STRUCTURE REPORTS

FOR 1954

Volume 18

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PUBLISHED FOR THE

INTERNATIONAL UNION OF CRYSTALLOGRAPHY

BY

N.V. A. OOSTHOEK'S UITGEVERS MIJ
UTRECHT

First published in 1961

Printed in the Netherlands
Kon. Drukkerij Van de Garde N.V., Zaltbommel

SYMBOLS

The letters a, b, c; α, β, γ are used consistently for the edges and angles of the unit cell. Other letters used consistently are as follow.

U	Volume of unit cell
D_m	Measured density or specific gravity
D_x	Density calculated from cell volume and contents
Z	Number of times the formula quoted is repeated in the unit cell (Number of atoms per unit cell in alloys of simple structure)
x, y, z	Atomic coordinates as fractions of cell edge (Occasionally u, v, w or other letters are used)
X, Y, Z	Atomic coordinates in Ångström units
X', Y, Z'	Atomic coordinates in Ångström units, referred to orthogonal axes (Used only in the Organic Section)
F.W.	Formula weight
A, B, C	Types of layer in layer structures
M, A, B	Variable metal atom(s) in a sequence of related structures
X, H	Variable non-metals, usually halogen, in a sequence of related structures
R	Variable organic radical
s, m, w, v, b	Strong, medium, weak, very, broad

LIMITS OF ERROR

Errors are quoted in units in the last place. Thus 4·8754 ± 3 means 4·8754 ± 0·0003, 4·87 ± 3 means 4·87 ± 0·03, and 4·875 ± 15 means 4·875 ± 0·015. Occasionally a very doubtful last digit has been placed in parentheses.

TRANSLITERATION OF RUSSIAN

а	a	и	i	р	r	ш	š
б	b	й	j	с	s	щ	šč
в	v	к	k	т	t	ы	y
г	g	л	l	у	u	ъ	″
д	d	м	m	ф	f	ь	′
е	e	н	n	х	kh	э	ė
ж	ž	о	o	ц	c	ю	ju
з	z	п	p	ч	č	я	ja

INTRODUCTION

Structure Reports are not intended to be abstracts in the ordinary sense. Ideally they extract only the material of structural interest in the paper reported, and attempt to do this so completely that no further structural information would be gained by consulting the paper itself. On the other hand, material of great interest from other standpoints may be ignored entirely, or dismissed in a few indicative words. The report of a short structural paper is occasionally longer than the paper itself, interatomic distances, say, having been added by the abstractor; long papers mainly of chemical, metallurgical or mineralogical interest may be represented merely by quotation of a cell dimension. The minimum criterion for the preparation of a report is ordinarily that the paper contains the determination or more accurate redetermination of a unit cell, but investigations of texture, papers containing powder data, and electron-diffraction studies have been reported when of some structural interest. Papers of this type in Russian and other journals not readily available have been included more freely than those in easily accessible sources.

The arrangement within individual reports is usually Name, Formula, Papers reported, Unit cell, Space group, Atomic positions and parameters, Interatomic and intermolecular distances, Material, Discussion, Details of analysis, References. The first, third and last of these are invariable, but deviations in the order of the rest occur whenever a gain in brevity or clarity is achieved. Editorial comments are enclosed in square brackets; it may be assumed that material not distinguished in this way is based directly on the papers reported.

This volume of *Structure Reports* is divided into three main sections: Metals, Inorganic Compounds, Organic Compounds. In the Metals section the arrangement is alphabetical; details are given on p. 2.

No simple alphabetical arrangement seemed practicable for the Inorganic and Organic sections. Classification according to structure type also seemed impracticable, and was in fact falling into disuse in the later volumes of *Strukturbericht*. Reports in these sections, therefore, are placed roughly in order of increasing complexity of composition, related substances and related structures being kept together as far as possible. Inorganic and organic compounds should be sought in the subject or formula index.

The subject index is arranged alphabetically by the names printed as the headings of reports, and some effort has been made to include other common names. It has not been possible to do this systematically, however, and if no entry is found for the name first thought of, search should be made under a reasonable alternative, or in the formula index. As a result of the experience gained in compiling vol. 14 some small improvements have been made in the subject index.

In the formula index the constituents are arranged in the *alphabetical order of the chemical symbols*; this is unique, and conventional orders such as the electrochemical series are likely to cause trouble to crystallographers not trained as chemists. At the request of certain organic chemists an additional index of carbon compounds is included, in which the primary classification is by the number of carbon atoms and the secondary classification is by the number of hydrogen atoms, without regard to the nature of the other atoms present.

The scheme of transliteration of Russian usually employed is reproduced on p. VI, and the usual abbreviations of journal titles are given on p. 792. Transliteration is in accordance with draft recommendation no. 6 of the International Organization for Standardization (which is, unfortunately, subject to revision), and the abbreviations are based on the World List of Scientific Periodicals.

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6 June 1961

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STRUCTURE REPORTS

SECTION I

METALS

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ARRANGEMENT

In the **Metals** section of *Structure Reports* the arrangement is strictly alphabetical, and metals and alloys are not included in the subject and formula indexes. Thus magnesium-copper alloys should be sought under **Copper Magnesium,** steels under **Carbon Iron** (not iron carbon), and solutions of hydrogen in tantalum under **Hydrogen Tantalum.** When there is a reasonable doubt whether a substance should be classed as a metal or as an inorganic compound a cross-reference is usually given, but this is not always practicable. To be sure that information regarding such substances is not overlooked, therefore, search should be made both in the appropriate place in the Metals section (for example, **Tellurium Vanadium**) and under the appropriate name in the subject index (for example, Vanadium telluride).

Miscellaneous reports (pp. 324—332), included in the Metals section for the first time, are fully indexed in the subject index.

The names and spellings aluminum, beryllium, caesium, niobium, sulphur and wolfram should be noted.

Aluminum

I. [On the study of the crystal lattice potential by the electron-diffraction method.] B. K. VAJNŠTEJN, 1954. *Trudy Inst. Krist. Akad. Nauk SSSR*, No. 9, 259—276.

Sections showing the lattice potential of Al, Cu and Ag along the ⟨100⟩, ⟨110⟩ and ⟨111⟩ directions are given (figs. 1, 2 and 3). The potential is spherically

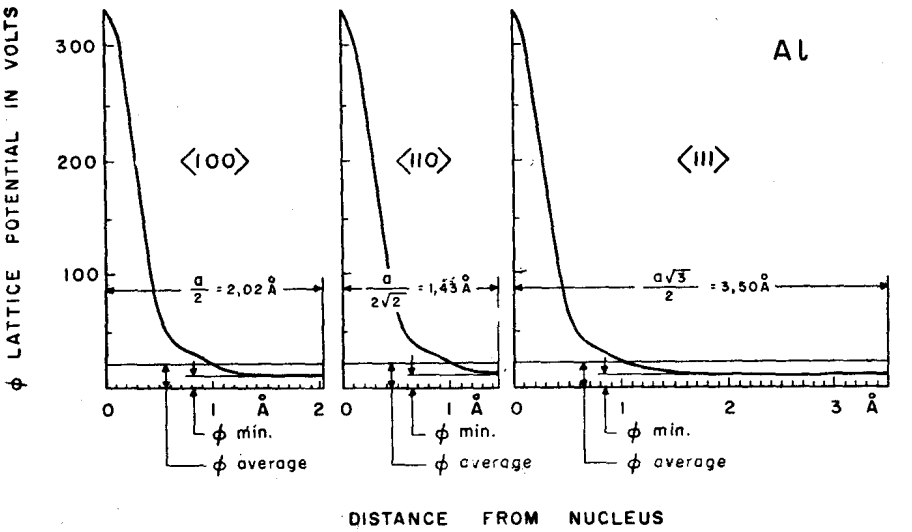

Fig. 1. Lattice potential of aluminum along the ⟨100⟩, ⟨110⟩ and ⟨111⟩ directions.

symmetrical near the nucleus and departs from this symmetry at a distance larger than about 0·4 Å. The maximum value of the potential [uncorrected for series-termination effect] is ~ 320 V for Al, ~ 750 V for Cu and ~ 850 V for Ag. Series-termination error was examined for Al along ⟨100⟩ and found to amount to about 20 V at the nucleus (see fig. 4).

Details of analysis

The lattice potential was derived by Fourier analysis from electron-diffraction data of I. I. YAZIN.

II. Röntgenographische Bestimmung der Elektronenverteilung im Aluminium. H. BENSCH, H. WITTE and E. WÖLFEL, 1954. *Z. phys. Chem.*, **1**, 256—258.

Reflexions up to $\Sigma h^2 = 100$, obtained with Mo radiation in transmission, were measured for single crystals of aluminum, and extinction was determined by comparison with reflexions from fine texture-free powders. The errors in the observed structure amplitudes were said to be 1% for the strongest reflexions and 1·5 to 2% for the weaker ones. The temperature factor, $B = 0{\cdot}78(1) \times 10^{-16}$ cm^2,

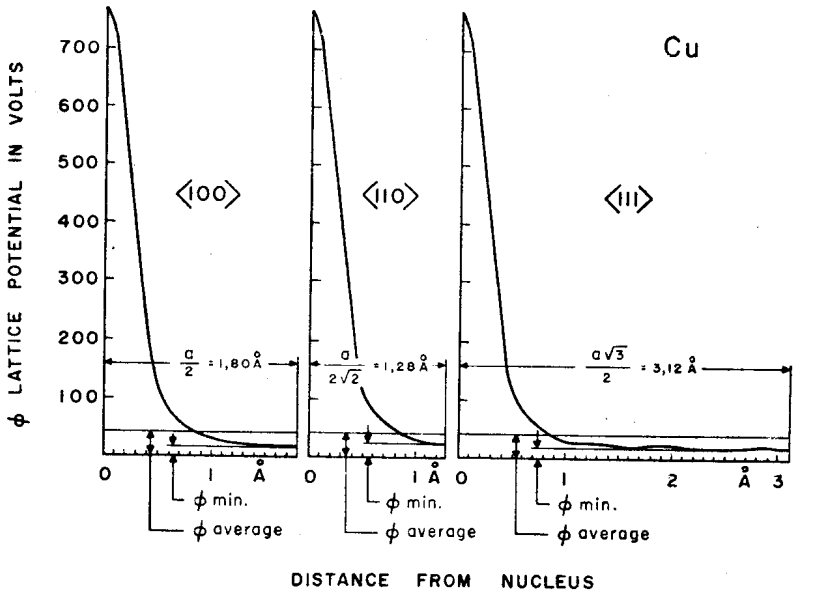

Fig. 2. Lattice potential of copper along the ⟨100⟩, ⟨110⟩ and ⟨111⟩ directions.

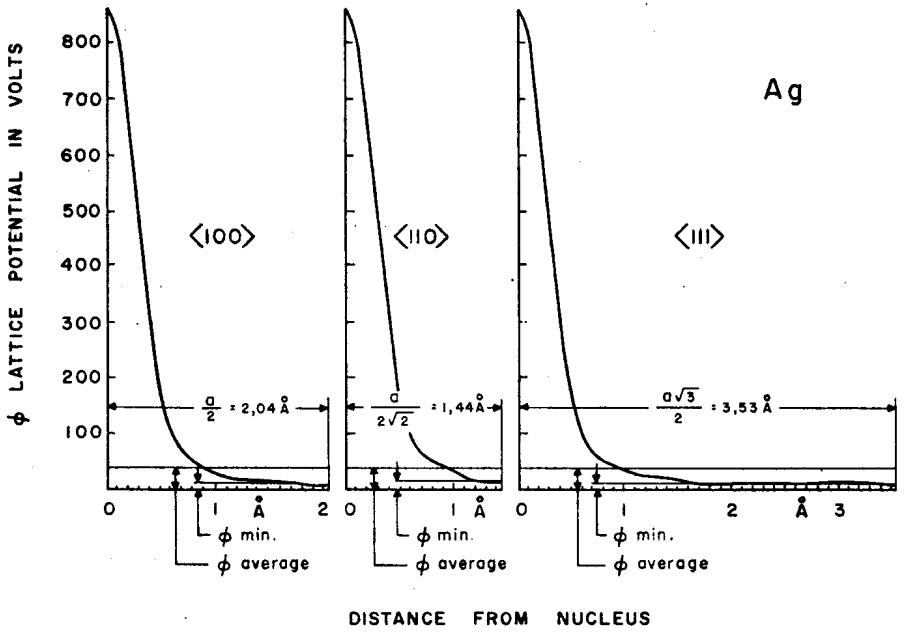

Fig. 3. Lattice potential of silver along the ⟨100⟩, ⟨110⟩ and ⟨111⟩ directions.

determined by comparison of experimental and theoretical structure amplitudes, was larger than that found by James *et al.* (**1**).

The electron density in the *xy*0 plane, obtained by a three-dimensional Fourier synthesis, was shown in a diagram. The electron density between the atoms was found to be practically constant, having an average value of 0·17(3) electrons per Å^3. (This average refers to the region bounded by the contour for 0·2 electrons

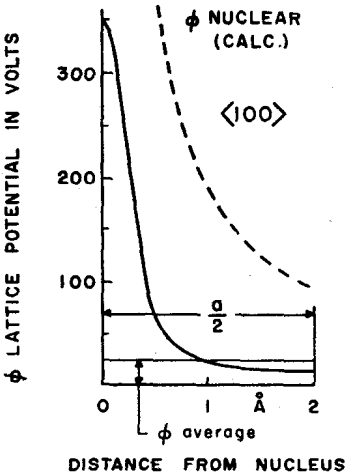

Fig. 4. Lattice potential of aluminum along the ⟨100⟩ direction. Calculations corrected for series-termination errors. – – – – Calculated lattice potential for nucleus alone.

per Å^3.) On the assumption that this is the density of the conduction electrons and that it is constant throughout the unit cell, a value of 2·8 conduction electrons per atom is obtained. The electrons specifically associated with each atom (those above the density contour for 0·2 electrons per Å^3) are then 10·2 per atom (see also **2**).

III. Measurement of electron diffraction intensities by means of Geiger counters. Experimental determination of relative values of the atomic factor for gold, silver and aluminium. S. LENNANDER, 1954. *Ark. Fys.*, **8**, 551—613.

See also **3**.

An electron-diffraction apparatus for accurate intensity measurements using Geiger counters is described. From measurements of the relative intensities of various Debye-Scherrer lines, the atomic factor curves for Au (30 kV and 18 kV radiation) Ag (29.5 kV radiation) and Al (27 kV radiation) were derived. In each case the curve of atomic factor for electrons against sin θ/λ is less steep than that predicted by kinematic theory.

Materials

Foils (about 75 Å thick) of Au, Ag and Al were examined. From the widths of the diffracted beams they were found to have mean crystallite sizes of 50, 60, and

110 Å respectively. Foils of Au and Ag were randomly oriented, but those of Al showed some preferred orientation.

IV. An X-ray study of the substructure of fine-grained aluminium. S. WEISSMANN and D. L. EVANS, 1954. *Acta Crystallogr.*, **7**, 733—737.

See also **4**.

The grain substructure of fine-grained Al was investigated in a 'double-crystal diffractometer'. For a given temperature of annealing, the angular tilt between adjacent sub-grains increases with increasing reduction by cold-rolling, and the lattice imperfection within a sub-grain also increases.

Material and Details of analysis

Al, cold-rolled to 96, 75 or 50% reduction, was examined after annealing at 300°C for one hour. Crystal-monochromatized radiation is incident on a fixed specimen, and discrete film shifts are made between each specimen position. Each crystallite thus gives an array of spots, similar to the rocking curve of a single crystal. From the intensity distribution in these spots, statistical parameters are computed, and these are a measure of the mean angular tilt between adjacent sub-grains, and of the angular misalignment within a sub-grain.

V. An X-ray microbeam study of polycrystalline specimens of aluminium and iron deformed in tension. A. KELLY, 1954. *Acta Crystallogr.*, **7**, 554—558.

See also **5** and **6**.

Particle size as a function of strain was determined by the method of counting spots. The results for Al specimens having original grain sizes of 27 μ, 37 μ and 53 μ are shown in fig. 5. The grain size appeared to have reached a limiting value of about 2·8 μ at a strain of about 30% when the specimens cracked and broke.

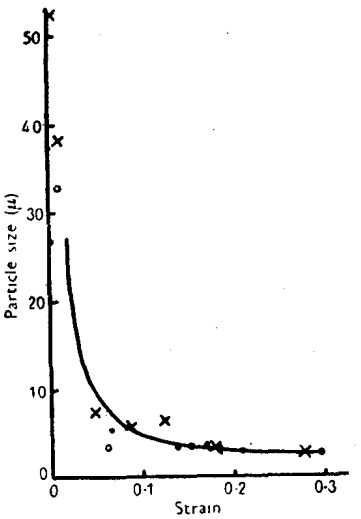

Fig. 5. Variation of particle size with plastic strain for three samples of aluminum.

The average results for three Fe specimens are given in Table I. The spots formed when Fe was strained were much less well resolved and the background connecting them was stronger than in the case of Al.

The total angular range of misorientation of the material within a deformed grain was determined from the angular extent of the arcs around the Debye-Scherrer rings. The average results for a number of Al and Fe specimens are shown in Tables I and II. The misorientation appears to increase up to the point of fracture; however, it is pointed out that the measurements after each straining are not made on the same grains.

Spot shapes were obtained from microbeam photographs by measuring the lengths of discrete spots in directions radial and tangential to the Debye-Scherrer ring (tangentially only for Fe). These were interpreted in the terms introduced by Hirsch (**7**).

Table I. Iron deformed in tension (V).

% strain	Particle size μ	Misorientation
0	~ 20 (grain size	...
3·9	3	2½°
8·9	4·9	4
13·4	1·6	6
Broken	1·5	7

Table II. Aluminum deformed in tension (V).

% strain	Misorientation
3	3°
6	8
13	12
20	16
30	18

Materials

Specimens of 99·994% Al were prepared and strained in tension, unloaded, examined by X-rays and then restrained. The procedure was repeated until the specimens broke, the time between successive strainings being about 2 days.

Fe specimens, prepared from 99·96% deoxidized Fe wire, were similarly treated and examined.

Discussion

The particles in the deformed materials are assumed to occupy the region between the slip bands, and this assumption is used together with the results of a dislocation theory due to Frank (**8**) to account for the stress-strain curves observed. On this basis an approximate agreement between theory and experiment is obtained (the agreement appears good for all but one of the few values calculated for Fe). Hence the shape of the stress-strain curves, for these fine-grained polycrystalline samples, is accounted for solely by the variation of particle size with

strain; the smaller the particle size the more barriers there are per unit length of slip plane.

Details of analysis

After straining the specimens were examined by X-rays in the centre of the gauge length; it was in this position that the specimens always finally fractured. Normal X-ray beams ($\sim$ 1 mm diameter) and microbeams down to a diameter of 30 μ were used for the examination. The Al specimens were photographed with Cu$K\alpha$ radiation and the {422} ring was studied in detail. Fe$K\alpha$ radiation was used for the Fe samples and the {220} ring was studied.

VI. X-ray line broadening from metals deformed at low temperatures. M. S. PATERSON, 1954. *Acta Met.*, **2**, 823—830.

The variation of the corrected diffraction breadths of Debye-Scherrer lines with plastic shear strain is shown in figs. 6, 7 and 8. For Cu, the low-temperature breadth did not change on annealing the specimen for nine months at room

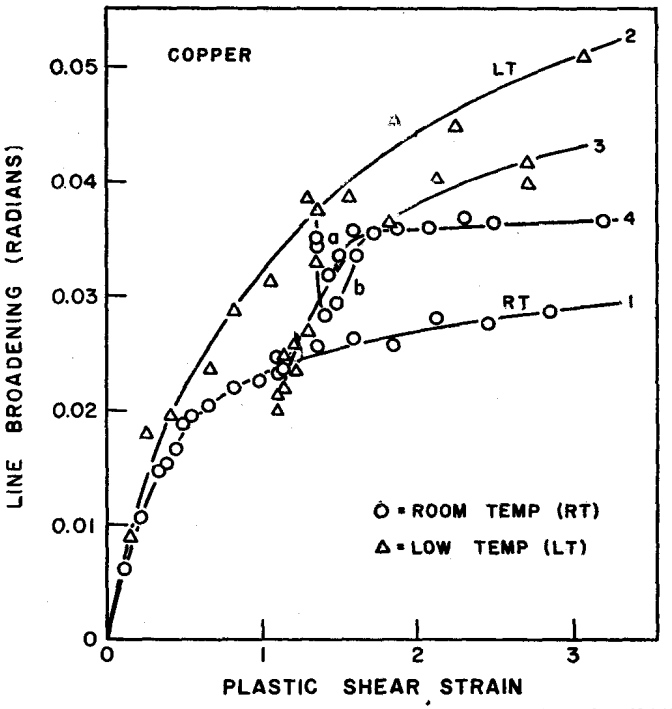

Fig. 6. Copper: the effect of plastic deformation on broadening the {311} reflexion.
Curve 1: Deformation at room temperature.
Curve 2: Deformation at liquid-nitrogen temperature.
Curve 3: Deformation at liquid-nitrogen temperature after a strain of 1·09 at room temperature.
Curve 4: Deformation at room temperature after strain of 1·36 at low temperature. For (*a*) and (*b*) see text.

temperature (allowing for the slight change in Bragg angle with temperature), nor was there any recovery after deforming at room temperature. Appreciable slow changes in line breadth were found when Al specimens were held at room temperature after either low-temperature or room-temperature deformation. A 10% recovery in line breadth was measured on a Ni specimen held for one month at room temperature. The curves 4(*a*) and 4(*b*) in fig. 6 represent separate experiments

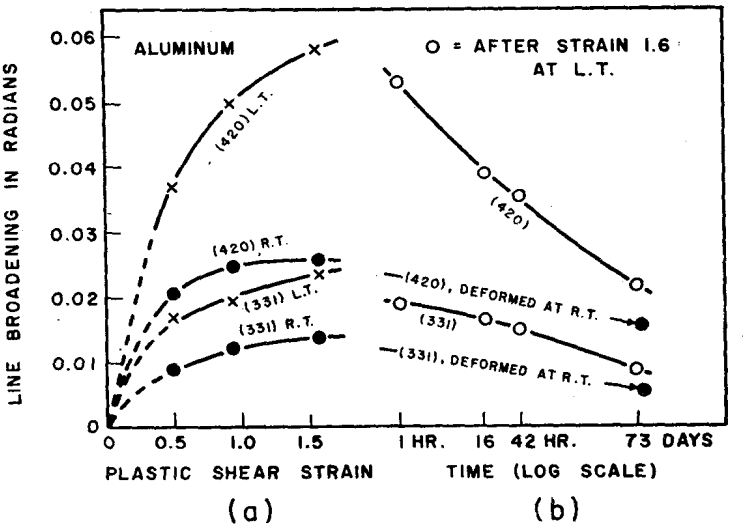

Fig. 7. Aluminum: (*a*) the effect of plastic deformation at room temperature (R.T.) and liquid-nitrogen temperature (L.T.) on the broadening of the {331} and {420} reflexions from aluminum; (*b*) the recovery of the line broadening of Al at room temperature.

to confirm the dip in the curve when the specimen was deformed first at low temperature, and the deformation continued at room temperature.

Torque-twist curves on duplicate specimens were converted to shear stress-strain curves, and were similar to the line-broadening curves. The breadth of the {331} line from Cu after a total surface plastic strain of 2·2, composed of successive increments of 0·05 in opposite senses, was 0·009 radians, about one-third of the breadth corresponding to the same total strain applied unidirectionally.

The results show the limiting line breadth at any temperature is not determined by a recovery process, nor by a limiting crystallite size. They support the hypothesis that the broadening is related to the yield stress of the work-hardened material, and is due to internal stresses which cannot exceed this stress. Internal stresses calculated from the results are of the same magnitude as measured yield stresses.

[Later work has shown that at liquid-nitrogen temperature the line broadening of Cu, and possibly Ni, includes an appreciable contribution from stacking faults if high stresses are attained.]

Material

High-conductivity Cu and commercially pure Al and Ni were examined.

Details of analysis

Wire specimens were deformed in torsion at liquid-nitrogen (liquid-oxygen for Ni) and at room temperature in an apparatus which allowed back-reflexion X-ray photographs to be taken at various stages of the deformation. The main reflexions studied were {311} for Cu (Mn radiation) and {331} and {420} for Al and Ni (Cu and

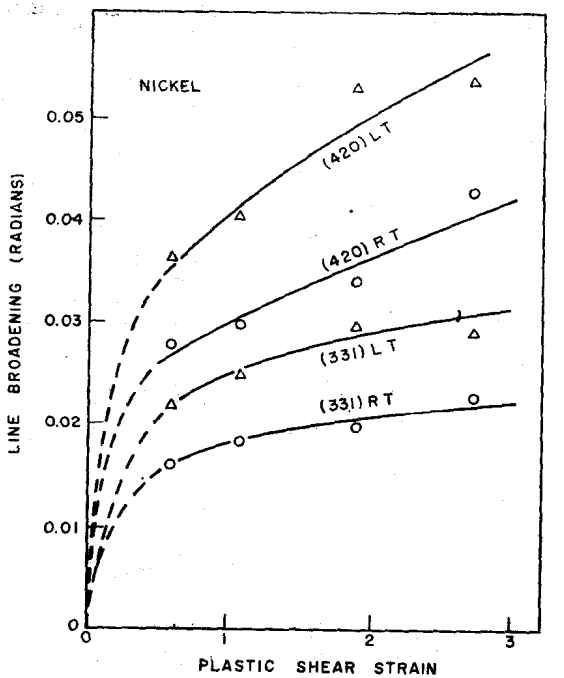

Fig. 8. Nickel: the effect of plastic deformation at room temperature (R.T.) and at liquid-oxygen temperature (L.T.) on the broadening of {331} and {420} reflexions from Ni.

Co radiation respectively). The lines were photometered, and measured integral breadths were corrected for $K\alpha$ doublets and for instrumental factors with the numerical method developed by the author (**9**).

VII. 'Mean strains' in worked aluminium. P. GAY and A. KELLY, 1954. *Acta Crystallogr.*, **7**, 333—336.

Radial displacement of reflexions on back-reflexion photographs have been attributed to variations of the lattice spacing of individual grains (**10**), but such an interpretation has been criticized (**11** and **12**). In the present experiments, using the microbeam technique to examine cold-worked Al, it was concluded that the radial separation of some reflexions on resolved microbeam photographs could only

be accounted for by the assumption that the particles had slightly different lattice parameters (although such effects are due in the main to the geometrical conditions under which the photographs are taken). The calculated difference in mean strain between two particles giving rise to adjacent radially displaced spots was of the same order as the yield stress of the material.

These conclusions were arrived at from the observed data after an analysis of all of the possible causes of the relative radial displacement of the spots on the back-reflexion photographs.

Material and Details of analysis

99·99% pure Al was deformed by rolling and then etched before examination.

Two experiments were undertaken. In the first a lightly (4%) deformed specimen was examined with a microbeam 110 μ in diameter, which had a divergence as small as possible. Two exposures of the {422} ring from the same irradiated volume were taken with Cu$K\alpha$ radiation, one at a specimen-film distance of 1 cm and the other at 1·6 cm. These showed that waviness of the Debye-Scherrer ring did not exist and that the angular divergence of the incident beam was very small. In some positions around the ring the centres of diffraction spots were radially displaced with respect to each other. Since the ratio of the angular displacements on the two rings (taken at 1·0 cm and 1·6 cm distances) did not have the constant value 10/16 the effect was angular and could not be due to position alone.

In the second experiment a heavily rolled specimen was oscillated over $\frac{3}{4}°$ on either side of a vertical axis perpendicular to the incident beam, which had the small diameter of 30 μ. The regions of maximum blackening of the observed streaks on the {422} Debye-Scherrer ring lay closely on a ring of definite radius. The maximum possible spread of the ring was calculated from the geometry of the experimental arrangement to be 15 μ. However, the most intense regions of some pairs of streaks occurring near the equator of the {422} ring were found to be separated by about 50 μ in a radial direction. This had to be attributed to the fact that these particles had different mean strains, since all other known causes of the displacement had been eliminated or allowed for.

VIII. On the strain figure in deformed aluminium crystals observed by X-ray diffraction microscopy. Z. NISHIYAMA and M. YAMAMOTO, 1954. *Mem. Inst. Sci. Res. Osaka Univ.*, **11**, 163—174.

An examination of single or coarse-grained 99·98% Al crystals strained from 1 to 12% in tension was carried out by optical and X-ray diffraction microscopy (Berg-Barrett method, **13** and **14**). The diffraction microscopy revealed two sets of lamellae consisting of light and dark bands. One set (referred to as K), which runs parallel to the kink bands observed by optical microscope, could be detected long before the kink bands could be seen optically. The other set (referred to as S) runs approximately parallel to the slip bands, although in some cases a considerable divergence in these directions was found. The S bands generally appear later in the deformation process than the K bands and they may be absent even though many slip bands can be seen by optical examination of the specimen. K lamellae alone are found in crystals oriented near the ⟨100⟩ zone, but both types of lamellae