

## Internal Strain of GaAs. I. Longitudinal Case

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(Received 20 September 1974; accepted 23 September 1974)

The theory of the internal strain, which has been verified experimentally for crystals with the diamond structure, is extended here to the zincblende structure. X-ray intensity measurements were taken on GaAs under a uniaxial stress along the [111] direction. It was found that this stress causes a slight change of the structure factor of the weak reflexion 006, from which the value  $\zeta = 0.046 \pm 0.002$  for the bond-bending constant was estimated. This means that in GaAs the effect of the internal strain is very weak, so that the tetrahedral bond changes its length almost according to the macroscopic strain tensor.

### Introduction

Macroscopically, the strain tensor is related to the stress tensor through the elastic compliance matrix  $s_{ij}$ . However, in some crystals, the strain within the unit cell does not coincide with the macroscopic strain (Born & Huang, 1954). When a crystal with tetrahedral bonds between its atoms is compressed along one of these bonds, the strain  $\varepsilon'$  of this bond is not equal to the macroscopic strain  $\varepsilon$  but:

$$\varepsilon' = \varepsilon - \varepsilon\zeta \quad (\varepsilon < 0)$$

where  $\zeta$  is the so-called bond-bending constant (Kleinman, 1962, 1963). If  $\zeta = 0$ , no internal strain occurs, and the bond changes its length  $b$  according to the strain tensor. If  $\zeta = 1$ , complete internal strain occurs and the bond keeps its length unchanged under stress; the strain  $\varepsilon$  is then due to the change of the angles.

In the present case the internal strain vector  $\varepsilon\zeta\mathbf{b}$  is antiparallel to the macroscopic strain vector  $\varepsilon\mathbf{b}$ , so that the case can be described as longitudinal. Uniaxial stress not parallel to the bond direction may produce internal strain with components transverse to the bond direction.

The theory has been verified experimentally for the diamond-structure crystals Si and Ge (Segmüller, 1963, 1964; Segmüller & Neyer, 1965). On the other hand, measurements on an InSb single crystal showed that in this material no internal strain exists, at least within the limit of the errors (Koumelis, 1965).

### Calculations

#### (a) Correlation between the bond-bending constant and the force constants.

Projecting the tetrahedral bond on the  $(1\bar{1}0)$  plane (Fig. 1), and assuming the existence of springs  $D_1$  and  $D_2$  between the (111) planes (Segmüller, 1964), a stress in the [111] direction leads to different strains  $\varepsilon'$ ,  $\varepsilon$  and  $\varepsilon\Psi$  for the lengths  $b$ ,  $X$ ,  $\Psi$ :

$$\varepsilon'b = \frac{F}{D_1} \quad \varepsilon X = \frac{F}{D_2} \quad \varepsilon\Psi = \varepsilon'b + \varepsilon X.$$

As  $b = 3X$ , these equations give:

$$\zeta = \frac{D_1 + \frac{1}{3}D_2}{D_1 + D_2} \quad (1)$$

If  $\alpha$  and  $\beta$  are the force constants (Begbie & Born, 1947; Begbie, 1947) between the nearest neighbours, and if the force  $F_{[111]}$  causes a displacement  $R_{[111]}$  of the nearest neighbours along the [111] direction, we will have (Smith, 1948; Herman, 1959):

$$\begin{pmatrix} F_{[111]x} \\ F_{[111]y} \\ F_{[111]z} \end{pmatrix} = \begin{pmatrix} \alpha & \beta & \beta \\ \beta & \alpha & \beta \\ \beta & \beta & \alpha \end{pmatrix} \cdot \begin{pmatrix} R_{[111]x} \\ R_{[111]y} \\ R_{[111]z} \end{pmatrix}.$$

Owing to the symmetry, the components of the force are all equal as are the components of the displacement. This system gives then:

$$F_{[111]} = (\alpha + 2\beta) \cdot R_{[111]}$$

and hence:

$$D_1 = \alpha + 2\beta.$$

On the atom  $B$  of Fig. 1 forces are further applied along the other bonds. For the force along the  $[1\bar{1}\bar{1}]$  direction

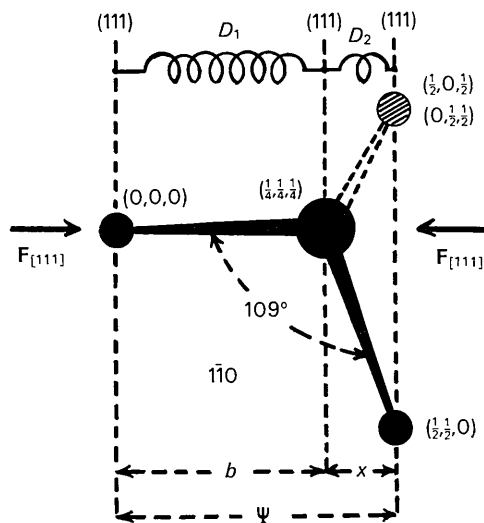


Fig. 1. Mechanical model for the tetrahedral bond.

we can resolve the displacement  $R_{[1\bar{1}\bar{1}]}$  into two components, parallel to the  $[111]$  direction and perpendicular to it, *i.e.* in the  $[2\bar{1}\bar{1}]$  direction. Then we will have (Herman, 1959):

$$\begin{pmatrix} F_{[1\bar{1}\bar{1}]_x} \\ F_{[1\bar{1}\bar{1}]_y} \\ F_{[1\bar{1}\bar{1}]_z} \end{pmatrix} = \begin{pmatrix} \alpha & -\beta & -\beta \\ -\beta & \alpha & \beta \\ -\beta & \beta & \alpha \end{pmatrix} \cdot \begin{pmatrix} R_{[1\bar{1}\bar{1}]_{x\parallel}} + R_{[1\bar{1}\bar{1}]_{x\perp}} \\ R_{[1\bar{1}\bar{1}]_{y\parallel}} + R_{[1\bar{1}\bar{1}]_{y\perp}} \\ R_{[1\bar{1}\bar{1}]_{z\parallel}} + R_{[1\bar{1}\bar{1}]_{z\perp}} \end{pmatrix}.$$

For the forces along  $[\bar{1}\bar{1}\bar{1}]$  and  $[\bar{1}\bar{1}\bar{1}]$  directions, similar equations can be written. Putting in the values of the direction cosines involved, and taking into account

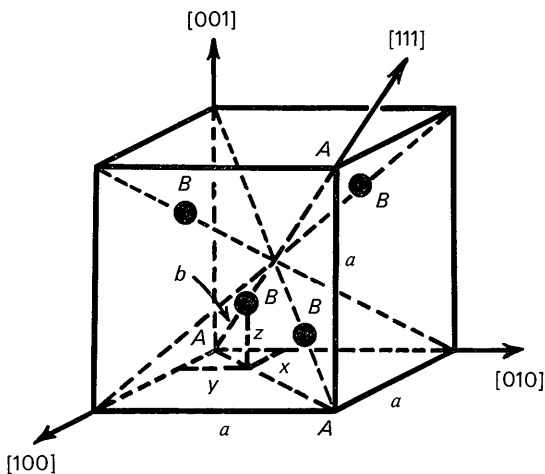


Fig. 2. The unstrained cell of GaAs. The A atoms are not shown.

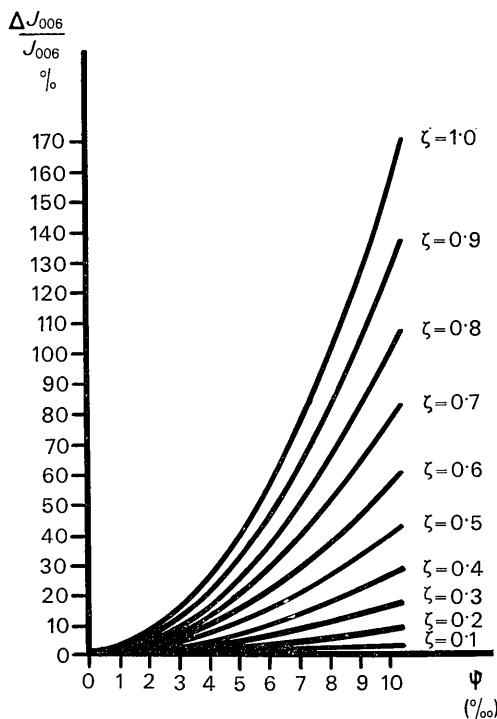


Fig. 3. Theoretical curves for the ratio  $\Delta J_{006}/J_{006}$  of GaAs versus  $\epsilon$ .

that the resultant of the components  $F_{\perp}$  is zero, we obtain from these equations

$$F_{\text{tot}\parallel} = \frac{9\alpha^2 + 9\alpha\beta - 18\beta^2}{3\alpha + 5\beta} R_{\text{tot}\parallel} = D_2 \cdot R_{\text{tot}\parallel}.$$

Substitution of expression (1) for  $D_1$  and  $D_2$  gives:

$$\zeta = \frac{2\beta}{3\alpha - \beta}. \quad (2)$$

If  $\beta=0$ , then  $\zeta=0$ . If  $\alpha=\beta$ , then  $\zeta=1$ .

For Ge and Si, the following values of  $\alpha$  and  $\beta$  have been published:

$$\begin{aligned} \alpha_{\text{Ge}} &= 3.71 \cdot 10^4 \text{ dyne cm}^{-1} \\ \beta_{\text{Ge}} &= 3.40 \cdot 10^4 \text{ dyne cm}^{-1} \text{ (Herman, 1959)} \\ \alpha_{\text{Si}} &= 5.35 \cdot 10^4 \text{ dyne cm}^{-1} \\ \beta_{\text{Si}} &= 3.83 \cdot 10^4 \text{ dyne cm}^{-1}, \text{ (Corbeau, 1964)} \end{aligned}$$

giving for the bond-bending constants:

$$\begin{aligned} \zeta_{\text{Ge}} &= 0.88 \\ \zeta_{\text{Si}} &= 0.63. \end{aligned}$$

These values are in good agreement with the experimental results (Segmüller, 1963, 1964, 1965). We notice that in Ge and Si the internal strain is very strong.

(b) Influence of the internal strain on the structure factor

The length  $b$  of the tetrahedral bond changes under the stress  $\tau$  along the  $[111]$  direction (Fig. 2) to:

$$b' = b(1 + \epsilon - \epsilon\zeta).$$

From the strained triangle  $AAA$  we obtain:

$$\frac{z'}{a} = \frac{b'}{d'} \quad \text{or} \quad \frac{z'}{a} = \frac{1}{4} - \frac{\epsilon\zeta}{4(1 + \epsilon)}.$$

Hence, the relative coordinates  $x/a$ ,  $y/a$ ,  $z/a$  of the point  $B$  are changed by the amount:

$$u = -\frac{\epsilon\zeta}{4(1 + \epsilon)}. \quad (3)$$

If  $\zeta=0$ , the relative coordinates of the point  $B$  remain unchanged under the stress  $\tau$ .

If the stress  $\tau$  changes the structure factor  $F_{hkl}$ , the ratio of the integrated intensities of the  $hkl$  reflexion without and under stress will be:

$$\frac{J_{hkl}^*}{J_{hkl}} = \frac{F_{hkl}^* \cdot F_{hkl}^{**}}{F_{hkl} \cdot F_{hkl}^*}. \quad (4)$$

In the unstrained zincblende cell, the two kinds of atoms  $A$  and  $B$  are in the positions:

$$\begin{aligned} A: & \begin{matrix} \text{-----} & Q_{j\kappa} & \text{-----} \\ 000 & 0\frac{1}{2}\frac{1}{2} & \frac{1}{2}0\frac{1}{2} & \frac{1}{2}\frac{1}{2}0 & j=1,2,3,4 \end{matrix} \\ B: & \begin{matrix} \text{-----} & r_{j\kappa} & \text{-----} \\ \frac{1}{4}\frac{1}{4}\frac{1}{4} & \frac{1}{4}\frac{3}{4}\frac{3}{4} & \frac{3}{4}\frac{1}{4}\frac{3}{4} & \frac{3}{4}\frac{3}{4}\frac{1}{4} & \kappa=1,2,3. \end{matrix} \end{aligned}$$

The structure factor is given by:

$$F_{hkl} = f_A \cdot \sum_1^j \prod_1^{\kappa} \exp(2\pi i Q_{j\kappa} H_{\kappa}) + f_B \cdot \sum_1^j \prod_1^{\kappa} \exp(2\pi i r_{j\kappa} H_{\kappa}) \quad (5)$$

where  $\Pi$  represents a product and  $H_\kappa = h, k, l$  for  $\kappa = 1, 2, 3$ . The coordinates  $q_{j\kappa}$  and  $r_{j\kappa}$  give in (5) for a weak reflexion:

$$F_{hkl} \cdot F_{hkl}^* = 16(f_A - f_B)^2.$$

For a cell under a stress along the [111] direction, the relative coordinates of the atoms  $A$  remain unchanged while the relative coordinates of the atoms  $B$  become:

$$r_{j\kappa}^u = r_{j\kappa} + u.$$

Substituting the new coordinates  $q_{j\kappa}$  and  $r_{j\kappa}^u$  in (5) we obtain for a weak reflexion:

$$F_{hkl}^u \cdot F_{hkl}^{u*} = 16 \cdot \{f_A^2 + f_B^2 - 2f_A f_B \cdot \cos [2\pi u(h+k+l)]\}.$$

As  $\varepsilon = s_{44}\tau/3$  (Segmüller, 1964), we have according to (3) and (4):

$$\frac{\Delta J_{hkl}}{J_{hkl}} = \frac{J_{hkl}^u - J_{hkl}}{J_{hkl}} = \frac{4f_A f_B}{(f_A - f_B)^2} \times \sin^2 \left[ \frac{1}{4}\pi \zeta (h+k+l) \cdot \frac{s_{44}\tau}{3 + s_{44}\tau} \right].$$

The determination of the ratio  $\Delta J/J$  is possible only for sufficiently large values of  $4f_A f_B / (f_A - f_B)^2$ ,  $\zeta$ ,  $s_{44}$ , and  $\tau$ . The maximum value of the stress that can be applied depends on the resistance of the crystal to fracture.

Table 1 gives information for various zincblende crystals. It is evident that only GaAs and InSb give the possibility for a successful experiment.

Fig. 3 is a plot of the calculated ratio  $\Delta J_{006}/J_{006}$  for GaAs for the weak reflexion 006 and for various values of  $\zeta$ , versus  $\varepsilon$ . These curves show that the method is very difficult if not impossible when  $\varepsilon_{\max}$  or  $\zeta$  is small. In InSb,  $\varepsilon_{\max}$  was found to be small ( $1.9\%$ ) (Koumelis, 1965), not allowing therefore the determination of  $\zeta$ . On the contrary, the method is promising for large enough values of  $\varepsilon_{\max}$  and  $\zeta$ . As there is no information on  $\zeta$  of GaAs, the attempt at such an experiment seems reasonable.

### Experimental details – results

The GaAs crystal in the form of a small  $5 \times 5 \times 5$  mm cube was cut to the proper orientation, by an impregnated diamond disc, from a larger piece obtained from M. C. P. Electronics Ltd. England. Before use, the (111) surfaces were polished.

The crystal  $C$  (Fig. 4) was placed in the window of a mechanical steel press specially constructed to allow compression along the [111] direction. The pliers-like

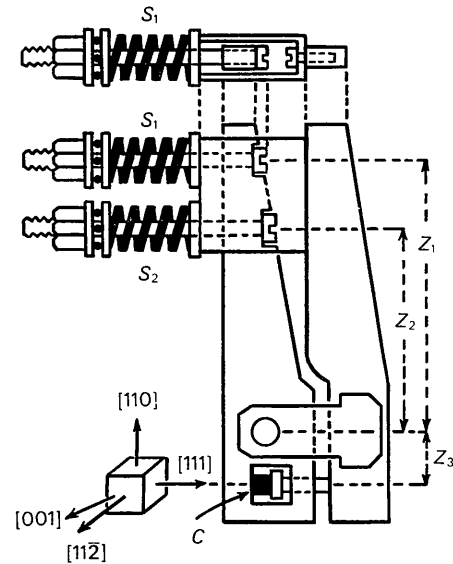


Fig. 4. The mechanical press and the orientation of the crystal fragment.

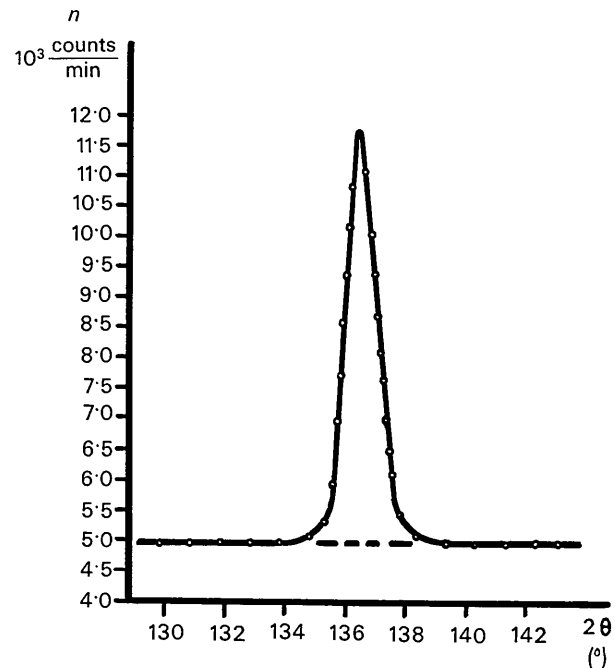


Fig. 5. The 006 line taken with Fe  $K\beta$  radiation. The statistical error is too small to be shown.

Table 1. Data for zincblende crystals

Material	$4f_A f_B / (f_A - f_B)^2$	$s_{44}$	Author
	For $\sin \theta / \lambda = 0$	$10^{-12} \text{ cm}^2 \text{ dyne}^{-1}$	
GaAs	1023.00	18.6	Huntington (1958)
InSb	2499.00	3.31	Huntington (1958)
InAs	25.27	2.532	Reifenberger, Keck & Trivissimo (1969)
GaSb	15.81	2.31	Huntington (1958)
GaP	7.27	1.419	Weil & Growes (1968)

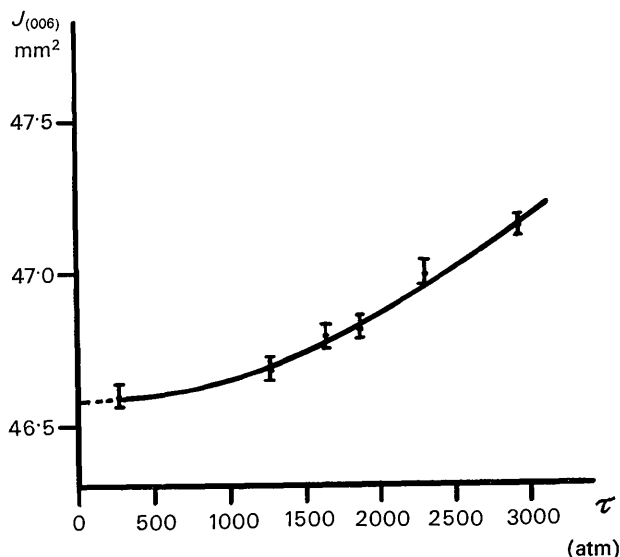


Fig. 6. The integrated intensity of the 006 line *versus*  $\tau$ .

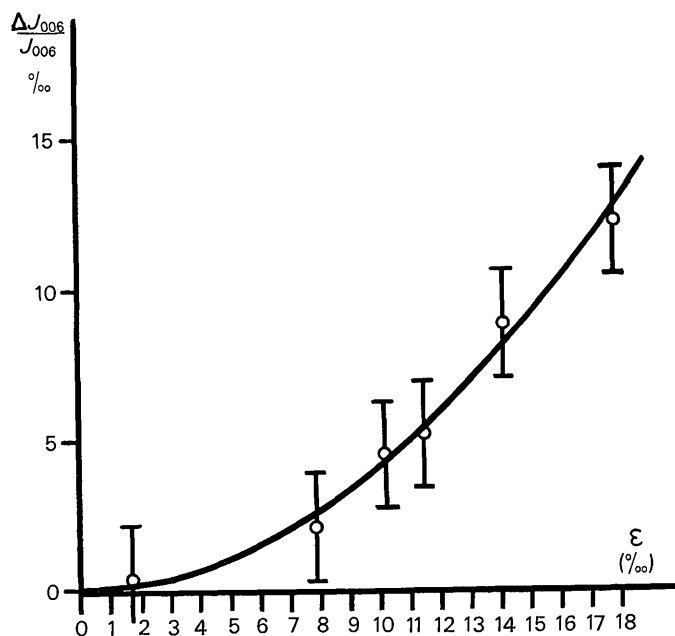


Fig. 7. The ratio  $\Delta J_{006}/J_{006}$  *versus*  $\epsilon$ .

press worked by the springs  $S_1, S_2$ . The pressure on the crystal was estimated from the lengths of the springs, the distances  $Z_1, Z_2, Z_3$ , and the area of the compressed surface of the crystal.

A modified Norelco Philips diffractometer was used for the measurements. As the standard goniostats were too weak to carry the weight of the press (2 kg), a strong brass goniostat providing the proper orientation was constructed.

Segmüller (1964) has pointed out that internal strain can be observed for the diamond structure only by using a forbidden reflexion; so in the present experiment the weak reflexion 006 was chosen.

Fig. 5 shows the 006 line taken with Fe  $K\beta$  radiation. Because of the high background, an automatic scan would not provide sufficient statistical accuracy, so that the  $(\theta, 2\theta)$  scan was made point by point. The statistical error for each point was 0.5% in the background, and 0.3% in the peak.

The values of  $J_{006}$  shown in Fig. 6 are the areas above the background line. The stress was increased step by step until the crystal fractured. The first measurements were taken at  $\tau = 270$  atm to fasten the crystal on the press. The integrated intensity corresponding to  $\tau = 0$  was found by extrapolation. The reproducibility was checked by repeating the measurement at  $\tau = 270$  atm after each step.

Table 2 gives the experimental results. Around  $\tau = 3025$  atm the crystal broke into pieces. Until fracture, the strain was found to be elastic.

Fig. 7 shows the ratio  $\Delta J_{006}/J_{006}$  *versus*  $\epsilon$ . The curve is in good agreement with the theoretical curve for  $\zeta = 0.045$ . The error  $\delta\zeta/\zeta$  is large for small values of  $\Delta J_{006}/J_{006}$  but small for large values of it. The most probable value of  $\zeta$  is that corresponding to  $\tau = 2930$  atm ( $\epsilon = 17.8\%$ ). Considering all the values of  $\zeta$  with their weights according to their errors, we obtain the mean value:

$$\zeta = 0.046 \pm 0.002 \quad \delta\zeta/\zeta = 4.3\%$$

Substituting in (2), we obtain for the ratio  $\alpha/\beta$ :

$$\frac{\alpha}{\beta} = 14.8 \pm 0.6 \quad \delta(\alpha/\beta)/\alpha/\beta = 4\%$$

The small value for the bond-bending constant indicates that the internal strain in GaAs is very weak, so that the tetrahedral bond changes its length almost according to the strain tensor.

Table 2. *Results*

$\tau$ at	$\epsilon$ %	$J$ mm <sup>2</sup>	$\delta J$ mm <sup>2</sup>	$\Delta J$ mm <sup>2</sup>	$\Delta J/J$ $\times 10^{-3}$	$\delta(\Delta J/J)$ $\times 10^{-3}$	$\zeta$	$\delta\zeta$	$\delta\zeta/\zeta$ %
270	1.7	4660	6	2	0.4	1.8	0.093	0.190	204
1280	7.8	4668	7	10	2.1	2.0	0.044	0.020	45
1660	10.1	4679	7	21	4.5	2.0	0.049	0.010	20
1880	11.4	4682	6	24	5.2	1.8	0.046	0.008	17
2320	14.1	4699	6	41	8.8	1.8	0.049	0.005	10
2930	17.8	4715	6	57	12.2	1.8	0.045	0.003	7

The authors thank Professor K. Alexopoulos and Dr S. Mourikis for helpful discussions.

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*Acta Cryst.* (1975). **A31**, 88

## Automorphismengruppen von Raumgruppen und die Zuordnung von Punktlagen zu Konfigurationslagen

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(Eingegangen am 25. April 1974; angenommen am 3. September 1974)

For all space groups the groups of inner automorphisms are given. They are isomorphic with groups of motions, but fall into four sets according to their dimension. In the triclinic and monoclinic systems, however, the corresponding groups of all automorphisms cannot be represented by groups of motions. These groups of automorphisms therefore are only tabulated for the other cases. The relation between groups of automorphisms and Cheshire groups is discussed. By means of automorphisms sets of equivalent points are combined to 'Konfigurationslagen'. For these complete tables are included.

### Einleitung

Die Automorphismen der Raumgruppen wurden von Fischer & Koch (1974) zur Definition des Begriffs Gitterkomplex verwendet. Insbesondere wurde vorgeschlagen, Punktlagen mit Hilfe von äusseren Automorphismen zu Konfigurationslagen zusammenzufassen. In diesem Zusammenhang erschien es jedoch nicht angebracht, alle Konfigurationslagen aufzuzählen, ohne dabei die Automorphismengruppen der Raumgruppen näher zu beschreiben. Beides soll an dieser Stelle nachgeholt werden. Ausserdem soll auf den Zusammenhang mit dem von Hirshfeld (1968) eingeführten Begriff Cheshire-Symmetrie und auf die Vertauschbarkeit von Punktlagen nach Boyle & Lawrenson (1973) eingegangen werden.

Dabei werden in Übereinstimmung mit dem üblichen Sprachgebrauch folgende Begriffe zugrunde gelegt: Eine umkehrbar eindeutige Abbildung  $\sigma$  einer Gruppe  $G$  auf sich selbst heisst ein *Automorphismus*, wenn dabei alle Gruppenrelationen erhalten bleiben. Ist  $a \in G$  ein beliebiges festes Gruppenelement, so stellt die Abbildung  $\sigma_a: g \rightarrow aga^{-1}$  für alle Elemente  $g \in G$  einen Automorphismus der Gruppe dar. Jeder derartige Automorphismus wird *innerer Automorphismus* genannt, alle übrigen heissen *äussere Automorphismen*. Die Men-

ge aller Automorphismen von  $G$  ist eine Gruppe, die *Automorphismengruppe*  $A$  von  $G$ . Die inneren Automorphismen für sich bilden eine Untergruppe von  $A$ , und zwar einen Normalteiler.

### Innere Automorphismen von Raumgruppen

Definitionsgemäss gibt jedes Element  $a$  einer Gruppe  $G$  Anlass zu einem inneren Automorphismus  $\sigma_a$  von  $G$ . Ist die Gruppe  $G$  speziell eine Raumgruppe,\* so ist  $a$  eine Bewegung des dreidimensionalen Raumes  $R^3$ . In diesem Fall erhebt sich die Frage nach dem Zusammenhang zwischen dieser Abbildung  $a$  des  $R^3$  auf sich und der damit verknüpften Abbildung  $\sigma_a$  der Symmetrioperationen von  $G$  auf sich.

$g$  und  $h$  seien zwei Symmetrioperationen von  $G$ , die durch den inneren Automorphismus  $\sigma_a$  aufeinander abgebildet werden, sodass gilt:  $\sigma_a(g) = h = aga^{-1}$ , d.h.  $ha = ag$ . Die Symmetrioperation  $g$  führt jeden Punkt  $x \in R^3$  in den Punkt  $g(x)$ , die Symmetrioperation  $h$

\* Im folgenden wird unter Raumgruppe immer ein Exemplar aus einer der 219 Raumgruppenklassen verstanden (vgl. Fischer & Koch, 1974). Wegen der Isomorphiebeziehungen zwischen allen Raumgruppen einer Klasse genügt es in diesem Zusammenhang, jeweils eine Raumgruppe als Vertreter der Klasse zu betrachten.