

die Abhängigkeit des *h*-Anteils von der Valenzelektronenkonzentration war früher (BS) hingewiesen worden.

Die Überstruktur der vorliegenden Phase Au₇₇Mg₂₃ gehorcht allerdings nicht dem einfachen Verwerfungsmechanismus mit unendlichen Verwerfungsebenen; die Verwerfungsflächen bilden hier Sechsecke, und diese Anordnung ist sehr ähnlich der, wie sie in der Struktur von Cu₁₀Sb₃(*h*) (Günzel & Schubert, 1958) gefunden worden war. Die Cu₁₀Sb₃(*h*)-Abart des Ni₃Sn-Typs besteht aus zwei dichtest-gepackten Schichten, die man in sechseckige Bereiche unterteilen kann, innerhalb derer die Ni₃Sn-Struktur vollständig erhalten bleibt. Auch an den Bereichsgrenzen wird nur die Koordination der zweitnächsten Nachbarn geändert, d.h. es entstehen zweitnächste Nachbarn der Art Sb-Sb. Ganz entsprechend ist es bei der Überstruktur von Au₇₇Mg₂₃. In Fig. 2 sind die Bereiche, in denen die Ni₃Sn-artige Schicht nicht gestört ist, eingezeichnet. Im Gegensatz zu den Stapelvarianten der einfachen Verwerfungen, wie sie z.B. in Au-Cd-In-Phasen (Wegst & Schubert, 1958), Au-Mg-Phasen (BS), Au-Mn-Phasen (STH) und anderen auftreten, kann man diese Schichten nicht durch einfaches Verschieben der Domänen in ungestörte Ni₃Sn-Schichten überführen. Dennoch kann man auch hier von einer Verwerfung sprechen, da zwar durch die Verwerfungsflächen, die in diesem Fall durch die nicht ebenen Bereichsgrenzen dargestellt werden, die Koordination der nächsten Nachbarn nicht geändert wird, jedoch die der zweitnächsten. Damit ist eine wesentliche Eigenschaft der Verwerfungsüberstrukturen auch in der hier besprochenen Struktur erfüllt. Die obige Verwerfungsart kann nicht als normale oder unnormale Verwerfung (SK S. 97) bzw. als Verwerfung 1. oder 2. Art (ST S. 303) bezeichnet werden, sondern stellt einen weiteren eigenen Verwerfungstyp dar. Die hier aufgeklärte Struktur zeigt ebenso wie die anderen Mitglieder dieser Strukturfamilie, dass die Ver-

werfungerscheinungen bindungsmässig verursacht sind, und dass die Reichweite der Bindungskräfte 20Å sicher übersteigt. Deutungsmöglichkeiten für diese Erscheinung findet man bei SK, ST und STH.

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An Investigation of the Crystal Structure of Antiferromagnetic Chromium

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A search has been made for evidence of the splitting of X-ray reflexions from polycrystalline antiferromagnetic chromium that would be expected if a single domain possessed tetragonal symmetry. An examination of integral line widths and Nelson-Riley plots for specimen temperatures above and below the Néel point has been found to yield no such evidence. A simple theoretical estimate of the sensitivities of these methods has been made and the upper limit of Δ set at 10^{-5} , where $a=c(1+\Delta)$ for the distorted structure.

Neutron-diffraction studies have shown that antiferromagnetic chromium has a periodicity of approximately 28 unit cells in its magnetic structure (see e.g. Bacon, 1961; Shirane & Takei, 1962). Overhauser (1962) has cited this and other evidence in proposing that the structure arises from static spin-density waves directed

along any one of the cube axes. Between the Néel temperature (39°C) and about 120°K the spins are perpendicular to the wave vector, and below 120°K they are parallel to this direction.

Above the Néel temperature Wilkinson, Wollan, Koehler & Cable (1962) were unable to observe para-

magnetic scattering and thus in any theoretical model the moments must be created in a self-consistent manner from the conducting $3d$ electrons. The observed symmetry of a single magnetic domain is a guide to the required theoretical model. For example one such model with tetragonal symmetry, that of a single helical wave, has been shown to be stable under certain conditions by Tachiki & Nagamiya (1963) although the measurements of the polarization of scattered neutrons by Brown, Wilkinson, Forsyth & Nathans (1965) indicate that this model is probably unacceptable. The neutron diffraction evidence cannot determine whether, in the upper phase structure, the ordinary multidomain material contains domains with a single spin wave along one axis or an admixture of such waves along all three axes. In the former case a single domain would possess tetragonal symmetry whereas in the latter overall cubic symmetry would be maintained. The purpose of this note is to report a search for the splitting of the X-ray diffraction lines of powdered chromium that would result from a tetragonal distortion of the normal cubic structure consistent with the first of these two models.

The angular positions of the three components of an hkl reflexion for a tetragonally distorted cubic structure, relative to the position of the reflexion for an undistorted structure of the same unit-cell volume, are given by

$$\delta_l = \Delta \left(\frac{1}{3} - \frac{l^2}{N} \right) \tan \theta_{hkl}$$

where $N = h^2 + k^2 + l^2$, $a = c(1 + \Delta)$ for the distorted structure, and θ_{hkl} is the Bragg angle for the undistorted structure. If Δ is small ($\sim 10^{-4}$ say) then it is impossible to resolve these three components but they produce an asymmetric broadening and a shift in the maximum of the line. By rewriting the above equation as

$$\delta_l = S \left(\frac{1}{3} - \frac{l^2}{N} \right)$$

and approximately expressing the intensity of each component by

$$I = \frac{I_0}{1 + (\varphi + \delta_l)^2}$$

some estimate can be made of the effect of the splitting on the integral breadth and position of the maximum of the composite line. The results of calculations based on these expressions are shown in Figs. 1 and 2. The shift in the maximum (x) of the composite line, the positions of the maxima (δ_l) of the three components, the angular variable (φ), and the splitting factor (S) are all measured in terms of the half-width at half maximum of the unsplit line. At large Bragg angles this is equivalent to a change in the lattice parameter of about one part in 10^4 . Thus if Δ is 10^{-5} (*i.e.* $S = 0.1$) the broadening of the 310 reflexion would be about 0.5% and the shift in the maximum negligible, which indicates that measurement of these two quantities would be insensitive to a distortion of this order or less.

The measurements on chromium were carried out using powdered specimens which had been annealed

at 1240°C for four hours. As each diffraction line for the distorted structure is shifted by a different amount from its position for a cubic structure, values of the lattice parameter calculated for different lines will be inconsistent with a linear Nelson–Riley (Nelson & Riley, 1945) extrapolation. This is the basis of the technique used by Bacon & Wilson (1963) in their study of distortion in Pt_3Fe alloys, and of the one followed here. With a 114.8 mm diameter camera a series of room temperature (23°C) measurements were made on the 211 reflexions for Cr $K\alpha$ and $K\beta$ radiations, the 222 reflexion for Cu $K\alpha$ and the 321 for Cu $K\beta$ radiation. The lattice parameter was calculated for each reflexion and a least-squares extrapolation made through these four points. The equation of this line was

$$a = 2.88506 - (0.002892)y \text{ \AA at } 23^\circ\text{C},$$

where y is the Nelson–Riley function. The extrapolated value of the lattice parameter agrees well with the value of $2.88506 \pm 0.00006 \text{ \AA}$ obtained at 20°C by Straumanis & Weng (1955). A Nelson–Riley plot was made for each film and a line with the same slope as that defined above was drawn through the point corresponding to the 222 reflexion, which, within the assumption of the invariance of unit-cell volume, should not be shifted. The amount by which the point for the 321 reflexion was displaced from this line was taken as the shift of that reflexion. For ten films taken in the temperature range -102° to $+23^\circ\text{C}$ the mean value of this displacement was $0.0001 \pm 0.0001 \text{ \AA}$ where the error is the standard deviation of the measurements. In comparison, eight films taken in a range (70° to 80°C) above the Néel temperature yielded a mean value of 0.00002

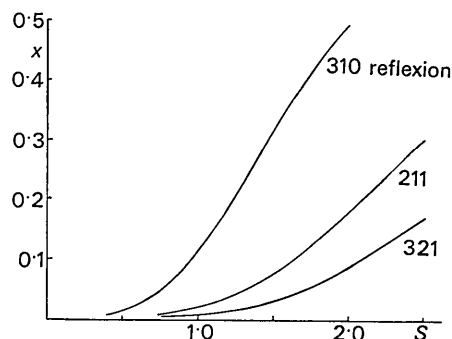


Fig. 1. The shift of the maximum (x) of the composite line as a function of the splitting factor (S) defined in the text.

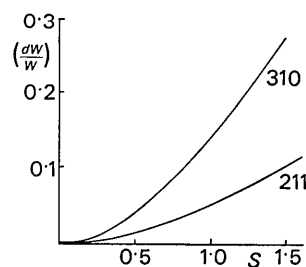


Fig. 2. The fractional broadening (dw/w) of the composite line as a function of S .

$\pm 0.00008 \text{ \AA}$. The value of the displacement appears to be larger below the Néel temperature but it is not significantly greater than the accuracy of the measurements. Further, the displacement might reasonably be expected to increase as the temperature is reduced below the Néel point, whereas the observed displacement showed no tendency to do so and in fact the room temperature value was about three times that obtained at -102°C .

To investigate the broadening effect for a powdered chromium specimen the 310 reflexion for Cu $K\alpha$ radiation was recorded with an X-ray diffractometer. The integral breadth of the reflexion was measured for 20 recordings in a range (40 to 70°C) above the Néel point, and below the Néel point for 21 recordings in the range 15 to 40°C and 6 in the range -70 to -40°C . The mean values of the breadth for all three ranges lie within 0.8%, the values in the higher and lower ranges being slightly larger than the values in the middle range. This latter indicates that the small observed broadening is more likely to be due to slight thermal instability than to a splitting of the reflexion.

The above results do not weight the argument in favour of the overall cubic symmetry of antiferro-

magnetic chromium but together with the previous discussion they point to an upper limit for Δ , in the specimens examined, of about 10^{-5} , where Δ is defined in the relation $a=c(1+\Delta)$ for the distorted structure.

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Monoclinic Diffraction Patterns Produced by Certain Triclinic Crystals and Diffraction Enhancement of Symmetry

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The triclinic mica polytype $10Tc_3$ produces an X-ray diffraction pattern monoclinic in symmetry. It is now established that if a triclinic structure, with a metrically monoclinic lattice, is composed of two kinds of layer, one being an integral multiple, in thickness, of the other and each bearing twofold rotational symmetry, its diffraction pattern should assume a rigorously monoclinic symmetry. The term *diffraction enhancement of symmetry* is proposed for phenomena of this kind. Some triclinic mica polytypes, though not in conformity with the above conditions, still give rise to diffraction patterns monoclinic in a very good approximation, and these cases are specified as *quasi-enhancement*. If the X-ray diffraction pattern of a crystal bears, only in part, a symmetry higher than that of the crystal, the case is designated *partial enhancement*.

Introduction

It has often been observed that some sets of X-ray reflections from a crystal exhibit, besides the centrosymmetry due to the Friedel law, a symmetry higher than that of the crystal. One of the notable examples is a case of triclinic wollastonite (Ito, 1950). It gives the b -axis rotation photograph in which spots on the even-order layer-lines are arranged, in intensity as well as position, quite symmetric against the zero layer. As far as these reflections are concerned, therefore, the pattern strictly assumes an appearance of that of a monoclinic

symmetry, though those on the odd-order layer-lines betray that the symmetry of the crystal is in fact triclinic. Boléite and monoclinic trinitrotoluene also exhibit features similar to the above in their X-ray patterns, some sets of reflections being strictly cubic in the former in spite of its tetragonal symmetry and orthorhombic in the latter.

These intricate phenomena have been dealt with by Ito (1950), who has given explanations of these based upon his theory of twinned space groups. In fact, in each of these examples, it has been confirmed experimentally that the crystal is a polysynthetic twin of a