3·5 Å in α-Se$_8$ as well as in β-Se$_8$. These distances are markedly

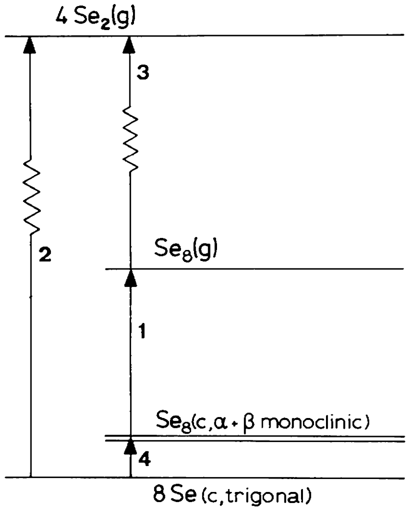

Fig. 1. Enthalpy scheme of selenium (g and c denote gaseous and crystalline phases respectively). Figures (1) to (4) denote enthalpy transitions as used in expressions (7) and (8) and in Table 1.

---

* Nauchitel' & Mirskaya (1972) mention a value $B = 45\,000$ kcal mol^{-1}, which is erroneous in view of equation (1) in Mirskaya & Nauchitel' (1972).

shorter than the predicted van der Waals distance of 4·0 Å for Se–Se interactions (Cherin & Unger, 1972), and types of interactions other than van der Waals might be present. These therefore will be included in the parameters derived. We note that the Se–Se parameters will be applied to systems which may also contain very different types of interactions (Govers, 1978*b*). The determination of the crystal structure of β-Se_8 has a residual reliability value of 0·19, whereas for α-Se_8 this value is 0·072. This high value for β-Se_8 introduces errors of 0·02 Å into the atomic positional parameters, which are, however, of the same order as the errors in crystal structures predicted by the atom–atom approximation (Kitaigorodskii, 1973).

The α and β room-temperature crystalline structures are very similar. α-Se_8 crystallizes in space group $P2_1/n$, β-Se_8 in $P2_1/a$. The unit cells of both structures contain four Se_8 molecules with nearly identical geometry. Both structures are defined by 10 intermolecular structural parameters p ($a,b,c,\beta,\varphi,\theta,\psi,T1,T2,T3$).

In the gaseous phase Se, Se_2, ..., Se_8 molecules are present in proportions determined by temperature and pressure (*e.g.* Rau, 1974). Because of this and because of the instability of monoclinic selenium with respect to the trigonal modification no direct experimental determination of the heat of sublimation of monoclinic selenium at room temperature is possible. The indirect way in which we were able to obtain an experimental value can be illustrated with the enthalpy scheme of Fig. 1.

The enthalpy difference of transition (**1**), $\Delta H(\mathbf{1}) = \Delta H^{\text{subl}}$, is needed for our purpose and can be found by the relations

$$\Delta H(\mathbf{1}+\mathbf{4}) = \overline{\Delta H(\mathbf{2})} - \Delta H(\mathbf{3}), \quad (7)$$

$$\Delta H^{\text{subl}} = \overline{\Delta H(\mathbf{1}+\mathbf{4})} - \Delta H(\mathbf{4}). \quad (8)$$

Experimental values for these enthalpy differences at 298 K are given in Table 1.

Transition (**4**) contains a further uncertainty, as it includes a mixture of α- and β-Se_8 in the determination by Gattow & Dräger (1966). These authors estimate this uncertainty to be less than the other experimental errors. Thus we were forced to use the same experimental values for both modifications. Moreover, this value is rather inaccurate as can be read from Table 1.

Table 1. *Experimental enthalpy differences* (kcal mol^{-1}) *for selenium at* 298 K (*cf. Fig.* 1)

The values are given per mol of Se_8 molecules. Values at 298 K, when not given in the references quoted, have been calculated using the heat-capacity values of Rau (1974) for gaseous Se_2 and Se_8 and of Grønvold (1973) for crystalline trigonal selenium.

Transition	ΔH	Comments
(**2**)	142·4	Mesmeyanov (1963)
(**2**)	137·2	Mesmeyanov (1963)
(**2**)	136·8	Berkowitz & Chupta (1966)
(**2**)	139·2	Rau (1974)
(**2**)	138·8	Average value
(**3**)	98·1	Mesmeyanov (1963)
(**4**)	8·0 ± 3·2	Gattow & Dräger (1966)
(**1** + **4**)	40·8	*Via* relation (7)
(**1** + **4**)	44·5	Berkowitz & Chupta (1966)
(**1** + **4**)	40·5	Rau (1974)
$\overline{(\mathbf{1}+\mathbf{4})}$	41·9 ± 1·3	Average value
(**1**)	33·9 ± 3·5	*Via* relation (8)

Derivation of the parameters

We applied the NM procedure to both α- and β-Se_8. The values of r_0 at the energy minimum were determined numerically in three stages. First, we varied r_0 from 2·4–4·9 Å in steps of 0·5 Å. We then refined the crude minimum at about 3·9 Å by varying r_0 from 3·80–4·30 Å in steps of 0·05 Å. Finally we obtained graphically the minima at $r_0 = 4{\cdot}066 \pm 0{\cdot}002$ Å for α-Se_8 and at $r_0 = 4{\cdot}023 \pm 0{\cdot}002$ Å for the β modification. The scaling factors K proved to be 6·031 and 7·129 for α- and β-Se_8 respectively. The resulting parameters A, B, C and the parameter Sl used form sets (I) and (II), respectively, as given in Table 2. The corresponding potential curves are drawn in Fig. 2.

In the six WG procedures we used the basic experimental information from both α- and β-Se_8 [sets (IV)

Table 2. *Derivation of* Se–Se-*potential parameters*

Set (III) is the S–S potential of Nauchitel' & Mirskaya (1972).

Set	Procedure	Compound	A (kcal mol^{-1})	B (kcal mol^{-1})	C (Å)	Sl ($\bar{\sigma}$%) (Å)
(I)	NM	α-Se_8	3550·0	277288	3·345	15 (–)
(II)	NM	β-Se_8	3596·5	299422	3·381	15 (–)
(III)	NM	S_8	2346	235000	3·49	15 (–)
(IV)	WG	$\alpha+\beta$-Se_8	2757·0	82632·0	3·345	6 (2·7)
(V)	WG	$\alpha+\beta$-Se_8	2737·8	91673·9	3·381	6 (2·7)
(VI)	WG	α-Se_8	2747·2	84657·0	3·345	6 (5·2)
(VII)	WG	β-Se_8	2797·9	84558·4	3·345	6 (3·2)
(VIII)	WG	α-Se_8	2723·6	93437·9	3·381	6 (5·3)
(IX)	WG	β-Se_8	2779·3	93985·3	3·381	6 (3·2)

Table 3. *Calculated heats of sublimation* (kcal mol^{-1})

Set	$\Delta H^{\mathrm{subl}}(\alpha\text{-Se}_8)$	$\Delta H^{\mathrm{subl}}(\beta\text{-Se}_8)$
(I)	33·9	36·5
(II)	31·1	33·9
(IV)	34·1	33·3
(V)	34·1	33·3

and (V) of Table 2; curves (IV) and (V) of Fig. 2], from α-Se$_8$ only [sets (VI) and (VIII) of Table 2] or from β-Se$_8$ only [sets (VII) and (IX) of Table 2]. Both values for $C = 13{\cdot}6/r_0$ Å^{-1}, found in the NM procedures, were applied in the WG procedures. The average of the percentage standard deviations of the derived parameters A and B, $\bar{\sigma}$%, is also given in Table 2. The latter values show clearly the improvement obtained when the 22 observational equations of $\alpha + \beta$-Se$_8$ were used [sets (IV) and (V)] instead of the 11 observational equations of either α- or β-Se$_8$ only [sets (VI)–(IX)]. In all calculations a weight of $1000/\Delta H^{\mathrm{subl}}$ (= 29·5) has been assigned to the observational equations of type (5) and a weight of 1 to those of type (6) (Williams, 1967; Govers, 1975). The heats of sublimation of both modifications were calculated by means of the best sets of parameters derived. The results are listed in Table 3.

Discussion of the results and conclusions

Sets (I) and (II), resulting from the NM procedures, are based only on the experimental information from either α- or β-Se$_8$. From Fig. 2 we can see that both sets look very similar to the S–S potential [set (III)] of Nauchitel' & Mirskaya (1972). Both predict a difference between the heats of sublimation of the α and β modifications of about −2·7 kcal mol^{-1}, as is shown in Table 3. This difference is so large that it would probably have also caused an error higher than ±3·2 kcal mol^{-1} in the determination of transition (**4**) by Gattow & Dräger (1966). Moreover, the β modification is predicted to be less unstable than the α phase; this conflicts with the experiments of, *e.g.*, Marsh *et al.* (1953), who found that α-Se$_8$ undergoes a spontaneous transformation to the stable trigonal form at a much lower rate than β-Se$_8$. There is no sharp criterion for preferring the one set to the other. However, when NM-type potentials have to be used, set (I) may be considered to be slightly better than set (II), as it is based on a more accurate structure determination.

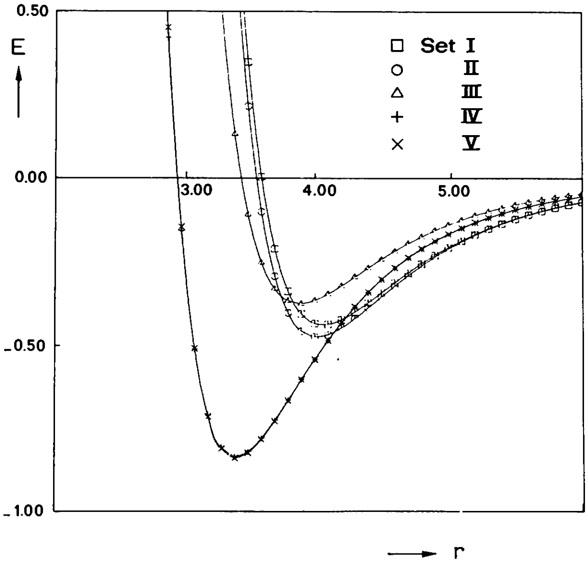

Fig. 2. Se–Se (I,II,IV,V) and S–S (III) potential curves. The roman figures are defined in Table 2 and in the text. Units are kcal mol^{-1} for E, and Å for r. Curves (IV) and (V) coincide almost exactly.

The difficulties mentioned above have been mainly solved in sets (IV) and (V), resulting from WG procedures. These sets are based on the simultaneous use of the experimental information from α- and β-Se$_8$. The parameters A and B derived in this way have the low average standard deviation of 2·7%, as can be read from Table 2. Both these sets predict heats of sublimation which are much closer to the experimental heat of sublimation of the monoclinic selenium mixture (*cf.* Tables 1 and 3) than those predicted by sets (I) and (II). A difference between the heats of sublimation of α- and β-Se$_8$ of +0·8 kcal mol^{-1} is predicted, which seems to be much more realistic in view of the experimental information as mentioned above. As these sets show identical values for the standard deviations of the parameters derived and as they predict identical heats of sublimation, we could hardly decide which was better. Their general appearance is quite similar (*cf.* Fig. 2). Both show a much deeper potential minimum at a markedly shorter distance than the NM potentials. Again there is a slight preference for set (IV) rather than set (V) as the former is based on the parameter C as obtained in set (I) of the NM procedure.

All sets of parameters derived need further tests; these can be performed only when more experimental information about, *e.g.*, the heats of sublimation and crystal structures becomes available for molecular crystals with a high selenium content.

References

Berkowitz, J. & Chupta, W. A. (1966). *J. Chem. Phys.* **45**, 4289–4302.

Cherin, P. & Unger, P. (1972). *Acta Cryst.* B**28**, 313–317.

Engler, E. M., Scott, B. A., Etemad, S., Penney, T. & Patel, V. V. (1977). *J. Am. Chem. Soc.* **99**, 5909–5916.

Gattow, G. & Dräger, M. (1966). *Z. Anorg. Allg. Chem.* **343**, 55–57.

Govers, H. A. J. (1974). *Calculation of Lattice Energies of Unitary and Binary Molecular Crystals.* Thesis, Rijksuniversiteit Utrecht, p. 15.

GOVERS, H. A. J. (1975). *Acta Cryst.* A**31**, 380–385.
GOVERS, H. A. J. (1978*a*). *Acta Cryst.* A**34**, 960–965.
GOVERS, H. A. J. (1978*b*). Conference on Quasi One-Dimensional Conductors, Dubrovnik. To be published.
GRØNVOLD, F. (1973). *J. Chem. Thermodyn.* **5**, 525–531.
KITAIGORODSKII, A. I. (1973). *Molecular Crystals and Molecules.* New York: Academic Press.
MARSH, R. E., PAULING, L. & MCCULLOUGH, J. D. (1953). *Acta Cryst.* **6**, 71–75.
MESMEYANOV, A. N. (1963). *Vapor Pressure of The Chemical Elements*, pp. 324–327. Amsterdam: Elsevier.
MIRSKAYA, K. V. & NAUCHITEL', V. V. (1972). *Sov. Phys. Crystallog.* **17**, 56–59.
NAUCHITEL', V. V. & MIRSKAYA, K. V. (1972). *Sov. Phys. Crystallogr.* **16**, 891–892.
RAU, H. (1974). *J. Chem. Thermodyn.* **6**, 525–535.
WILLIAMS, D. E. (1967). *J. Chem. Phys.* **47**, 4680–4684.
WILLIAMS, D. E. (1974). *Acta Cryst.* A**30**, 71–77.

Acta Cryst. (1979). A**35**, 240–243

Third-Order Elastic Constants of Cubic Sodium Cyanide and Potassium Cyanide

BY S. HAUSSÜHL AND W. MICHAELIS

Institut für Kristallographie der Universität zu Köln, Zülpicher Strasse 49, 5000 *Köln* 1, *Federal Republic of Germany*

(*Received* 16 *March* 1978; *accepted* 13 *September* 1978)

Abstract

The complete third-order elasticity tensors of cubic NaCN and KCN have been determined from stress-shifted resonance frequencies of thick plates at 293 K. The two cyanides exhibit quite similar nonlinear elastic properties which, however, differ strongly from those of comparable alkali halides such as NaCl and KCl. The 'longitudinal' constants c_{111} are *ca* five times smaller and the 'transverse' constants c_{112} and c_{123} *ca* eight times larger than those in NaCl and KCl. The Cauchy relations are strongly violated, as is already known for the second-order elastic constants. The critical shear resistance c_{44}, which is connected with the phase transitions observed at 283 K (NaCN) and 168 K (KCN), exhibits a considerable dependence on hydrostatic pressure only in the case of NaCN: c_{44} drops rapidly with increasing pressure. The absolute change of c_{44} per hydrostatic pressure unit, however, is comparable to that in alkali halides. The nonlinear elastic behaviour of NaCN and KCN is qualitatively interpreted by interactions of volume-conserving type (as existing in fluids).

Introduction

In continuation of earlier investigations on elastic and thermoelastic properties of alkali cyanides (Haussühl, 1957, 1973; Haussühl, Eckstein, Recker & Wallrafen, 1977) we have now determined the third-order elastic constants (TOEC) of cubic NaCN and KCN. These constants are strongly related to other anharmonic properties, such as thermal expansion, thermoelastic constants, and thermal conductivity. The knowledge of TOEC may provide further critical data for testing the models which have been developed recently to interpret the extremely anomalous thermoelastic properties originating from thermally activated rotational movements of the cyanide ions (Michel & Naudts, 1977).

Furthermore, we expected to obtain additional data for the discussion of the influence of asymmetric ions on nonlinear elastic properties, in particular for crystals of rock salt type.

The experimental method employed has been described in detail in a previous paper (Haussühl & Preu, 1978), where stress-induced shifts of resonance frequencies f of thick plates in the range between 14 and 28 MHz are used for the evaluation of TOEC. The states of resonance are detected by diffraction of monochromatic light by the grating of ultrasonic waves which attain maximum amplitudes at the resonance frequencies. For the generation of longitudinal and transverse waves we used *X*-cut and *Y*-cut quartz plates respectively. This method has been proved to be well suited to nonlinear acoustic studies owing to its high accuracy and its simple handling. The basic equations which combine TOEC and observed derivatives $d[\ln(f)]/dP$ have been elaborated by Thurston & Brugger (1964), Brugger (1965*a*,*b*), and Wallace (1970). P is the appropriate quantity of uniaxial or hydrostatic mechanical stress.

Experimental

Single crystals of NaCN of optical quality, grown by the Czochralski method (Haussühl, Eckstein, Recker & Wallrafen, 1977), were provided by K. Recker and his group. Crystals of KCN were grown from aqueous

0567-7394/79/010240-04$01.00 © 1979 International Union of Crystallography