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On the structure of fibrous sulfur. By JERRY DONOHUE, *Department of Chemistry and Laboratory for Research on the Structure of Matter, University of Pennsylvania, Philadelphia, Pennsylvania, U.S.A.*, STEWART H GOODMAN, *General Dynamics Corporation, Pomona, California, U.S.A.* and MICHAEL CRISP, *Department of Chemistry, University of California, Los Angeles, California, U.S.A.*

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A structure recently proposed by Tuinstra for fibrous sulfur cannot be correct because it predicts a strong equatorial reflection at $d=4.60 \text{ \AA}$; this reflection is, in fact, in large part the β contribution of the very intense equatorial reflection at $d=4.04 \text{ \AA}$.

In a recent paper Tuinstra (1966) has described the results of his interpretation of the diffraction pattern of fibrous sulfur. This pattern is notable for a very intense equatorial reflection at $d=4.04 \text{ \AA}$. This reflection has been described as 'broad' (Prins & Tuinstra, 1963); its position is accordingly difficult to measure precisely.

Tuinstra's description of the structure includes structural details of the infinite helical chains of sulfur atoms together with the way in which they pack together. Evidence for the correctness of this structure is presented in the form of a table which includes observed and calculated values of the intensities and of $4 \sin^2 \theta / \lambda^2$. The agreement between the observed intensities and the corresponding calculated values is apparently quite good. For example, the second most intense reflection on the equator, at $d=4.60 \text{ \AA}$, is, in the text, stated to have about one-tenth the intensity of the strongest equatorial reflection (referred to above); the respective calculated intensity values for the proposed structure are 120 and 1000.

We have prepared samples of fibrous sulfur, following the procedure of Prins, Schenk & Hospel (1956). Fiber diagrams of these preparations, taken with Cu radiation, are presented in Fig. 1. These photographs, which were deliberately underexposed, were taken with (a) no Ni filter, (b) one Ni filter (thickness 0.00035 in), and (c) two Ni filters, and were timed so that intensity of the strongest reflection would be very nearly the same on all three. The general appearance of the three photographs resembles closely those of fibrous sulfur which have been published previously (Prins, Schenk & Hospel, 1956; Prins, Schenk & Wachters, 1957) and are as well in agreement with tabulated diffraction data (Prins & Tuinstra, 1963; Tuinstra, 1966), with, however, one crucial exception: the reflection at $d=4.60 \text{ \AA}$ is obviously largely the β of the reflection at 4.04 \AA .

A structure for fibrous sulfur which requires a strong reflection to be observed at 4.60 \AA cannot, therefore, be accepted. This conclusion is supported by the recent work of Geller & Lind (1969) and Lind & Geller (1969) who examined single crystals of pressure-induced sulfur, and

concluded that this material is the same as fibrous sulfur prepared at atmospheric pressure by the method of Prins *et al.* The details of the structure deduced by Lind & Geller are not the same as those presented by Tuinstra.

The reflection at $d=4.60 \text{ \AA}$ is indexed by Geller & Lind as 002, with an observed F of 284, and the reflection at $d=4.04 \text{ \AA}$ is a combination of 080 and 042, both with observed F values of 858. The ratio of the intensities* to be expected on a fiber diagram is thus 1:27, a value which is in serious disagreement with the ratio 1:8 calculated for Tuinstra's structure, but is in satisfactory agreement with the ratio 1:25 calculated for the structure of Geller & Lind. It is difficult to estimate this ratio from Fig. 1(c), but it appears possible from this and other photographs that it may be as small as 1:50 or less, a result which suggests that fibrous and pressure-induced sulfur might have slightly different structures. As pointed out by Geller & Lind, the correspondence between the two diffraction patterns is very close, so this difference, if it exists, cannot be very large.

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* This calculation omits both absorption and Lorentz-polarization effects which, however, tend to cancel each other.

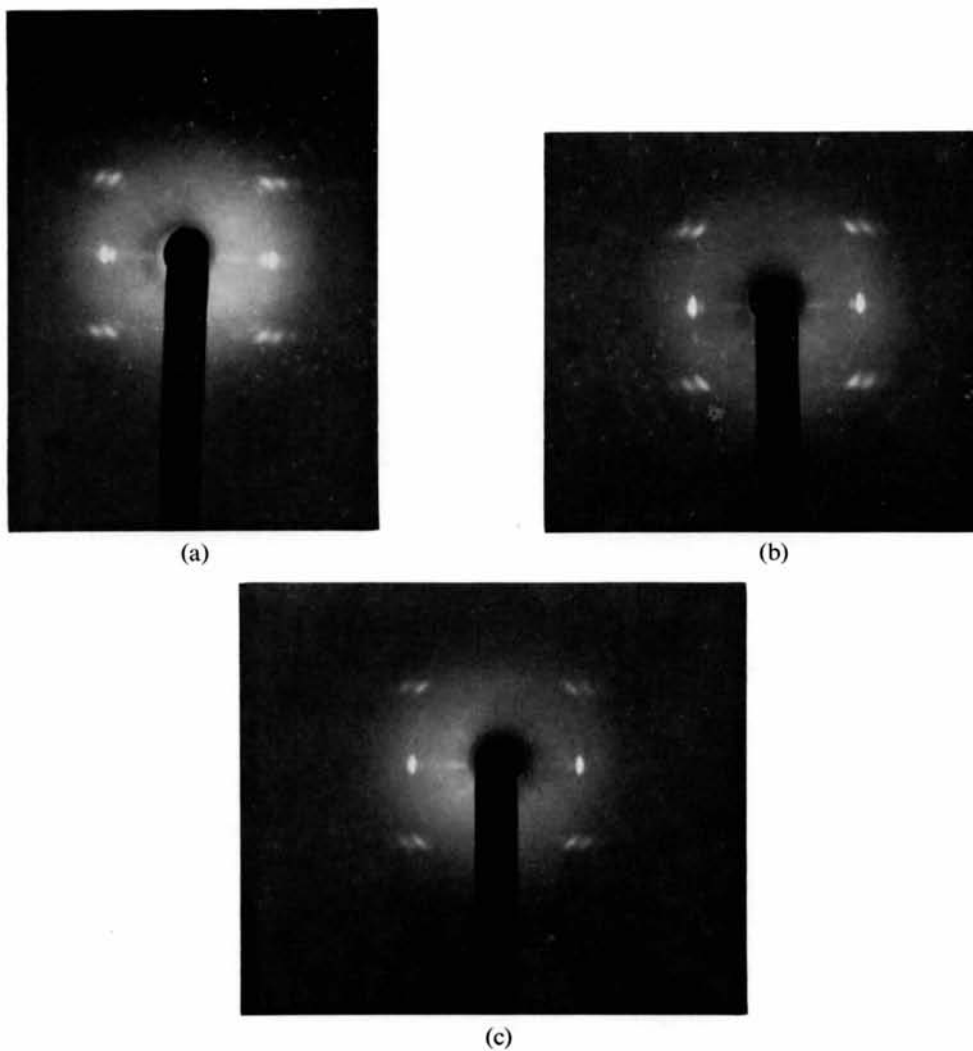


Fig.1. Fibrous sulfur, Cu *K* radiation. (a) No filter, exposure 1 hour, (b) one Ni filter, exposure 1 hour 35 min, and (c) two Ni filters, exposure 2 hours 30 min.