

Our thanks are due to Dr B. Raistrick, of Scottish Agricultural Industries Ltd, for suggesting this problem, and to the Agricultural Research Council for a grant to purchase apparatus. One of us (G. M.) is indebted to the Department of Scientific and Industrial Research for a maintenance allowance during the period of this research.

References

- BEEVERS, C. A. & MACINTYRE, D. (1946). *Miner. Mag.* **27**, 254.
 BEEVERS, C. A. & RAISTRICK, B. (1954). *Nature, Lond.* **173**, 542.
 BEEVERS, C. A. & ROBERTSON, J. H. (1950). *Acta Cryst.* **3**, 164.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 DICKSON, E. C. S. & BINKS, W. (1926). *Phil. Mag.* (7), **2**, 114.
 GROTH, P. (1908). *Chemische Krystallographie*, vol. 2, p. 820. Leipzig: Engelmann.
 HOWELLS, E. R., PHILLIPS, D. C. & ROGERS, D. (1950). *Acta Cryst.* **3**, 210.
 LEHR, J. R., SMITH, J. P. & BROWN, W. E. (1952). S. E. Regional Meeting, American Chemical Society, October 1952.
 SMITH, J. V. (1953). *Acta Cryst.* **6**, 9.
 WELLS, A. F. (1945). *Structural Inorganic Chemistry*. Oxford: Clarendon Press.

Acta Cryst. (1955). **8**, 583

The Crystal Structure of Hydroxylamine

BY EDWARD A. MEYERS AND WILLIAM N. LIPSCOMB

School of Chemistry, University of Minnesota, Minneapolis 14, Minnesota, U.S.A.

(Received 25 April 1955)

Four molecules of hydroxylamine are in an orthorhombic unit cell of symmetry $P2_12_12_1$ and dimensions $a = 7.29$, $b = 4.39$, $c = 4.88$ Å. The coordinates $x_O = 0.060$, $y_O = -0.062$, $z_O = -0.023$, $x_N = 0.121$, $y_N = 0.244$ and $z_N = 0.063$ lead to the N-O bond distance of $1.47_6 \pm 0.03$ Å, and to the closest intermolecular contacts of $N \cdots O = 2.74$, 3.07 , 3.11 and 3.18 Å. Hydrogen bonds are presumed to lie in the 2.74 and 3.07 Å contacts, thus leaving the third hydrogen atom of the molecule uninvolved, and indicating a *trans* configuration for the molecule. No residual entropy is indicated, and no transition occurs when the solid is cooled to -185° C.

Introduction

Two spectroscopic investigations of hydroxylamine, one of the solid and gas by Giguère & Liu (1952), and one of the solid at low temperature by Nightingale & Wagner (1954), have recently been made. These studies differ somewhat in the observations, and the assignments of the bands are different. In particular, Nightingale & Wagner assigned the broad, intense band at 2867 cm.^{-1} to a strong hydrogen bond.

In the hope that we could provide some information relating to these spectroscopic studies, and in the expectation that the structure might be closely related to those shown by hydrazine (Collin & Lipscomb, 1950, 1951), hydrogen peroxide (Abrahams, Collin & Lipscomb, 1951), methanol (Tauer & Lipscomb, 1952), and methylamine (Atoji & Lipscomb, 1953), we have carried out a study of the crystal structure as described below. Low-temperature techniques were employed partly because of the low melting point of 33° C., but chiefly because of the tendency towards rapid decomposition near room temperature.

Experimental

Hydroxylamine, prepared by the method of Hurd (1939), was transferred to a vacuum line and was

partially further purified by pumping out volatile impurities for periods up to 30 min. The usual techniques of sublimation into capillaries produced impure samples, so that a modified technique was used. A section of glass tubing between the sample and vacuum pumps was drawn down to capillary diameter. With the pumps maintained in operation, a short length of this constricted region was cooled to near liquid-nitrogen temperature, allowed to warm for a short time, cooled again, with the low-temperature stream of nitrogen, and then sealed on both sides of the small slug of solid hydroxylamine. Thus prepared, the samples were stored in dry ice.

X-ray diffraction data were collected on the precession camera from a single crystal, grown with the use of a warm air stream, and maintained at -60° C. during photography. Mo $K\alpha$ radiation was used, and precession angles of 21° for the $\{h0l\}$ zone and 30° for the $\{hko\}$, $\{0kl\}$, $\{hkh\}$ and $\{2h,k,h\}$ zones were employed. No X-ray diffraction evidence of a phase transition was observable at temperatures down to -185° C.

Intensities were estimated visually with the use of a standard scale of timed exposures of a reflection from a crystal of NaCl of comparable size. The usual Lorentz and polarization corrections (Waser, 1951)

were made, the resulting reduced intensities were correlated to the same relative scale with the use of common reflections, and observed structure amplitudes were then calculated.

Structure determination

Reciprocal-lattice symmetry D_{2h} , and the systematic extinctions of only the axial reflections having odd indices, lead uniquely to the space group $D_{2h}^1-P2_12_12_1$. Unit-cell dimensions are

$$a = 7.29_2, b = 4.39_2, c = 4.87_5 \text{ \AA}.$$

The assumption of four molecules of NH_2OH in this unit cell leads to a calculated density of 1.40 g.cm.^{-3} , in agreement with the value of 1.35 g.cm.^{-3} observed by De Bruyn (1892). No molecular symmetry is demanded by the space group, since the molecule necessarily occupies the general position.

Ignoring, for the start, the hydrogen atoms and the difference between N and O, an approximate structure was found by trial-and-error methods. Refinement by

Fourier methods, using the well-resolved c -axis projection (Fig. 1(a)) and the poorly resolved a -axis (Fig. 2(a)) and $[10\bar{1}]$ -axis (Fig. 3(a)) projections, yielded values of coordinates for N and O. These values eventually proved to be within an average deviation of ± 0.001 and a maximum deviation of 0.002 of the final values.

The c -axis projection indicated a significant difference between the electron densities of the two heavy atoms. The model indicated by this projection (Fig. 1(b)) is designated as Model I, while that obtained by reversing the positions of N and O is called Model II. A careful comparison of these two models was then made. Because of lack of resolution in the projections along b , a and $[10\bar{1}]$, an analytical comparison was made by calculation of

$$S = \frac{\sum (|F_o| - |F_c|)^2}{\sum |F_o|^2} \quad \text{and} \quad R = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|},$$

assuming temperature factors $\exp(-B \sin^2 \theta / \lambda^2)$ with $B = 1.5$ and 3.0 \AA^2 . The results are, for Models I and II:

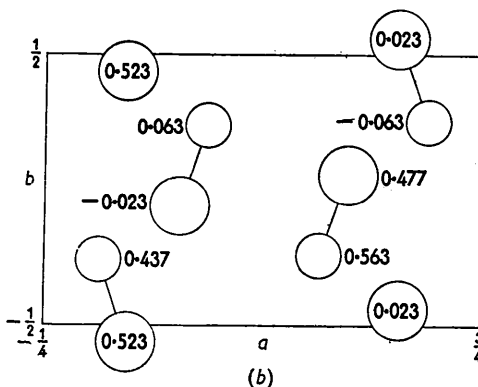
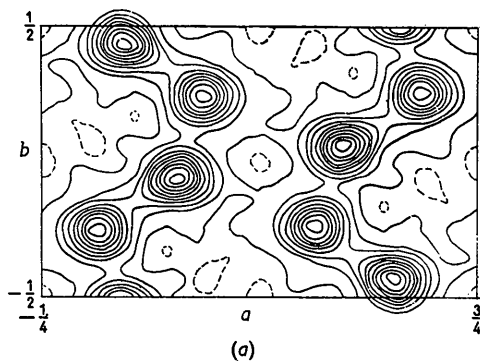


Fig. 1. (a) Projection of the electron density along the c axis. Contours are in intervals of $1 \text{ e.}\text{\AA}^{-2}$. The contour for $1 \text{ e.}\text{\AA}^{-2}$ is broken. (b) Explanation of (a), showing out-of-plane coordinates. The smaller circles represent N and the larger circles O atoms.

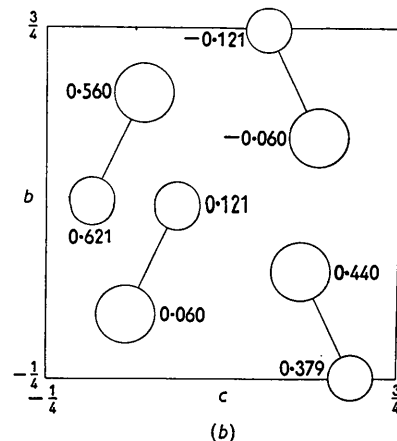
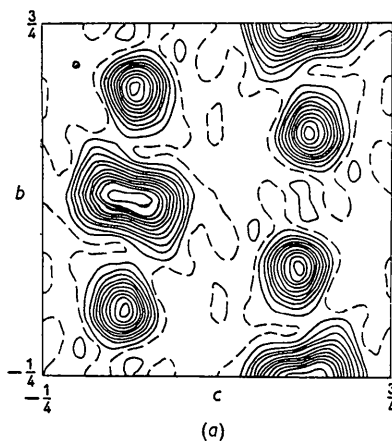


Fig. 2. (a) Projection of the electron density along the a axis. Contours are in intervals of $1 \text{ e.}\text{\AA}^{-2}$. The contour for $1 \text{ e.}\text{\AA}^{-2}$ is broken. (b) Explanation of (a), showing out-of-plane coordinates. The smaller circles represent N and the larger circles O atoms.

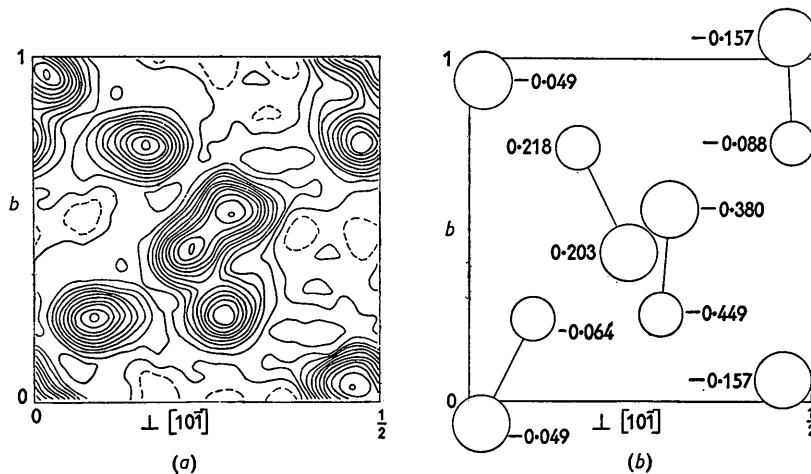


Fig. 3. (a) Projection of the electron density along the $[10\bar{1}]$ axis. Contours are in intervals of $1 \text{ e.}\text{\AA}^{-2}$. The contour for $1 \text{ e.}\text{\AA}^{-2}$ is broken. (b) Explanation of (a), showing out-of-plane coordinates. The smaller circles represent N and the larger circles O atoms.

For $B = 1.5$:

$$S_{\text{I}} = 0.033, R_{\text{I}} = 0.18, S_{\text{II}} = 0.046, R_{\text{II}} = 0.21;$$

For $B = 3.0$:

$$S_{\text{I}} = 0.046, R_{\text{I}} = 0.21, S_{\text{II}} = 0.062, R_{\text{II}} = 0.25.$$

Thus, in agreement with the c -axis projection, Model I is favoured.

A series of difference projections along a and c were then calculated in which both models were tested. Both values of B were employed. For the quantitative comparison the method of Cruickshank (1949) was used. In summary, the difference in peak heights for Model I is 1.5σ while that for Model II is 4σ , where σ is the standard deviation of electron density in the difference synthesis. Details of this calculation are given elsewhere (Meyers, 1955). Again the results support Model I.

Backshift corrections were then calculated, assuming Model I but omitting hydrogen atoms. The largest correction was 0.004 , for the z_{O} parameter, and the corrections were essentially independent of the choice of B at 1.5 or 3.0 \AA^2 . In addition, a least-squares calculation of z_{O} and z_{N} was made with the use of the $\{0kl\}$ data. The final parameter values are

$$x_{\text{O}} = 0.060, y_{\text{O}} = -0.062, z_{\text{O}} = -0.023;$$

$$x_{\text{N}} = 0.121, y_{\text{N}} = 0.244, z_{\text{N}} = 0.063.$$

The final value of $B = 2.3 \text{ \AA}^2$ was found from plots of $\log(F_{\text{O}}/F_{\text{c}})$ versus $(\sin \theta/\lambda)^2$. Comparison of structure factors, without the inclusion of hydrogen atoms, is shown in Table 1. The value of R is 0.17 when only observed reflections are included. However, inclusion of the hydrogen atoms halfway between the non-bonded contacts reduced R from 0.17 to 0.14 for the $\{hk0\}$, $\{0kl\}$ and $\{h0l\}$ reflections.

Location of hydrogen atoms by use of the various difference syntheses described above proved unsuccessful. Aside from the presence of an unresolved maximum in the difference projection along the c axis where packing considerations suggest the overlapping of two hydrogen atoms, we cannot be sure of any direct evidence regarding hydrogen positions from our data.

Discussion

The N–O bond distance is $1.47_{\text{e}} \text{ \AA}$, with an estimated probable error of $\pm 0.03 \text{ \AA}$. This error is meant to include the effect of omission of hydrogen atoms in the refinement, a procedure which may be responsible for the bond being unexpectedly long. The value expected from tables of bond radii is $1.43_{\text{e}} \text{ \AA}$ (Schomaker & Stevenson, 1941) and is somewhat shorter than our value, which, however, is in good agreement with the N–O bond distance of 1.47 \AA in hydroxylamine hydrochloride (Jerslev, 1948; Donohue, 1952). It may be added that an estimate of 1.46 \AA was made by Giguère & Liu from the force constant of the N–O stretching frequency and Badger's rule.

The next longest interatomic distances are $\text{O}_1\text{N}_2 = \text{N}_1\text{O}_2 = 2.74 \text{ \AA}$, $\text{O}_1\text{N}_3 = \text{N}_1\text{O}_3 = 3.07 \text{ \AA}$, $\text{O}_1\text{N}_5 = \text{N}_1\text{O}_5 = 3.11 \text{ \AA}$, $\text{O}_1\text{N}_4 = \text{N}_1\text{O}_4 = 3.18 \text{ \AA}$, and $\text{O}_1\text{O}_3 = 3.24 \text{ \AA}$. All other contacts are greater than 3.5 \AA . The angles are

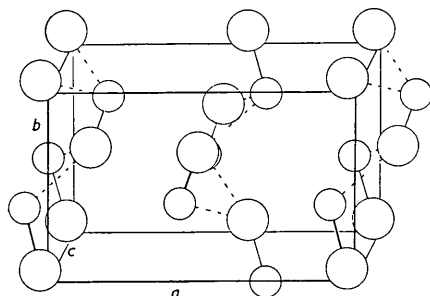


Fig. 4. Isometric drawing of the hydroxylamine structure. Probable hydrogen bonds are indicated by broken lines connecting the smaller circles (N) and the larger circles (O).

Table 1. Comparison of $|F_o|$ and $|F_c|$ Values of $|F_c|$ include contributions only of N and O.

hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_c $	hkl	$ F_o $	$ F_c $
200	17.5	19.0	414	1.7	1.6	333	2.3	1.5
400	9.8	10.1	015	3.0	2.8	633	2.4	1.7
600	6.4	5.7	016	1.5	1.9	034	3.2	1.0
101	3.9	2.4				434	3.1	2.4
201	28.5	30.8	020	4.2	1.2	035	2.8	1.3
301	4.3	4.5	120	12.4	10.3			
401	14.6	13.9	220	8.4	7.0	040	5.5	5.0
501	<i>a</i>	1.8	320	4.9	4.1	140	6.6	6.3
601	<i>a</i>	0.4	420	7.1	7.9	240	<i>a</i>	0.3
002	24.6	28.7	520	<i>a</i>	1.3	340	<i>a</i>	1.7
102	6.5	5.1	620	<i>a</i>	2.0	440	4.0	3.7
202	10.5	11.7	720	<i>a</i>	2.8	540	1.9	1.5
302	<i>a</i>	2.1	820	3.2	5.2	041	<i>a</i>	0.6
402	6.5	5.0	021	3.1	2.0	141	5.1	2.9
502	5.2	4.8	121	7.1	5.9	241	3.7	4.2
602	6.0	4.3	221	4.0	3.2	042	4.2	3.0
103	2.1	1.4	022	1.3	1.8	242	<i>a</i>	0.5
203	12.8	9.8	222	5.6	5.5	442	2.7	2.6
303	6.0	5.9	422	3.9	4.6	043	<i>a</i>	1.2
403	8.8	7.2	023	3.9	3.0	343	4.3	3.5
503	3.8	2.8	323	5.1	4.6			
004	6.6	6.6	623	2.7	3.2	150	<i>a</i>	0.1
104	3.6	2.4	024	4.0	3.6	250	<i>a</i>	0.9
204	5.1	4.2	424	<i>a</i>	1.6	350	<i>a</i>	0.6
			025	3.2	2.0	450	2.3	2.3
110	9.6	8.7	525	3.3	2.3	550	<i>a</i>	1.1
210	13.4	11.4	026	3.7	2.8	650	3.0	3.2
310	13.0	14.6				051	<i>a</i>	0.4
410	1.5	3.9	130	<i>a</i>	0.9	151	<i>a</i>	1.2
510	5.7	8.3	230	13.0	13.0	251	2.7	2.0
610	5.5	7.5	330	2.9	2.3	052	<i>a</i>	0.7
011	11.0	8.6	430	6.0	6.8	452	1.6	2.0
111	16.9	19.9	530	2.2	2.3	053	1.4	1.3
211	4.5	4.9	031	17.1	15.9	353	3.0	2.3
012	2.2	4.2	131	4.4	3.2			
212	5.5	5.0	231	5.7	6.3	060	3.8	3.5
412	2.3	4.1	032	4.1	1.4	061	<i>a</i>	0.4
013	<i>a</i>	0.7	232	9.0	8.4	161	<i>a</i>	0.4
313	5.6	6.5	432	4.3	5.1	261	3.0	2.5
014	3.3	3.4	033	7.8	7.0	062	2.7	2.4

$$N_1ON_2 = 101^\circ 9', \quad N_1O_1N_3 = 128^\circ 50',$$

$$N_1O_1N_4 = 100^\circ 52', \quad O_1N_1O_2 = 110^\circ 46',$$

$$O_1N_1O_3 = 83^\circ 7', \quad N_1O_1O_3 = 70^\circ 1',$$

$$O_4N_1O_2 = 84^\circ 54', \quad O_4N_1O_3 = 158^\circ 15',$$

$$O_3N_1O_2 = 114^\circ 9', \quad N_3O_1N_2 = 114^\circ 9',$$

$$N_4O_1N_2 = 142^\circ 32', \quad N_4O_1N_3 = 107^\circ 26',$$

$$N_1O_1N_5 = 144^\circ 12', \quad O_1N_1O_4 = 99^\circ 55'$$

$$\text{and } O_1N_1O_5 = 144^\circ 12'.$$

It seems reasonable to discard the O_1O_3 contact and the N_1O_5 and O_1N_5 contacts as possibilities for hydrogen bonding because of their lengths, and because of their very large deviations of $-39^\circ 27'$, $+34^\circ 44'$, $+34^\circ 44'$ of the corresponding angles, $N_1O_1O_3$, $O_1N_1O_5$ and $N_1O_1N_5$, from the approximately tetrahedral hybridization expected about the N and O atoms in NH_2OH . The value of 3.1 Å for $N_1O_5 = O_1N_5$ is indeed very nearly that expected for van der Waals contact between N and O in molecular crystals, in which the O radius of 1.45 Å is suggested from H_2O_2 and the N radius of 1.65 Å is suggested from hydrazine. Indeed, this value of 3.1 Å makes doubtful the oc-

currence of a hydrogen bond in the $O_1N_4 = N_1O_4$ distance of 3.18 Å, thus leaving the 2.74 Å and 3.07 Å distances as the most likely positions for hydrogen bonding.

If hydrogen bonds are assumed in the 2.74 and 3.07 Å distances, the structure bears a strong resemblance to that of H_2O_2 and a striking resemblance to that of N_2H_4 . In all of these structures, chains of hydrogen bonds extend approximately along major crystallographic axes. These bonds link both ends of these three molecules in each of their structures, and, in a similar way, the bonds in methanol and in methylamine link the polar ends of these molecules strongly.

The effect of assuming an additional hydrogen bond in the 3.18 Å distance is not so satisfactory. Although the angles defining hydrogen bonds do lie within the relatively large range summarized by Donohue (1952), the resulting effort to use up the remaining hydrogen atom and electron pair of the molecule in what would be an unusually long hydrogen bond produces apparently unacceptable deviations of the hybridization about N and O from the expected roughly tetrahedral

angles. Although a somewhat similar arrangement occurs in *p*-aminophenol (Brown, 1951) in which distances of 2.83, 3.13 and 3.18 Å are found at considerably more favourable angles than those shown by hydroxylamine, it seems best to us to leave one hydrogen atom of NH₂OH uninvolved in hydrogen bonding and to assume such bonds only in the 2.74 and 3.07 Å distances.

It is of interest to ask what is the configuration of the molecule, and where are the hydrogen atoms. Considerable effort was made to see if our data were capable of yielding any direct information, with results described in detail elsewhere (Meyers, 1955). In summary, a detailed examination of structure factors, not given here, for three different possible arrangements of hydrogen bonds

- (a) O₁-H...N₂ = 2.74 Å, N₁-H...O₃ = 3.07 Å;
 (b) N₁-H...O₂ = 2.74 Å, O₁-H...N₃ = 3.07 Å;
 (c) N₁-H...O₂ = 2.74 Å, N₁-H...O₃ = 3.07 Å

yielded, respectively, values of $R = 0.16, 0.16$ and 0.17 for all observed reflections, thus supplying no direct evidence regarding the hydrogen positions. Nevertheless, all three of these possible models lead to NH₂OH molecules which, if isolated from the crystal, would have very nearly the *trans* configuration of symmetry C_s . This result lends some support to a model of C_s symmetry in the gas phase, assumed by Giguère & Liu, in so far as extrapolations of from solid to gas are valid.*

* While normally the same geometry occurs in the solid and gas, the binding forces in the solid are occasionally sufficient to produce some modifications of orientation about

It is a pleasure to acknowledge support of this research by the Office of Naval Research and to thank Dr Peter A. Howell for assistance in obtaining the diffraction patterns.

References

- ABRAHAM, S. C., COLLIN, R. L. & LIPSCOMB, W. N. (1951). *Acta Cryst.* **4**, 15.
 ATOJI, M. & LIPSCOMB, W. N. (1953). *Acta Cryst.* **6**, 770.
 BROWN, C. J. (1951). *Acta Cryst.* **4**, 100.
 COLLIN, R. L. & LIPSCOMB, W. N. (1950). *J. Chem. Phys.* **18**, 566.
 COLLIN, R. L. & LIPSCOMB, W. N. (1951). *Acta Cryst.* **4**, 10.
 CRUICKSHANK, D. W. J. (1949). *Acta Cryst.* **2**, 65.
 DE BRUYN, L. (1892). *Rec. Trav. chim. Pays-Bas*, **11**, 18.
 DONOHUE, J. (1952). *J. Phys. Chem.* **56**, 502.
 GIGUÈRE, P. A. & LIU, I. D. (1952). *Canad. J. Chem.* **30**, 948.
 HURD, C. D. (1939). *Inorganic Synthesis*, vol. 1, p. 87. New York: McGraw-Hill.
 JERSLEV, B. (1948). *Acta Cryst.* **1**, 21.
 MEYERS, E. A. (1955). Ph.D. Thesis, University of Minnesota.
 NIGHTINGALE, R. E. & WAGNER, E. L. (1954). *J. Chem. Phys.* **22**, 203.
 SCHOMAKER, V. & STEVENSON, D. P. (1941). *J. Amer. Chem. Soc.* **63**, 37.
 TAUER, K. J. & LIPSCOMB, W. N. (1952). *Acta Cryst.* **5**, 606.
 WASER, J. (1951). *Rev. Sci. Instrum.* **22**, 567.

single bonds. In hydrazine an eclipsed form was found. Presumably the singly eclipsed form of hydrazine is only a small deviation from the geometry presumed to exist in the gas phase as indicated in the first drawing of Fig. 1 in the paper by Collin & Lipscomb (1950).

Acta Cryst. (1955). **8**, 587

The Structure of Guinier-Preston Zones. I. The Fourier Transform of the Diffuse Intensity Diffracted by a Guinier-Preston Zone

By KAREL TOMAN

The Research Institute of Metals, Panenské Břežany, P.O. Odolena Voda, Czechoslovakia

(Received 24 January 1955 and in revised form 4 March 1955)

The expression for the diffuse intensity diffracted by the Al-Cu alloy with Guinier-Preston zones is derived as a trigonometrical series with coefficients dependent on the structure. It is shown that the coefficients can be determined with the aid of the Fourier transform of the integrated diffuse intensity in relrod (00 l). From these coefficients it is possible to deduce the features which are characteristic of the structure of Guinier-Preston zones.

1. Introduction

The anomalous diffraction effects in Al-Cu and Al-Cu-Mg alloys in the age-hardened stage are well known (Preston, 1938; Guinier, 1938). They corre-

spond approximately to diffraction by a two-dimensional lattice and they are usually connected with the formation of two-dimensional copper-rich regions in the (001) planes of the matrix. The asymmetrical intensity distribution around the reciprocal lattice