Reactions were run at pressures of 1, 2, and 3 kb at 1000°C, hold 3 hr, cool 3 hr to 700°C, and quenched. The products were washed with CS_2 to remove excess S, leaving yellow-orange crystalline material. The Guinier x-ray diffraction patterns of the products of reactions run at 2 kb and 3 kb were similar and could be indexed on the basis of cubic unit cells $a = 9.938 \pm 0.001$ Å in which only 16 of 24 reflections were used. The pattern was completely indexed when a tetragonal cell was used similar to that of β-In_2S_3 in which a tetragonal = a cubic/$\sqrt{2}$ and c tetragonal = $3a$ cubic. The refined parameters are $a = 7.026 \pm 0.001$, $c = 29.819 \pm 0.001$ Å. In order to prove that the structure is similar to that of βIn_2S_3, intensities of the powder diffraction pattern were calculated (*9*) and compared to observed intensities. Intensities were gathered by tracing the peaks of a diffractometer pattern on to Cronaflex® drafting film No. IDF4, cutting out the peaks and weighing them. The diffractometer chart was obtained using a Norelco diffractometer with a bent crystal monochromator and CuKα radiaton. Background was estimated by drawing a smooth curve. For the calculated intensities, position parameters reported for β-In_2S_3 were used (*4*). No attempt was made to refine the parameters. The R factor defined as $R = |I_{obsd} - I_{calc}|/I_{obsd}$ is 17% which is sufficient to establish the similarity of the structure. The data are shown in Table I.

The product of the reaction run at 1 kb did not show the spinel type phase; thus, the pressure necessary for formation at 1000°C. is somewhere between 1 and 2 kb. A reaction run at 1200°C, 65 kb, 10 min, cool to 1000°C., slow cool 3 hr to 700°C yielded a spinel type phase similar to that prepared at 2 kb. Good crystal growth occurred, and electrical resistivity measurements were made on a crystal. The resistivity showed semiconducting behavior $\rho_{0.298°K} = 1 \times 10^9$ Ωcm with an activation energy $E_a = 0.3$ eV.

B. $MnAl_2S_4$

A reaction starting with the elements in the ratio 2Al/Mn/5S at 1000°C, 3 kb held for 5 hr, cool 3 hr to 700°C, and quench yielded a mixture of phases. After washing with CS_2 and 1:1 HCl, orange crystals remained which gave a spinel type powder diffraction pattern $a = 10.052 \pm 0.001$ Å. The best samples of the compound were formed at higher pressure. The reaction of 2Al/Mn/4S at 1200°C, 65 kb, held 1 hr, cool 3 hr to 1000°C, and quench yielded orange and green material. The orange material showed a spinel type diffraction pattern, $a = 10.092$ Å, while the green material showed the cubic α-MnS pattern. The density of the crystals was measured by a displacement technique in bromoform. Found 2.95 g/cm³; calculated for $MnAl_2S_4$: 3.06 g/cm³. It is apparent that the compound tolerates a large degree of nonstoichiometry.

Two reactions run at 30 kb, 1000°C hold 2 hr, quench, and starting with the reagents 0.5 MnS/-2Al/3S and 0.25 MnS/2Al/3S yielded nearly homogeneous products. The spinel type unit cell dimensions are $a = 10.050 \pm 0.001$ Å and $a = 10.010$ Å respectively, again illustrating nonstoichiometry.

Magnetic and electrical measurements were made on a sample prepared at 1000°C and 45 kb, held 2 hr/Q. The unit cell was refined to $a = 10.052$ Å, and a trace of α-MnS was seen in the powder pattern. Resistivity measurements were made on a polycrystalline piece and showed semiconducting behavior $\rho_{298°K} = 1.2 \times 10^{10}$ Ωcm, $E_a = 0.7$ eV. The magnetic measurements showed paramagnetic behavior from 77–300°K, with $C = 16.5 \times 10^{-3}$ emu °K/gOe and $\theta = -116$°K. Assuming the formula $MnAl_2S_4$, $\mu^2_{eff} = 31.4$ μB^2/f wt. $\pm 2\mu B^2$/f wt. When μ^2_{eff} is calculated for $MnAl_2S_4$ using the formula for electron spin only and assuming high spin Mn^{2+}, then it is 35 μB^2/f wt. The difference is consistent with the observed nonstoichiometry.

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