with the observed heat of fusion of lead, 1·3 kcal.mole^{-1}. Some free-energy curves calculated in this way are given in Fig. 9, and the corresponding phase diagram is represented in Fig. 10. The discrepancy in the lead-rich region between the theoretical liquidus and solidus curves and the experimental ones is probably due to the fact that the occupancy of the position 0, 0, 0 by lead atoms alone could not be retained at very small percentages of thallium; the dilute alloys may well have a random or nearly random replacement of lead atoms by thallium atoms in all positions.

There seem to be many binary metallic systems in which there are phases of this sort. In the sodium–lead system there are two such phases. One of them, based on the ideal structure Na_3Pb, extends from 27 to 30 atomic percent lead, with its maximum at about 28 atomic percent lead; and the other, corresponding to the ideal composition $NaPb_3$, extends from 68 to 72 atomic percent lead, with maximum at about 70 atomic percent. The intensities of X-ray reflection have verified that in the second of these phases sodium atoms occupy the positions 0, 0, 0, and the other three positions in the unit cell are occupied by lead atoms isomorphously replaced to some extent by sodium atoms (Zintl & Harder, 1931). These two phases are interesting in that the ranges of stability do not include the pure compounds Na_3Pb and $NaPb_3$.

It seems likely that there are many other phases of this sort. Among them is probably the γ phase of the mercury–thallium system, extending from 21 to 32 atomic percent thallium, and with maximum melting-point at 28 atomic percent thallium; this phase, which usually is described as having the ideal composition Hg_5Tl_2, presumably should be described as having the ideal composition Hg_3Tl.

We express our gratitude to Prof. J. H. Sturdivant for his help in this work. The investigation was carried out with the aid of a grant from the Carbide and Carbon Chemicals Corporation.

References

GUERTLER, W. & SCHULZE, A. (1923). *Z. phys. Chem.* **104**, 269.
HALLA, F. & STAUFER, R. (1928). *Z. Krystallogr.* **67**, 440.
HANSEN, M. (1936). *Der Aufbau der Zweistofflegierungen.* Berlin: Springer.
KURNAKOW, N. S. & PUSHIN, N. A. (1907). *Z. anorg. Chem.* **52**, 430.
KURNAKOW, N. S. & SCHEMTSCHUSHNY, S. F. (1909). *Z. anorg. Chem.* **64**, 149.
LEWKONJA, K. (1907). *Z. anorg. Chem.* **52**, 452.
MCMILLAN, E. & PAULING, L. (1927). *J. Amer. Chem. Soc.* **49**, 666.
NELSON, H. R. & RILEY, D. P. (1945). *Proc. Phys. Soc.* **57**, 160.
ÖLANDER, A. (1934). *Z. phys. Chem.* (A), **168**, 274.
PAULING, L. (1949). *Proc. Roy. Soc.* A, **196**, 343.
TANG, Y.-C. (1951). *Acta Cryst.* **4**, 377.
ZINTL, E. & HARDER, A. (1931). *Z. phys. Chem.* (A), **154**, 47.

Acta Cryst. (1952). **5**, 44

Physical Properties of Crystals: The Direct-Inspection Method

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(*Received* 26 *December* 1950 *and in revised form* 22 *May* 1951)

The independent non-zero components of physical properties of crystals can be obtained by *direct inspection* in all crystal classes in which one can find Cartesian orthogonal co-ordinates that do not transform into linear combinations of themselves under the symmetry operations, i.e. in the groups S_2–$\bar{1}$; C_{1h}–m, C_2–2, C_{2h}–$2/m$; C_{2v}–$2mm$, D_2–222, D_{2h}–mmm; C_4–4, S_4–$\bar{4}$, C_{4h}–$4/m$, C_{4v}–$4mm$, D_{2d}–$\bar{4}2m$, D_4–42, D_{4h}–$4/mmm$; C_3–3, S_6–$\bar{3}$, C_{3v}–$3m$; T–23, T_h–$m3$, T_d–$\bar{4}3m$, O–432, O_h–$m3m$.

The method is applied to a general third-order tensor (polar or axial) in C_3, S_6, C_{3v}, T_d, O, O_h; to a fourth-order polar tensor t_{rs} (r, $s=1, 2, 3, 4, 5, 6$) in C_4, S_4, C_{4h}, C_3, S_6, T, T_h (correcting the erroneous results of Pockels on photoelastic constants); and to a sixth-order polar tensor $t_{ikl}=t_{ilk}$ (i, k, $l=1, 2, 3, 4, 5, 6$) in monoclinic and orthorhombic groups and in C_{4v}, D_{2d}, D_4, D_{4h}.

1

Some of the components of tensor properties of matter are zero in crystalline bodies and some are equal between themselves owing to the symmetry of the system. This reduction is additional to the reduction of components of a general tensor of a given order,

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already intrinsic in the definition of a particular physical property.

Methods for determining the independent non-zero components of tensor properties in crystals are given in various text-books (Pockels, 1906; Love, 1906; Voigt, 1910; Mathieu, 1945; Cady, 1946; Wooster, 1949; Mason, 1950); they are lengthy and algebraically involved. Hermann (1934) has simplified the equations that one obtains imposing invariance on each component by using the principal axes of the symmetry operations, generally complex. Jahn (1949) and Bhagavantam & Suryanarayana (1949) have treated the problem by group theory; however, their methods do not enumerate the independent non-zero components and represent only a way of checking their numbers. The main successes achieved by Bhagavantam (1942; see also Bhagavantam & Suryanarayana, 1947) with his method consisted in detecting errors in the number of photoelastic constants attributed by Pockels (1906) to many crystal classes, and in the number of third-order elastic coefficients attributed by Birch (1947) to T_d–$\bar{4}3m$. His results were confirmed by Jahn (1949).

Here we shall show that the components of tensor properties can be listed by *direct inspection* in 23 crystal classes: the method eliminates any algebraic calculation, and so the possibility of errors.

2

The tensor properties of crystals can be classified according to their transformation behaviour under proper and improper rotations of the Cartesian orthogonal frames; in such reference frames the covariant and controvariant representations coincide. Inspection of the tensor transformation equations (Wooster, 1949, chap. 1, § 1) shows that the components of a tensor transform under proper rotations as do products of co-ordinates; the order of the products coincides with the order of the tensor, and the particular product of interest for a certain component coincides with the index of the component (e.g. the component t_{xyzz} of a fourth-order tensor transforms as does xyz^2). There are tensor properties (polar) whose sign is determined by the standard sense along directions in space; for others (axial) the sign is determined by the standard sense of rotation around directions in space. Thus the components of polar properties transform as do products of co-ordinates also under improper rotations; the transformation equations for components of axial properties under improper rotations, however, differ from those for products of co-ordinates by a factor -1.

The components of tensor properties of crystals must be invariant under the symmetry of the crystal, i.e. under the generating elements of its symmetry group. Therefore all the components of polar properties whose index changes sign under a proper or improper symmetry operation, and all the components of axial properties whose index changes sign under proper symmetry operations, or remains invariant under improper ones, vanish; all components of polar properties of odd order and all components of axial properties of even order vanish identically in centrosymmetrical crystals, while the components of polar properties of even order and of axial properties of odd order are centrosymmetrical by nature. The components of polar and axial properties whose indices transform into one another under symmetry operations are equal and not independent; the sign relation is the same one for the indices for polar properties and for axial properties under proper symmetry operations, the opposite one for axial properties under improper symmetry operations.

Clearly the independent non-zero components of physical properties of crystals can be obtained by *direct inspection* for all classes in which one can find orthogonal Cartesian co-ordinates that do not transform into linear combinations of themselves under the symmetry operations of the crystal, i.e. for the groups S_2–$\bar{1}$; C_{1h}–m, C_2–2, C_{2h}–$2/m$; C_{2v}–$2mm$, D_2–222, D_{2h}–mmm; C_4–4, S_4–$\bar{4}$, C_{4h}–$4/m$, C_{4v}–$4mm$, D_{2d}–$\bar{4}2m$, D_4–42, D_{4h}–$4/mmm$; C_3–3, S_6–$\bar{3}$, C_{3v}–$3m$; T–23, T_h–$m3$, T_d–$\bar{4}3m$, O–432, O_h–$m3m$. The reference frames to be used coincide with those commonly applied for the triclinic, monoclinic, orthorhombic, tetragonal and cubic classes, but not for C_3, S_6 and C_{3v}. The results obtained are directly comparable with those given in the literature, except for the trigonal classes; for these only the number of components is the result immediately useful.

We shall index tensor components with Voigt's (1910) convention starting with the digit referring to the first member of the defining equation. Wooster (1949) uses the opposite convention; one must keep this in mind in comparing results.

3. Applications

(*a*) *Third-order tensor* t_{ikl} $(i, k, l=1, 2, 3)$

$$\left.\begin{matrix} t_{xxx} & t_{xyy} & t_{xzz} & t_{xyz} & t_{xzy} & t_{xzx} & t_{xxz} & t_{xxy} & t_{xyx} \\ t_{yxx} & t_{yyy} & t_{yzz} & t_{yyz} & t_{yzy} & t_{yzx} & t_{yxz} & t_{yxy} & t_{yyx} \\ t_{zxx} & t_{zyy} & t_{zzz} & t_{zyz} & t_{zzy} & t_{zzx} & t_{zxz} & t_{zxy} & t_{zyx} \end{matrix}\right\}. \qquad (1)$$

Symmetry C_3:

$$C_3 \qquad x \rightarrow y, \quad y \rightarrow z, \quad z \rightarrow x. \qquad (2)$$

There is no difference between a polar and an axial tensor since there are no improper rotations. The independent components are nine:

$$\left.\begin{matrix} t_{xxx}=t_{yyy}=t_{zzz} & t_{xyy}=t_{yzz}=t_{zxx} & t_{xzz}=t_{yxx}=t_{zyy} \\ t_{xyz}=t_{yzx}=t_{zxy} & t_{xzy}=t_{yxz}=t_{zyx} & t_{xzx}=t_{yxy}=t_{zyz} \\ t_{xxz}=t_{yyx}=t_{zzy} & t_{xxy}=t_{yyz}=t_{zzx} & t_{xyx}=t_{yzy}=t_{zxz} \end{matrix}\right\}. \qquad (3)$$

The addition of a center of symmetry

$$i \qquad x \rightarrow -x, \quad y \rightarrow -y, \quad z \rightarrow -z \qquad (4)$$

leads to S_6, introducing a substantial difference between a polar and an axial third-order tensor; for the first, all the components vanish; for the second, they satisfy the same relations (3).

Symmetry C_{3v}:

$$C_3 \qquad x\to y, \quad y\to z, \quad z\to x, \tag{2}$$

$$\sigma_v \qquad x\to x, \quad y\to z, \quad z\to y. \tag{5}$$

For a polar third-order tensor four additional relations hold among the nine components (3):

$$t_{xyy}=t_{xzz} \quad t_{xyz}=t_{xzy} \quad t_{xzx}=t_{xyx} \quad t_{xxz}=t_{xxy}, \tag{6}$$

so that one has five independent components. For an axial third-order tensor there are five additional relations among the nine components (3):

$$\begin{gathered} t_{yyy}=-t_{zzz} \quad t_{xyy}=-t_{xzz} \quad t_{xyz}=-t_{xzy} \\ t_{xzx}=-t_{xyx} \quad t_{xxz}=-t_{xxy}. \end{gathered} \tag{7}$$

The first of these requires

$$t_{xxx}=t_{yyy}=t_{zzz}=0. \tag{7'}$$

The number of independent non-zero components is four.*

Symmetry T_d:

$$C'_3 \qquad x\to y, \quad y\to z, \quad z\to x, \tag{2}$$

$$C''_3 \qquad -x\to y, \quad y\to z, \quad z\to -x, \tag{8}$$

$$\sigma_d \qquad x\to x, \quad y\to z, \quad z\to y. \tag{5}$$

A polar third-order tensor has only one independent non-zero component:

$$t_{xyz}=t_{xzy}. \tag{9}$$

The other non-zero components for symmetry C_{3v} vanish owing to the relations imposed by C''_3:

$$t_{xxx}=-t_{yyy} \quad t_{xyy}=-t_{yzz} \quad t_{xzx}=-t_{yxy} \quad t_{xxz}=-t_{yyx}.$$

For the same reason also an axial third-order tensor has only one independent non-zero component:

$$t_{xyz}=-t_{xzy}. \tag{10}$$

Symmetry O_h $(T_d\times i=O\times i)$ is equivalent to T_d for an axial third-order tensor while it equates to zero all the components of a polar one. Symmetry O is equivalent to T_d for an axial third-order tensor and therefore also for a polar one since it does not distinguish between the two, not containing any improper rotation.

(b) *Polar fourth-order tensor* $t_{iklm}=t_{kilm}=t_{ikml}$ $(i, k, l, m=1, 2, 3)$

Examples are photoelastic constants and piezo-optical effect (Szivessy, 1929; Pockels, 1906), piezoresistive effect (Cookson, 1935), thermal conductivity under stress (Pockels, 1906), dielectric constant under strain (Pockels, 1904–22):

$$\left.\begin{matrix} t_{xxxx} & t_{xxyy} & t_{xxzz} & t_{xxyz} & t_{xxzx} & t_{xxxy} \\ t_{yyxx} & t_{yyyy} & t_{yyzz} & t_{yyyz} & t_{yyzx} & t_{yyxy} \\ t_{zzxx} & t_{zzyy} & t_{zzzz} & t_{zzyz} & t_{zzzx} & t_{zzxy} \\ t_{yzxx} & t_{yzyy} & t_{yzzz} & t_{yzyz} & t_{yzzx} & t_{yzxy} \\ t_{zxxx} & t_{zxyy} & t_{zxzz} & t_{zxyz} & t_{zxzx} & t_{zxxy} \\ t_{xyxx} & t_{xyyy} & t_{xyzz} & t_{xyyz} & t_{xyzx} & t_{xyxy} \end{matrix}\right\}. \tag{11}$$

Symmetry C_4:

$$C_4 \qquad x\to y, \quad y\to -x, \quad z\to z. \tag{12}$$

The independent non-zero components are 10:

$$\left.\begin{matrix} t_{xxxx}=t_{yyyy} & t_{xxyy}=t_{yyxx} & t_{xxzz}=t_{yyzz} \\ t_{xxxy}=-t_{yyxy} & t_{zzxx}=t_{zzyy} & t_{zzzz} \\ t_{zzxy}=-t_{zzxy}=0 & t_{yzyz}=t_{zxzx} & t_{yzzx}=-t_{zxyz} \\ t_{xyxx}=-t_{xyyy} & t_{xyzz}=-t_{xyzz}=0 & t_{xyxy} \end{matrix}\right\}. \tag{13}$$

The 16 components with indices odd in x or in y vanish. Symmetries C_{4h} $(C_4\times i=S_4\times i)$ and S_4 are equivalent to C_4.

Symmetry C_3:

$$C_3 \qquad x\to y, \quad y\to z, \quad z\to x. \tag{2}$$

There are 12 independent components:

$$\left.\begin{matrix} t_{xxxx}=t_{yyyy}=t_{zzzz} & t_{xxyy}=t_{yyzz}=t_{zzxx} & t_{xxyz}=t_{yyzx}=t_{zzxy} \\ t_{xxzx}=t_{yyxy}=t_{zzyz} & t_{xxxy}=t_{yyyz}=t_{zzzx} & t_{yyxx}=t_{zzyy}=t_{xxzz} \\ t_{yzxx}=t_{zxyy}=t_{xyzz} & t_{yzyy}=t_{zxzz}=t_{xyxx} & t_{yzzz}=t_{zxxx}=t_{xyyy} \\ t_{yzyz}=t_{zxzx}=t_{xyxy} & t_{yzzx}=t_{zxxy}=t_{xyyz} & t_{yzxy}=t_{zxyz}=t_{xyzx} \end{matrix}\right\}. \tag{14}$$

Symmetry $S_6=C_3\times i$ is equivalent to C_3.

Symmetry T:

$$C'_3 \qquad x\to y, \quad y\to z, \quad z\to x, \tag{2}$$

$$C''_3 \qquad -x\to y, \quad y\to z, \quad z\to -x. \tag{8}$$

Eight of the 12 components for C_3 vanish owing to the presence of C''_3:

$$\left.\begin{matrix} t_{xxyz}=-t_{yyzx}=-t_{zzxy} & t_{xxzx}=t_{yyxy}=-t_{zzyz} \\ t_{xxxy}=-t_{yyyz}=t_{zzzx} & t_{yzxx}=-t_{zxyy}=-t_{xyzz} \\ t_{yzyy}=-t_{zxzz}=-t_{xyxx} & t_{yzzz}=-t_{zxxx}=-t_{xyyy} \\ t_{yzzx}=-t_{zxxy}=t_{xyyz} & t_{yzxy}=t_{zxyz}=-t_{xyzx} \end{matrix}\right\}. \tag{15}$$

Symmetry $T_h=T\times i$ is equivalent to T.

The groups C_4, S_4, C_{4h}; C_3, S_6; T, T_h are seven of the ten crystal classes for which Bhagavantam (1942), by

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* An axial third-order tensor has not been considered either by Bhagavantam & Suryanarayana (1949) or by Jahn (1949). We here apply Bhagavantam's method to give the numbers of its components in C_{3v} and T_d to show that they agree with our results. The character of a rotation or of a rotation-reflection of an angle ϕ around z, in the reducible representation based on the 27 components of the tensor is given by

$$8\cos^3\phi\pm 12\cos^2\phi+6\cos\phi\pm 1$$

(Bhagavantam & Suryanarayana, 1949). The character tables of interest are

$$\begin{array}{llllll} C_{3v}: & E & 2C_3 & 3\sigma_v & & \\ & 27 & 0 & 1 & & \\ T_d: & E & 8C_3 & 3C_2 & 6\sigma_d & 6S_4 \\ & 27 & 0 & -1 & 1 & -1 \end{array}$$

To obtain the numbers of independent components we must look for the number of times that the irreducible representation symmetric in proper rotations and antisymmetric in improper ones is contained in these reducible representations: the results are

$$C_{3v}, \quad 4; \quad T_d, \quad 1.$$

group theory, has found errors in the number of photoelastic constants given by Pockels (1906); the other classes are C_{3h}, C_6, C_{6h}. Here this result (plus the explicit enumeration of the constants) is immediately obvious.

(*c*) *Polar sixth-order tensor** $t_{ikl}=t_{ilk}$ ($i, k, l=1, 2, 3, 4, 5, 6$)

An example is the photoelastic coefficients (Bhagavantam & Suryanarayana, 1949).

The total number of components as they appear in the defining equations is $6\times 21=126$. They are:

$$\left.\begin{array}{lllll}
t_{xxxxxx} & t_{xxxxyy} & t_{xxxxzz} & t_{xxxxyz} & t_{xxxxzx} \\
t_{xxxxxy} & t_{xxyyyy} & t_{xxyyzz} & t_{xxyyyz} & t_{xxyyzx} \\
t_{xxyyxy} & t_{xxzzzz} & t_{xxzzyz} & t_{xxzzzx} & t_{xxzzxy} \\
t_{xxyzyz} & t_{xxyzzx} & t_{xxyzxy} & t_{xxzxzx} & t_{xxzxxy} \\
t_{xxxyxy} & t_{yyxxxx} & t_{yyxxyy} & t_{yyxxzz} & t_{yyxxyz} \\
t_{yyxxzx} & t_{yyxxxy} & t_{yyyyyy} & t_{yyyyzz} & t_{yyyyyz} \\
t_{yyyyzx} & t_{yyyyxy} & t_{yyzzzz} & t_{yyzzyz} & t_{yyzzzx} \\
t_{yyzzxy} & t_{yyyzyz} & t_{yyyzzx} & t_{yyyzxy} & t_{yyzxzx} \\
t_{yyzxxy} & t_{yyxyxy} & t_{zzxxxx} & t_{zzxxyy} & t_{zzxxzz} \\
t_{zzxxyz} & t_{zzxxzx} & t_{zzxxxy} & t_{zzyyyy} & t_{zzyyzz} \\
t_{zzyyyz} & t_{zzyyzx} & t_{zzyyxy} & t_{zzzzzz} & t_{zzzzyz} \\
t_{zzzzzx} & t_{zzzzxy} & t_{zzyzyz} & t_{zzyzzx} & t_{zzyzxy} \\
t_{zzzxzx} & t_{zzzxxy} & t_{zzxyxy} & t_{yzxxxx} & t_{yzxxyy} \\
t_{yzxxzz} & t_{yzxxyz} & t_{yzxxzx} & t_{yzxxxy} & t_{yzyyyy} \\
t_{yzyyzz} & t_{yzyyyz} & t_{yzyyzx} & t_{yzyyxy} & t_{yzzzzz} \\
t_{yzzzyz} & t_{yzzzzx} & t_{yzzzxy} & t_{yzyzyz} & t_{yzyzzx} \\
t_{yzyzxy} & t_{yzzxzx} & t_{yzzxxy} & t_{yzxyxy} & t_{zxxxxx} \\
t_{zxxxyy} & t_{zxxxzz} & t_{zxxxyz} & t_{zxxxzx} & t_{zxxxxy} \\
t_{zxyyyy} & t_{zxyyzz} & t_{zxyyyz} & t_{zxyyzx} & t_{zxyyxy} \\
t_{zxzzzz} & t_{zxzzyz} & t_{zxzzzx} & t_{zxzzxy} & t_{zxyzyz} \\
t_{zxyzzx} & t_{zxyzxy} & t_{zxzxzx} & t_{zxzxxy} & t_{zxxyxy} \\
t_{xyxxxx} & t_{xyxxyy} & t_{xyxxzz} & t_{xyxxyz} & t_{xyxxzx} \\
t_{xyxxxy} & t_{xyyyyy} & t_{xyyyzz} & t_{xyyyyz} & t_{xyyyzx} \\
t_{xyyyxy} & t_{xyzzzz} & t_{xyzzyz} & t_{xyzzzx} & t_{xyzzxy} \\
t_{xyyzyz} & t_{xyyzzx} & t_{xyyzxy} & t_{xyzxzx} & t_{xyzxxy}
\end{array}\right\} \quad (16)$$

$$t_{xyxyxy}.$$

For symmetry C_{1h}:

$$\sigma_h \qquad x\rightarrow x, \quad y\rightarrow -y, \quad z\rightarrow z, \qquad (17)$$

the 58 components with indices odd in y must vanish:

$$\begin{aligned}
& t_{xxxxyz}=t_{xxxxxy}=t_{xxyyyz}=t_{xxyyxy}=t_{xxzzyz}=t_{xxzzxy} \\
& =t_{xxyzzx}=t_{xxzxxy}=t_{yyxxyz}=t_{yyxxxy}=t_{yyyyyz}=t_{yyyyxy} \\
& =t_{yyzzyz}=t_{yyzzxy}=t_{yyyzzx}=t_{yyzxxy}=t_{zzxxyz}=t_{zzxxxy} \\
& =t_{zzyyyz}=t_{zzyyxy}=t_{zzzzyz}=t_{zzzzxy}=t_{zzyzzx}=t_{zzzxxy} \\
& =t_{yzxxxx}=t_{yzxxyy}=t_{yzxxzz}=t_{yzxxzx}=t_{yzyyyy}=t_{yzyyzz} \\
& =t_{yzyyzx}=t_{yzzzzz}=t_{yzzzzx}=t_{yzyzyz}=t_{yzyzxy}=t_{yzzxzx} \\
& =t_{yzxyxy}=t_{zxxxyz}=t_{zxxxxy}=t_{zxyyyz}=t_{zxyyxy}=t_{zxzzyz} \\
& =t_{zxzzxy}=t_{zxyzzx}=t_{zxzxxy}=t_{xyxxxx}=t_{xyxxyy}=t_{xyxxzz} \\
& =t_{xyxxzx}=t_{xyyyyy}=t_{xyyyzz}=t_{xyyyzx}=t_{xyzzzz}=t_{xyzzzx} \\
& =t_{xyyzyz}=t_{xyyzxy}=t_{xyzxzx}=t_{xyxyxy}=0. \qquad (18)
\end{aligned}$$

Symmetries C_{2h} ($C_{1h}\times i=C_2\times i$) and C_2 ($C_2=C_2(y)$) are equivalent to C_{1h}.

For symmetry C_{2v}:

$$\sigma_v \qquad x\rightarrow -x, \quad y\rightarrow y, \quad z\rightarrow z, \qquad (19)$$

$$\sigma_v' \qquad x\rightarrow x, \quad y\rightarrow -y, \quad z\rightarrow z, \qquad (17)$$

also the 29 components with indices odd in x vanish:

$$\begin{aligned}
& t_{xxxxzx}=t_{xxyyzx}=t_{xxzzzx}=t_{xxyzxy}=t_{yyxxzx}=t_{yyyyzx} \\
& =t_{yyzzzx}=t_{yyyzxy}=t_{zzxxzx}=t_{zzyyzx}=t_{zzzzzx}=t_{zzyzxy} \\
& =t_{yzxxxy}=t_{yzyyxy}=t_{yzzzxy}=t_{yzyzzx}=t_{zxxxxx}=t_{zxxxyy} \\
& =t_{zxxxzz}=t_{zxyyyy}=t_{zxyyzz}=t_{zxzzzz}=t_{zxyzyz}=t_{zxzxzx} \\
& =t_{zxxyxy}=t_{xyxxyz}=t_{xyyyyz}=t_{xyzzyz}=t_{xyzxxy}=0. \qquad (20)
\end{aligned}$$

Symmetries D_{2h} ($C_{2v}\times i=D_2\times i$) and D_2 are equivalent to C_{2v}.

For symmetry C_{4v}:

$$C_4 \qquad x\rightarrow y, \quad y\rightarrow -x, \quad z\rightarrow z, \qquad (12)$$

$$\sigma_v \qquad x\rightarrow x, \quad y\rightarrow -y, \quad z\rightarrow z, \qquad (17)$$

the independent non-zero components are 22 since C_4 imposes that the 29 non-zero components for symmetry C_{1h} having indices odd in x vanish and that

$$\left.\begin{array}{lll}
t_{xxxxxx}=t_{yyyyyy} & t_{xxxxyy}=t_{yyxxyy} & t_{xxxxzz}=t_{yyyyzz} \\
t_{xxyyyy}=t_{yyxxxx} & t_{xxyyzz}=t_{yyxxzz} & t_{xxzzzz}=t_{yyzzzz} \\
t_{xxyzyz}=t_{yyzxzx} & t_{xxzxzx}=t_{yyyzyz} & t_{xxxyxy}=t_{yyxyxy} \\
t_{zzxxxx}=t_{zzyyyy} & t_{zzxxzz}=t_{zzyyzz} & t_{zzyzyz}=t_{zzzxzx} \\
t_{yzxxyz}=t_{zxyyzx} & t_{yzyyyz}=t_{zxxxzx} & t_{yzzzyz}=t_{zxzzzx} \\
t_{yzzxxy}=t_{zxyzxy} & t_{xyxxxy}=t_{xyyyxy} &
\end{array}\right\}. \quad (21)$$

Symmetries D_{4h} ($C_{4v}\times i=D_{2d}\times i=D_4\times i$), D_{2d} and D_4 are equivalent to C_{4v}.

The writer is indebted to the reviewer, Prof. P. P. Ewald, for his interest in the paper and to his colleague Dr R. Shuttleworth for useful discussion. He wishes to thank Prof. Bhagavantam of Osmania University, India, Dr Mason of the Bell Telephone Laboratories, U.S.A., and Dr Mathieu of the University of Paris, France, for reading critically the manuscript of the paper and making suggestions.

Note added in proof, 29 *October* 1951. Since this manuscript was circulated in September 1950 Dr Mason (1951, Appendix I) has published a paper which profits somewhat from ideas presented in it; however, Mason's procedure and results should be criticized. The number of symmetry conditions imposed is redundant since the independent symmetry elements of T_d (and of O) are only 2. Two orthogonal quaternary axes, e.g. $C_4(x)$, $C_4(y)$, are sufficient to obtain the independent non-zero components of the sixth-order tensor $R_{abc}(a, b, c=1, 2, 3, 4, 5, 6)$ (216 components) in O: T_d and O_h are equivalent to O for polar properties of even order. The 156 components odd in x, y or z vanish; the re-

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* A simpler type of polar sixth-order tensor (the third-order elastic coefficients) has been discussed by the writer elsewhere (Fumi, 1951).

maining 60 components are connected by the following relations:

111 = 222 = 333
121 = 131 = 212 = 232 = 313 = 323
123 = 132 = 213 = 231 = 312 = 321
155 = 166 = 244 − 266 = 344 = 355
441 = 552 = 663
442 = 443 = 551 = 553 = 661 = 662
112 = 113 = 221 = 223 = 331 = 332
122 = 133 = 211 = 233 = 311 = 322
144 = 255 = 366
414 = 525 = 636
424 = 434 = 515 = 535 = 616 = 626
456 = 465 = 546 = 564 = 645 = 654

If $R_{abc} = R_{bac}$ (126 components) these 12 independent components reduce to 9 in agreement with Bhagavantam's result (Bhagavantam & Suryanarayana, 1949). To obtain the independent components of the tensor N one must start from those of $R_{abc} \neq R_{bac}$: they are 111, 112, 122, 123, 414, 424, owing to the possibility of interchanging at random the last four indices. The results obtained by Dr Mason for the tensor N are incorrect.

Correspondence with Dr Mason on this matter is acknowledged.

References

Bhagavantam, S. (1942). *Proc. Indian Acad. Sci.* **16**, 359.

Bhagavantam, S. & Suryanarayana, D. (1947). *Nature, Lond.*, **160**, 750.

Bhagavantam, S. & Suryanarayana, D. (1949). *Acta Cryst.* **2**, 21.

Birch, F. (1947). *Phys. Rev.* **71**, 809.

Cady, W. G. (1946). *Piezoelectricity.* New York: McGraw Hill.

Cookson, J. W. (1935). *Phys. Rev.* **47**, 194.

Fumi, F. G. (1951). *Phys. Rev.* **83**, 1274.

Hermann, C. (1934). *Z. Krystallogr.* **89**, 32.

Jahn, H. A. (1949). *Acta Cryst.* **2**, 30.

Love, A. E. H. (1906). *Mathematical Theory of Elasticity.* Cambridge University Press.

Mason, W. P. (1950). *Piezoelectric Crystals and their Applications to Ultrasonics.* New York: Van Nostrand.

Mason, W. P. (1951). *Phys. Rev.* **82**, 715.

Mathieu, J. P. (1945). *Spectres de Vibration et Symétrie.* Paris: Hermann.

Pockels, F. (1904–22). *Encyklopädie der Mathematischen Wissenchaften,* 5 (2), 359. Leipzig: Teubner.

Pockels, F. (1906). *Lehrbuch der Krystalloptik.* Leipzig: Teubner.

Szivessy, G. (1929). *Handbuch der Physik,* **21**, 839. Berlin: Springer.

Voigt, W. (1910). *Lehrbuch der Krystallphysik.* Leipzig: Teubner.

Wooster, W. A. (1949). *A Textbook on Crystal Physics.* Cambridge University Press.

Acta Cryst. (1952). **5**, 48

Crystal-Structure Determination by Means of a Statistical Distribution of Interatomic Vectors

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(*Received* 16 *January* 1951)

The structure-factor equations are interpreted as coupled, closed-vector polygons. This interpretation permits the application of the random-walk problem to yield the probability distribution of the structure factors and of the co-ordinate differences between specified pairs of atomic centers in the case of rigid crystals. In practice the intensities must be corrected for vibrational motion. All crystals may be treated with the probability formula for the general asymmetric case, and the symmetry which exists in the crystal will automatically be obtained. Probability distributions which make use of an *a priori* knowledge of the crystal symmetry may also be obtained, and the case of the centrosymmetric crystal is worked out in detail. The relationship between the probability distribution for the interatomic vectors and the Patterson synthesis is derived.

A mathematical analysis (Hauptman & Karle, 1950*a*, *b*; Karle & Hauptman, 1951) of the crystal-structure problem shows that the atomic co-ordinates are generally greatly overdetermined by the observed X-ray intensities, provided the atomic scattering factors are known. This calls for a procedure which leads from the experimental data directly to the atomic co-ordinates. In this paper a statistical method will be described which appears to make efficient use of the observed intensities and the known atomic scattering factors.

From the geometric point of view, the structure-factor equations may be regarded as a system of coupled, closed-vector polygons, the sides of each of