These new $AlN-Al_2O_3$ compounds derived above completely confirm two of the 'sialon' phases postulated by Jack (1976) in the Si–Al–O–N system. In fact they can be considered as prototypes of his tetrahedral AlN 'polytypes' having $M/X$ ratios of 10/11 and 9/10, respectively. In his phase diagram for $Si_3N_4-AlN-Al_2O_3-SiO_2$, the $27R$ line should now be extended to the join between $Al_2O_3$ and AlN. Furthermore, another line for the $20H$ structure should intersect this join to account for the existence of $Al_{10}N_8O_3$. It is of interest to note that although many crystals of this $20H$ compound were well ordered, others from the same preparation showed considerable streaking along the $h0l$ rows on Weissenberg photographs. This indication of disorder is caused by mistakes in the stacking arrays along the $c$ axis. The rhombohedral crystals of $Al_9N_7O_3$ exhibited a higher degree of order, probably because less faulting occurs for shorter 9Al-atom segments which characterize the structure of this compound. This type of disorder is common in SiC and other such polytypic compounds (Verma & Krishna, 1966).

Although the crystal structure has not been refined from single-crystal Weissenberg photographs, the idealized arrangement postulated by Jack (1976) gives reasonably good agreement with the observed intensities. Projections of the $20H$ and $27R$ structures on the hexagonal (110) plane are illustrated in Fig. 1. Their X-ray diffraction patterns are given in Table 2. Because of the large number of possible reflections only those observable are listed.

We expect further work will reveal other aluminum oxynitride repeated-layer structures. So far these exist for $m = 4, 5, 6, 7$, and 8.

The authors thank W. S. Knapp for his assistance in growing the crystals.

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## On the space groups of two thiospinels.

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### Abstract

Single crystals of $CuIn_5S_8$ and $AgIn_5S_8$ thiospinels have been examined by X-ray diffractometry, in order to assign the space groups. The $\psi$ scan of some high-angle reflections, forbidden in the conventional space group $Fd3m$, showed that $CuIn_5S_8$ belongs to the alternative space group $F\bar{4}3m$.

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In the last few years stimulating discussions have been reported in the literature on the correct assignment of space group to the spinel-type compounds. The problem has been described by Thompson & Grimes (1977), who reviewed the results of previous work with electron and neutron diffraction techniques.

The alternative to space group $Fd3m$, usually assigned to spinels, is $F\bar{4}3m$, where the octahedral-site metal ions are displaced along the [111] directions and the tetrahedral ones split into two crystallographically independent sites, namely $4(a)$ and $4(c)$. The space-group assignment is usually based on the detection of $hk0$ reflections with $h + k = 4n + 2$, forbidden in $Fd3m$, but allowed in $F\bar{4}3m$. The difficulty
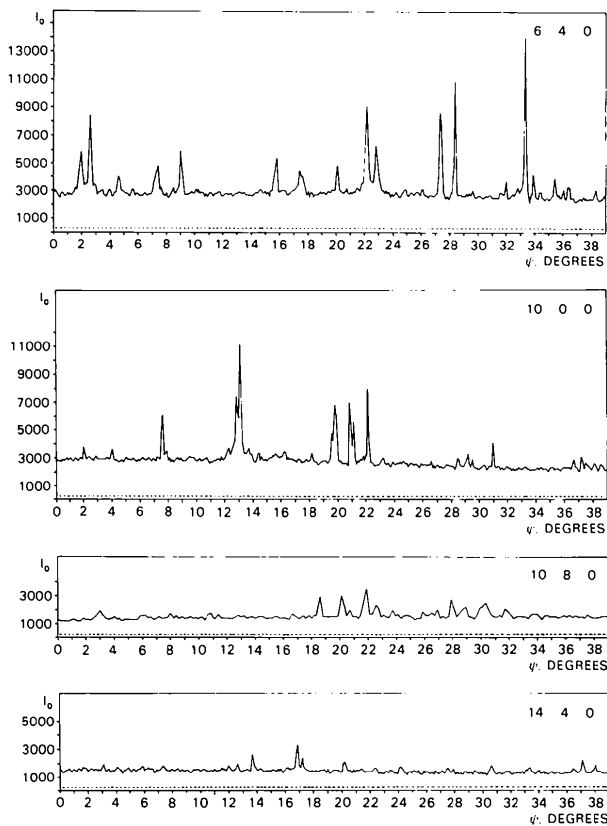
Fig. 1. Intensities of four reflections of $CuIn_5S_8$, taken with the $\theta$–$2\theta$ scan technique at various angles, $\psi$, around their scattering vectors, with $\Delta\psi = 0.1°$. The continuous curve represents the integrated intensity $I_0$, corrected for the background, and the dotted line indicates the $3\sigma(I)$ value.

Debye–Scherrer powder films of $CuIn_5S_8$ and $AgIn_5S_8$ showed that both have cubic spinel-type structures. For precise determination of lattice constants a Philips camera with the asymmetric Straumanis film mounting was used. Four reflections with $\theta > 65°$ gave the following final cell constants: $AgIn_5S_8$: $a = 10.8268\ (5)$ Å; $CuIn_5S_8$: $a = 10.6858\ (3)$ Å (the Nelson–Riley function was plotted). Single crystals were mounted on a four-circle Syntex $P2_1$ diffractometer; Mo $K\alpha$ ($\lambda = 0.71073$ Å) radiation was used ($\mu = 11.54$ and $12.21$ mm$^{-1}$ respectively). The crystal was rotated about the scattering vector of each reflection ($\psi$ angle) and a $\theta$–$2\theta$ scan collection carried out at fixed intervals ($0.1°$) of $\psi$. Two background values were measured at $1°$ below and $1°$ above the $K\alpha_1$ and $K\alpha_2$ peaks respectively.

The copper compound shows the presence of a considerable number of forbidden reflections, even at relatively high $\theta$ values. Four of these, chosen for their remarkable intensities, are plotted in Fig. 1. There are many Renninger peaks, separated by approximately flat regions, where the intensity variations are of the order of three or four times $\sigma(I)$.

The diagrams show, from top to bottom, two plots for each reflection: the intensity $I_0$ corrected for the background, and the $3\sigma(I)$ level.

On the basis of these results $CuIn_5S_8$ can be assigned to space group $F\bar{4}3m$. However, these results could be explained by a non-random distribution of copper and indium ions in the two tetrahedral sites $4(a)$ and $4(c)$, so a complete structural determination of this compound has been undertaken.

No forbidden reflections were detected for the silver compound, so we believe that, on the basis of the X-ray diffraction analysis, it must be assigned to the conventional space group $Fd3m$.

**Reference**

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arises from the fact that these reflections are affected by the Renninger effect. Since low-angle reflections (e.g. 200) are affected more in X-ray diffraction than in other techniques, we have examined some high-angle forbidden reflections.

# International Union of Crystallography

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