Acta Cryst. (1969). A**25**, 627

On the Contribution of Thermal Diffuse X-ray Scattering to the Integrated Bragg Intensities of Single Crystals

By B. W. Lucas*

*Crystallography Laboratory, Department of Physics, The City University, London, E.C.*1, *England*

(*Received* 1 *August* 1968 *and in revised form* 30 *October* 1968)

The effect of including first-order and second-order thermal diffuse scattering contributions on the theoretical treatment for integrated Bragg intensities of single crystals is given for crystals belonging to any crystal system and with any number of atoms per unit cell. With certain restricting approximations and assumptions, the modified integrated intensity is found to be a product of the Bragg scattering and a factor, exp $(C \sin^2 \theta_0/\lambda^2)$, where C is a simple function of the X-ray wavelength, the temperature, the angular peak-width, and a quantity related to the elastic properties of the crystal. For cubic crystals, C is found to be approximately constant and thus confirms the result obtained by Nilsson (1957, *Ark. Fys.* **12**, 247) for simple cubic crystals. The theory is applied to Al and KCl crystals, and calculated values for the ratio of uncorrected to corrected integrated Bragg intensities show reasonable agreement with some experimental values obtained using the Mössbauer effect.

Introduction

The thermal motion of atoms in crystals, which modifies their X-ray scattering behaviour, has been investigated since the earliest studies of X-ray diffraction; an historical review has been given by Wooster (1962). Laval (1939) predicted and verified that the thermal diffuse scattering of X-rays by crystals exhibits intensity maxima in the diffraction directions corresponding to the Bragg maxima.

The integrated Bragg intensity is usually evaluated by consideration of the total X-ray energy scattered over a small angular range of the crystal setting on either side of the Bragg position, after the 'background scattering' has been subtracted, as illustrated in Fig. 1. The background includes Compton scattering, air scattering, instrumental scattering and any contribution due to the relatively high-frequency 'optic modes' of lattice vibration. The importance of the angular-dependent thermal diffuse scattering components in, and very close to, the Bragg diffraction directions has recently been shown experimentally using the Mössbauer effect (O'Connor & Butt, 1963; Butt & O'Connor, 1967). Nilsson (1957) has theoretically considered the effect of the first-order diffuse scattering on the integrated Bragg intensities of simple cubic crystals, while Warren (1953) and Chipman & Paskin (1959) have considered, in a similar way, the effect for powdered crystals. Recently, Cooper & Rouse (1968) have described some improvements to the approximations made in the Nilsson (1957) treatment.

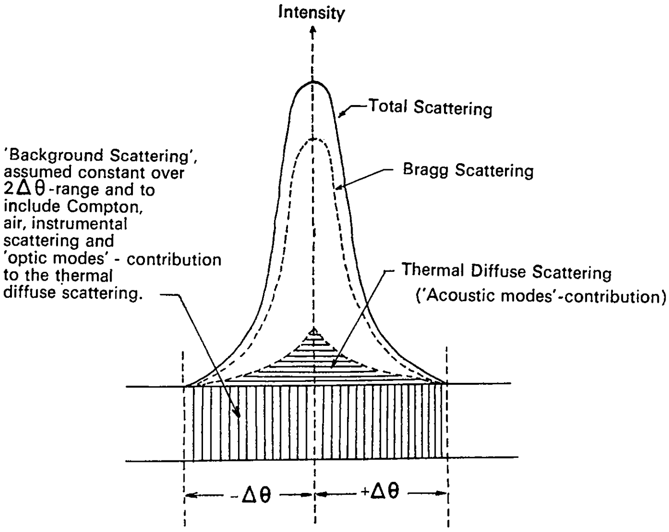

Fig. 1. A representation of the various component contributions to the total scattering close to the Bragg maxima directions.

---

* Present address: Department of Physics, University of Queensland, St. Lucia, Brisbane, Qld. Australia.

In the present paper, the effect of first-order and second-order thermal diffuse scattering contributions on the theoretical treatment for integrated Bragg intensities of single crystals belonging to any crystal system and with any number of atoms per unit cell is given. With certain restricting approximations and assumptions, a simplification of this expression is obtained. The theory is applied to cubic crystals, and calculated values for the ratio of uncorrected to corrected integrated Bragg intensities are compared with some experimental values obtained using the Mössbauer effect (Butt & O'Connor, 1967).

The theory of integrated Bragg intensities, including the effects of first-order and second-order thermal diffuse X-ray scattering

The treatment of the general theory of thermal diffuse scattering has been given by Cochran (1963), and by Cochran & Pawley (1964). If the treatment of the integrated Bragg intensities described by James (1962) is extended to include contributions due to first-order and second-order thermal diffuse scattering and the concept of 'Diffuse Scattering Power', D, (Ramachandran & Wooster, 1951) is introduced, the modified integrated Bragg intensity, ϱ', for any number of atoms in the unit cell may be written as:

$$\varrho' = \frac{E\omega}{I_0} = \int_{\theta_0-\Delta\theta}^{\theta_0+\Delta\theta} P(\theta)d\theta = N\Delta v \left(\frac{e^2}{mc^2}\right)^2 p \int_\varepsilon \int_\Omega (D_0+D_1+D_2+\ldots)d\Omega d\varepsilon\,, \tag{1}$$

where

$$D_0 = \left| \sum_{k=1}^{n} f_k \exp\left(-M_k\right) . \exp\left[i\mathbf{q} . \mathbf{r}(k)\right] \right|^2 (\mathscr{I}_L/N\Delta v)$$

$$= |F_T(\mathbf{q})|^2 (\mathscr{I}_L/N\Delta v)\,,$$

$$D_1 = \sum_{j=1}^{3n} \left(\frac{E_j(\mathbf{R})}{\omega_j^2(\mathbf{R})}\right) \left| \sum_{k=1}^{n} f_k \exp\left(-M_k\right) . \exp\left[i\mathbf{q} . \mathbf{r}(k)\right] \times \frac{\mathbf{S} . \mathbf{e}_j(k,\mathbf{R})}{\sqrt{\mu_k}} \right|^2,$$

$$D_2 = \tfrac{1}{2} \sum_{j=1}^{3n} \sum_{j'=1}^{3n} \left(\frac{E_j(\mathbf{R}_1)}{\omega_j^2(\mathbf{R}_1)}\right) \left(\frac{E_{j}'(\mathbf{R}_2)}{\omega_{j'}^2(\mathbf{R}_2)}\right) \left| \sum_{k=1}^{n} f_k \exp(-M_k) \times \exp\left[i\mathbf{q} . \mathbf{r}(k)\right] \times \left[\frac{\mathbf{S} . \mathbf{e}_j(k,\mathbf{R}_1)}{\sqrt{\mu_k}}\right] \left[\frac{\mathbf{S} . \mathbf{e}_{j'}(k,\mathbf{R}_2)}{\sqrt{\mu_k}}\right] \right|^2 .$$

E = the total energy diffracted,
ω = the uniform angular velocity of the crystal rotation,
I_0 = the intensity per unit area of cross-section of the direct beam,
$P(\theta)$ = the reflecting power of the crystal,
θ_0 = the Bragg angle,
$\Delta\theta$ = the half angular-width of the peak,
N = the number of unit cells per unit volume of the crystal,
Δv = the volume of the crystal,
e = the electronic charge,
m = the mass of the electron,

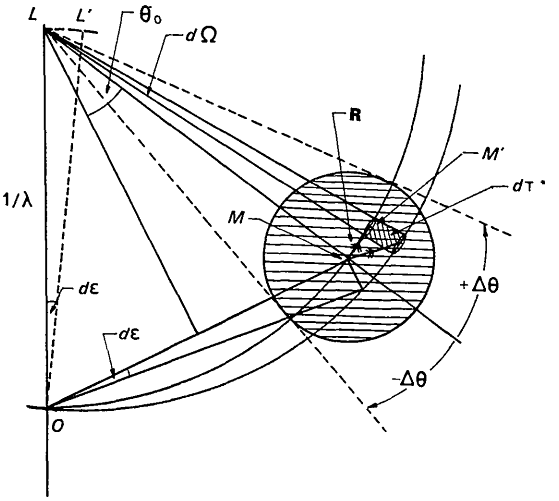

Fig. 2. Part of the Ewald sphere (in two positions) differing by rotation of an angle, $d\varepsilon$, about an axis through the reciprocal lattice origin, O, and normal to the plane of the paper. The shaded area around the reciprocal lattice point M denotes the region within which the Laue interference function $\mathscr{I}_L$, as modified by geometrical resolution effects, has appreciable values.

Table 1. *The evaluation of* $2\Delta B$ *for* Al *and* KCl
($\lambda = 0{\cdot}86$ Å; $T = 290$ °K)

Substance	Elastic constants ($\times 10^{11}$ dyne cm^{-2})		$\langle K[ABC]_{hkl}\rangle$ ($\times 10^{12}$dyne^{-1} cm^2)	$\Delta\theta$	$\frac{\pi^2 2!\langle K'[ABC]_{hkl}\rangle}{16\,(\langle K[ABC]_{hkl}\rangle)^2}$	$2\Delta B$ (Å^2)
	c_{11}	10·68				
Aluminum	c_{12}	6·07	2·89	1·75°	~0·94	$0{\cdot}20_6$
	c_{44}	2·82				
	Kamm & Alers (1964)					
	c_{11}	4·03				
Potassium chloride	c_{12}	0·66	8·22	1·50°	~1·51	$0{\cdot}50_3$
	c_{44}	0·63				
	Norwood & Briscoe (1958)					

c = the velocity of light,

p = the polarization factor,

D_0 = the 'Diffuse Scattering Power' associated with the Bragg scattering,

D_1 = the first-order thermal Diffuse Scattering Power,

D_2 = the second-order thermal Diffuse Scattering Power,

$d\Omega$ = a small solid angle containing a given diffraction direction, LM' (Fig. 2),

$d\varepsilon$ = a small angular change of crystal position, about the axis of rotation (Fig. 2),

n = the number of atoms in the unit cell,

f_k = the atomic scattering factor of the kth atom at rest,

M_k is associated with the Debye–Waller factor of the kth atom,

$\mathbf{q}$ = the vector distance in reciprocal space of the lattice point to the origin,

$\mathbf{r}(k)$ = the vector distance of the kth atom from the origin of the unit cell,

$\mathscr{I}_L$ = the Laue 'interference function',

$E_j(\mathbf{R})$ = the energy of the jth mode of vibration,

$\omega_j(\mathbf{R})$ = the circular frequency of the jth mode of vibration,

$\mathbf{S}$ = the difference vector between the incident and diffracted wave-vectors of the scattered X-radiation, so that $|\mathbf{S}| = 4\pi \sin\theta/\lambda$,

$\mathbf{e}_j(k,\mathbf{R})$ = the polarization vector of the kth atom, vibrating in the jth mode,

μ_k = the mass of the kth atom.

Fig. 2 shows part of the Ewald sphere of reflexion, in two positions differing in orientation by a small angle, $d\varepsilon$, around the crystal rotation axis. The rotation axis passes through O and is normal to the plane containing LOM. The shaded area represents a section of the spherical volume (see *Discussion*) of reciprocal space over which the Laue interference function, $\mathscr{I}_L$, is considered to result in a measurable contribution to the Bragg intensity (James, 1962). M is the reciprocal lattice point and LO is the direction of the incident X-ray beam. The total scattering entering the solid angle $d\Omega$, containing the direction of diffraction, LM', consists of the Bragg scattering together with the first-order and second-order thermal diffuse scattering.

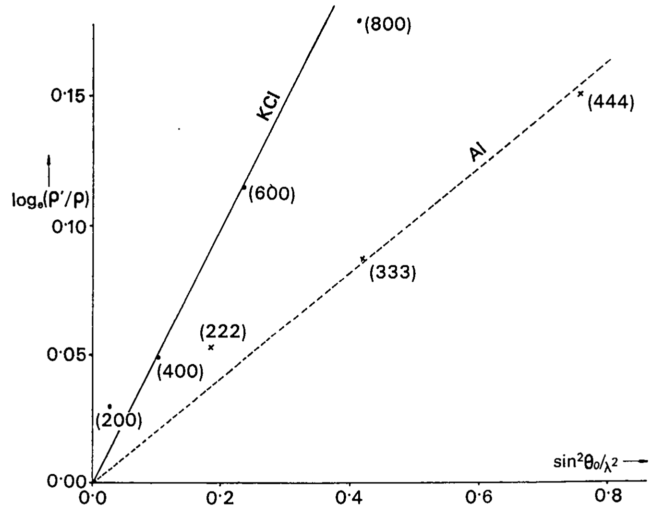

Fig. 3. Comparison of theoretical and experimental variation of $\log_e(\varrho'/\varrho)$ with $\sin^2\theta_0/\lambda^2$.

The contribution to integrated Bragg intensities due to the acoustic modes of vibration

Evaluation of the integrals containing D_1 and D_2 would require a detailed knowledge of the vibration modes for the crystal, which is not at present generally available. Certain restricting assumptions and approximations are, therefore, necessary and are made as follows:

(i) As only the acoustic modes of vibration are important close to the reciprocal lattice point ($|\mathbf{R}|$ is small), the normalized polarization vectors, $\mathbf{e}_j(k,\mathbf{R})/\sqrt{\mu_k}$, for the different atoms in the unit cell may be made equal.

(ii) The atoms are in harmonic vibration and the temperature is such that the mean energy, $\langle E_j(\mathbf{R})\rangle = \hbar\omega_j(\mathbf{R}) . [\frac{1}{2} + \{\exp(\hbar\omega_j(\mathbf{R})/kT) - 1\}^{-1}]$, associated with each mode of vibration may be replaced by kT (k is the Boltzmann constant). Dispersion effects for the acoustic modes of vibration may be neglected.

(iii) The crystal may be considered as 'ideally mosaic', with an approximately spherical shape, and completely bathed in a parallel, monochromatic incident beam of uniform intensity.

(iv) 'Background scattering' may be allowed for by the method shown in Fig. 1.

With these approximations, and noting that $d\Omega d\varepsilon = \lambda^3 d\tau^*/\sin 2\theta_0$, equation (1) now becomes:

$$\varrho' = \varrho\left[1 + kTq^2\int_{\text{sphere}} K[ABC]_{hkl}/R^2 d\tau^* + (\pi^3/2)k^2T^2q^4\int_{\text{sphere}} K'[ABC]_{hkl}/R d\tau^* + \dots\right] \quad (2)$$

where the unmodified integrated Bragg intensity, ϱ, is given by:

$$\varrho = \left(\frac{e^2}{mc^2}\right)^2 p\lambda^3 N^2 \Delta v |F_T|^2/\sin 2\theta_0$$

and

$$K[ABC]_{hkl} = \sum_{j=1}^{3} \frac{\cos^2(\mathbf{q},\xi_j)}{\delta . V_j^2},$$

$$K'[ABC]_{hkl} = \sum_{j=1}^{3} \frac{\cos^4(\mathbf{q},\xi_j)}{\delta^2 V_j^4}.$$

δ = crystal density,

ξ_j ($j = 1,2,3$) are the amplitudes of the three acoustical waves having the wave vector, $\mathbf{R}$,

V_j ($j = 1,2,3$) are their corresponding velocities.

Lonsdale (1942) has shown experimentally that the thermal diffuse scattering intensity close to a reciprocal lattice point is usually anisotropic. Evaluation of the integrals by numerical means with allowance for this variation, although possible in principle, would be particularly lengthy. Average values, $\langle K[ABC]_{hkl}\rangle$ and $\langle K'[ABC]_{hkl}\rangle$, are therefore introduced. On transforming the variables of the integrand to spherical polar coordinates (with M as origin) and performing the integrations, equation (2) becomes:

$$\varrho'/\varrho=[1+16\pi kT(\Delta\theta/\lambda)\,\langle K[ABC]_{hkl}\rangle \sin^2\theta_0/\lambda^2 + 16\pi^4k^2T^2\langle K'[ABC]_{hkl}\rangle\,(\Delta\theta/\lambda)^2\sin^4\theta_0/\lambda^4+\ldots] \quad (3a)$$

which may be re-written as:

$$\varrho'/\varrho=\left[1+\frac{1}{1!}(16\pi kT(\Delta\theta/\lambda)\,\langle K[ABC]_{hkl}\rangle\sin^2\theta_0/\lambda^2) + \frac{1}{2!}(16\pi kT(\Delta\theta/\lambda)\,\langle K[ABC]_{hkl}\rangle\sin^2\theta_0/\lambda^2)^2 \times\left(\frac{\pi^2\,2!}{16}\,\frac{\langle K'[ABC]_{hkl}\rangle}{(\langle K[ABC]_{hkl}\rangle)^2}\right)+\ldots\right]. \quad (3b)$$

Equation (3*b*) shows a rapidly converging series, which, on approximating the expression

$$\left(\frac{\pi^2\,2!}{16}\,\frac{\langle K'[ABC]_{hkl}\rangle}{(\langle K[ABC]_{hkl}\rangle)^2}\right)\sim 1$$

(Prasad & Wooster, 1956; Lucas, 1968), becomes the first three terms of the exponential series;

$$\varrho'/\varrho=\exp\,(2\Delta B\sin^2\theta_0/\lambda^2)\,, \quad (4)$$

where

$$\Delta B=8\pi kT\langle K[ABC]_{hkl}\rangle\Delta\theta/\lambda\,.$$

Table 1 shows the value of

$$\left(\frac{\pi^2 2!}{16}\,\frac{\langle K'[ABC]_{hkl}\rangle}{(\langle K[ABC]_{hkl}\rangle)^2}\right)$$

for Al and KCl.

The general relationship between $\langle K[ABC]_{hkl}\rangle$ and the elastic constants of a crystal is the following:

$$\langle K[ABC]_{hkl}\rangle=\langle\,\Sigma\, g_ig_k(A^{-1})_{ik}\rangle\,,$$
$$A_{ik}=\Sigma\, c_{ilmk}f_lf_m\,,\ (c_{ilmk}=c_{ik})$$

g_1,g_2,g_3 are the direction cosines of the reciprocal lattice vector, $\mathbf{q}$;
f_1,f_2,f_3 are the direction cosines of the wave-vector, $\mathbf{R}$;
c_{ilmk} $(i,l,m,k=1,$ 2 or 3) are the elastic constants of the crystal (Wooster, 1962).

(Some approximate methods of estimating

$$\langle K[ABC]_{hkl}\rangle\,,$$

for cubic crystals, are compared in the *Appendix*.)

Comparison of the derived expression for (ϱ'/ϱ) with the experimentally measured values for some cubic single crystals

Equation (4) and the approximate relationship for $\langle K[ABC]_{hkl}\rangle$ given in the Appendix would appear to suggest that, at one particular temperature, $\log_e(\varrho'/\varrho)$ should be linearly related to $\sin^2\theta_0/\lambda^2$ by the constant, $2\Delta B$. In Fig. 3, the straight lines follow the calculated variation, while the points are experimentally obtained by use of the Mössbauer effect (Butt & O'Connor, 1967). (Table 1 includes values for the appropriate quantities used in the calculation of $2\Delta B$.)

Discussion

The method used to simplify the expression for the modified integrated Bragg intensity involves essentially an averaging procedure around each lattice point and an integration over a spherical volume centred upon it. The actual size and shape of the reciprocal volume contributing to the total scattering will, in general, be much more complex (Cooper & Rouse, 1968) and will depend on the instrumental method by which the experimental data is measured, the geometrical configuration of the apparatus used, and the size and shape of the crystal. Integrations over volumes with such forms usually require a numerical method for their evaluation and a separate application for each reflexion. Approximation to the spherical volume would appear reasonable, with the restricting assumptions made here, provided that the limiting apertures placed before the diffracted-beam detector and the angular oscillation range of the crystal about the Bragg angle are sufficiently large for the actual volume to be somewhat greater than the spherical volume. The contribution from the volume difference could then be considered

Table 2. *Comparison of approximate methods for calculating* $\langle K[ABC]_{hkl}\rangle$

Substance	T (°K)	$\frac{1}{3}\bar{\kappa}^*\times 10^{12}$	$\frac{1}{3}\bar{\kappa}_{\text{approx}}\times 10^{12}$	$\langle K[ABC]_{hkl}\rangle_{\text{approx}}\times 10^{12}$
		Nilsson (1957)		
KCl	86	7·43	7·04	7·61
	280	8·21	7·89	8·34
	290	8·27	7·95	8·38
NaCl	86	4·73	4·68	4·71
	290	5·31	5·29	5·39

* Schwartz (1964) has pointed out a possible difficulty, in some special cases, with the method of evaluation used by Nilsson (1957) and has suggested an alternative method.

as part of the 'background' and would be deducted from the total scattered intensity (Fig. 1).

For cubic crystals, the effect of neglecting thermal diffuse scattering contributions to the integrated intensities results in a systematic error, increasing in magnitude with diffraction angle. The overall result is to decrease appreciably the Debye–Waller temperature factors (*e.g.* Al ~ 11%; KCl ~ 15%, for the examples given in Table 1).

Although the Mössbauer measurements may be subject to some uncertainty, the reasonable agreement obtained with the predicted values for Al and KCl would appear to make further such measurements worthwhile.

The author gratefully acknowledges the help of Dr E. G. Steward for valuable discussion and kindly interest during the progress of this work.

APPENDIX

Approximate relationships to calculate $\langle K[ABC]_{hkl}\rangle$ for cubic crystals

(i) A direct method for calculating an approximate value for $\langle K[ABC]_{hkl}\rangle$ is to find the arithmetic mean, with appropriate weighting, for values of $K[ABC]_{hkl}$ over the $\langle 100\rangle$, $\langle 110\rangle$, and $\langle 111\rangle$ directions, which results in the expression:

$$\langle K[ABC]_{hkl}\rangle_{\text{approx}} = 1/13\,.\,(s_1+4(s_2+s_3+s_4+s_5)+8s_6)\,.$$

$s_1=1/c_{11}$, $s_2=1/c_{44}$, $s_3=1/(c_{11}-c_{12})$, $s_4=1/(c_{11}+c_{12}+2c_{44})$, $s_5=1/(c_{11}+2c_{12}+4c_{44})$, $s_6=1/(c_{11}-c_{12}+c_{44})$ (Ramachandran & Wooster, 1951).

(ii) Nilsson (1957) has also approximated a quantity, $\bar{\kappa}$, (it can readily be shown that $K[ABC]_{hkl}=\frac{1}{3}\,.\,\kappa$) and suggested the expression:

$$\bar{\kappa}_{\text{approx}}=\frac{\frac{1}{5}\,.\,b_1(c_{11}+c_{12})+c_{44}(2c_{11}+c_{44})}{1/105\,.\,b_1^2b_2+\frac{1}{5}\,.\,(c_{11}+c_{12})c_{44}+c_{11}c_{44}^2}\,,$$

where

$$b_1=c_{11}-c_{12}-2c_{44}\,,\ b_2=c_{11}+2c_{12}+c_{44}\,.$$

Both methods of approximation are compared in Table 2 with the more exact evaluation of Nilsson (1957).

References

Butt, N. M. & O'Connor, D. A. (1967). *Proc. Phys. Soc.* **90**, 247.
Chipman, D. R. & Paskin, A. (1959). *J. Appl. Phys.* **30**, 1992, 1998.
Cochran, W. (1963). *Rep. Progr. Phys.* **26**, 1.
Cochran, W. & Pawley, G. S. (1964). *Proc. Roy. Soc.* A**280**, 1.
Cooper, M. J. & Rouse, K. D. (1968). *Acta Cryst.* A**24**, 405.
James, R. W. (1962). *The Optical Principles of the Diffraction of X-rays.* London: Bell.
Kamm, G. N. & Alers, G. A. (1964). *J. Appl. Phys.* **35**, 327.
Laval, J. (1939). Thesis, Paris.
Lonsdale, K. (1942). *Proc. Phys. Soc.* **54**, 314.
Lucas, B. W. (1968). *Acta Cryst.* A**24**, 336.
Nilsson, N. (1957). *Ark. Fys.* **12**, 247.
Norwood, M. H. & Briscoe, C. V. (1958). *Phys. Rev.* **112**, 45.
O'Connor, D. A. & Butt, N. M. (1963). *Phys. Letters*, **7**, 233.
Prasad, S. C. & Wooster, W. A. (1956). *Acta Cryst.* **9**, 38.
Ramachandran, G. N. & Wooster, W. A. (1951). *Acta Cryst.* **4**, 335, 431.
Schwartz, L. H. (1964). *Acta Cryst.* **17**, 1614.
Warren, B. E. (1953). *Acta Cryst.* **6**, 803.
Wooster, W. A. (1962). *Diffuse X-ray Reflexions from Crystals.* London: Oxford Univ. Press.

Acta Cryst. (1969). A**25**, 631

Thermal Etching of Dislocations in Zinc Crystallites Grown from the Vapour

By Ram Bilas Sharma*

Applied Sciences Department, Punjab Engineering College, Chandigarh, India

(*Received* 9 *October* 1968 *and in revised form* 22 *January* 1969)

Small single crystals of zinc of 99·99% purity were grown from the vapour at a temperature slightly less than the melting point. The dislocation structure of these crystallites was studied by thermal etching, which occurs when the crystals are cooled from the growth temperature to 10 to 15 °C below the melting point in a few minutes. Various types of etch figures were observed and the mechanisms of their formation are discussed. It seems, on the basis of the available evidence, that the etch figures correspond to dislocations.

Introduction

It is known that thermal etching can be applied to reveal dislocations in crystals of a number of metals and alloys, with the important exceptions of Zn, Cd, Mg and their alloys, which have a high vapour pressure at high temperatures.

It is shown here for the first time that thermal etching can also be applied to reveal dislocations in zinc crystals if the conditions of high vacuum and low undersaturation of vapour are obtained. The latter condition

---

* Present address: Physics Department, Shyam Lal College, Delhi University, Shahdara, Delhi-32, India.