Structure and magnetic features of molybdenum triple sulfide Mo_5GaS_6

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X-ray diffraction investigations were made of the magnetic compound Mo_5GaS_6 in the temperature range from 15 to 300°K. A structural transition is observed below 50°K and appears also in measurements of the magnetic susceptibility and of the electric resistance.

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A new class of superconducting compounds, the so called Chevrel phases with composition $M_xMo_6S_8$, which include, for example, Mo_3CuS_4, Mo_5SnS_6, Mo_6PbS_8,[1–4] have been intensively studied recently. These compounds, as established in a number of studies,[5,6] have a rhombohedral structure (space group R3), which constitute a system of octahedrons Mo_6S_8, between which the atoms of the first component M are located.

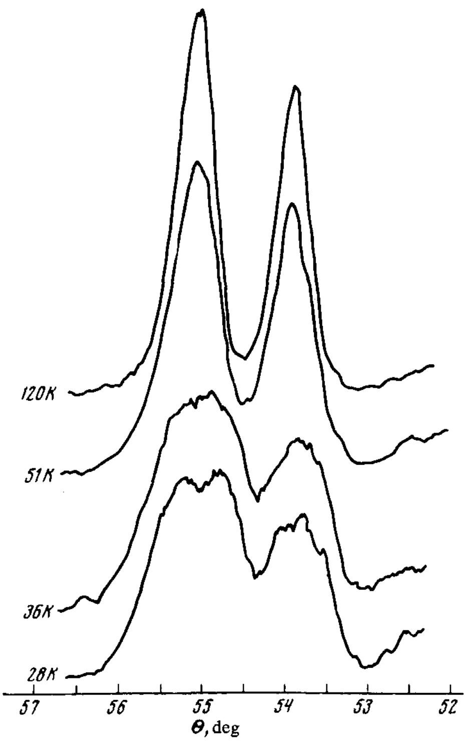

FIG. 1. Section of diffraction pattern obtained at different temperatures.

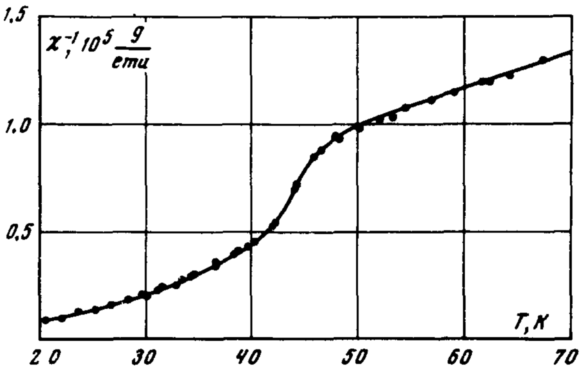

FIG. 2. Dependence of the reciprocal susceptibility on the temperature in the region of the structural transition.

It was shown by us in[7] that triple molybdenum sulfides with elements of the third group as the third component, such as Mo_5GaS_6 and Mo_5AlS_6 have a semiconductor-type temperature dependence of the resistance and a nonlinear dependence of the magnetic moment on the field at $T < 30$ °K. The plots of $M(T)$ and $\chi^{-1}(T)$ had shapes typical of ferromagnetic compounds.

In the present study we have carried out x-ray diffraction investigations of the structure of powders of the compound Mo_5GaS_6. The investigations were carried out with a standard x ray diffractometer using CuK_α radiation. The computer reduction of the diffraction patterns obtained at room temperature show that the latter can be indexed in a rhombohedral syngony with $a = 6.17$ Å and $\alpha = 104°17'$. From this fact we can conclude that the Mo_5GaS_6 samples have a rhombohedral structure which is apparently analogous to the Chevrel-phase structure. In contrast to most superconducting Chevrel phases (for which $\alpha \approx 90°$), in our case the rhombohedral angle α greatly exceeds 90°.[1)]

As a result of a low-temperature x-ray investigation we have observed that cooling the Mo_5GaS_6 samples leads to a strong change in the diffraction pattern. Below 50 °K, certain x-ray diffraction maxima are split, apparently as a result

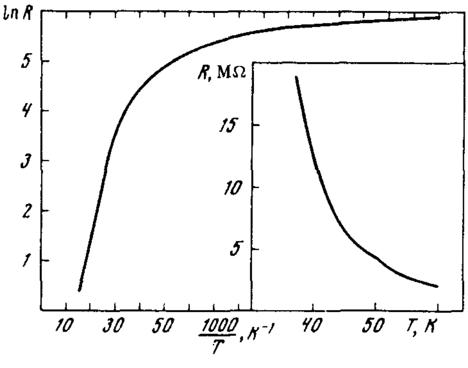

FIG. 3. Dependence of the logarithm of the resistance on the reciprocal temperature for one of the Mo_5GaS_6 samples. In the right-hand side is shown a plot of $R(T)$ in the region of the structural transition.

of distortions in the crystal lattice of the Mo_5GaS_6 compound (see Fig. 1). It is characteristic that the temperature region in which the structural transition is observed preceeds the temperature region in which the magnetic properties change.

Detailed measurements of the dependence of the magnetic moment on the temperature in different magnetic fields, carried out with a setup using a string magnetometer, have revealed a break on the plot of the reciprocal susceptibility against the temperature in the region of the structural transition (see Fig. 2). This behavior of $\chi^{-1}(T)$ does not make it possible to determine the paramagnetic Curie point Θ_p by extrapolating the $\chi^{-1}(T)$ plot.[2)] Extrapolation of the temperature dependences of the magnetic moment $M(T)|_{H=\text{const}}$ to the region of weak magnetic fields yielded for the ferromagnetic Curie point a value $\Theta_f = 19 \pm 1$ °K.

We have also measured the temperature dependence of the electric resistance of the Mo_5GaS_6 samples. The results for one of the samples are shown in Fig. 3. As seen from Fig. 3, the plot $R(T)$ has an exponential form with $\Delta = 220$ °K,[3)] a strong deviation from the exponential form begins below 30 °K, while a weak anomaly is observed on the $R(T)$ curve in the region of the structural transition.

The magnetic properties of the four-component superconducting samples $Mo_5SnGa_xS_6$, as already indicated many times,[7,8] are apparently connected with magnetism in the system Mo_5GaS_6, which system is present in the four-component samples as a second phase. Indeed, at $x \geq 0.5$ the diffraction pattern of the four-component samples $Mo_5SnGa_xS_6$ reveal lines of the compound Mo_5GaS_6, with intensities that increase with increasing x. At lower concentrations, however, it appears that Ga is soluble in the Mo_5Sn_6. This is confirmed by the data obtained by us from x-ray measurements, which indicate that the lattice constant increases, and can explain the noticeable growth of the temperature of the superconducting transition in the $Mo_5SnGa_xS_6$ system at $x \sim 0.2$—0.3.[7,9]

It was suggested in[10] that the magnetic properties of the four-component system $Mo_5SnGa_{0.5}S_6$ [4] are determined by the presence in the samples of the $Ga_{0.5}Mo_2S_4$ phase, which has a spinel structure and the magnetic properties of which were observed in[11]. We have carried out x-ray investigations of powders with composition $Ga_{0.5}Mo_2S_4$, which have shown that the diffraction patterns of this compound contain practically all the lines of the rhombohedral structure of Mo_5GaS_6 and the lines of the unknown phase. The magnetic measurements carried out on samples with composition $Ga_{0.5}Mo_2S_4$, have shown that the saturation moment at 4.2 °K is much less than the corresponding moment for the compound Mo_5GaS_6, while the Curie point practically coincides with that obtained in the present paper for Mo_5GaS_6. Therefore the magnetic properties of samples with composition $Ga_{0.5}Mo_2S_4$, which were published in[11], are apparently due to the presence in these samples of the rhombohedral phase Mo_5GaS_6. As already noted, the onset of magnetism in the Mo_5GaS_6 system is outwardly reminiscent of the situation in weak ferromagnets such as $ZrZn_2$. However, whereas in the case of $ZrZn_2$ we are dealing with a metal, and the magnetic order apparently sets in as a result of indirect exchange, in our case Mo_5GaS_6 is a semiconductor and the mechanism that determines the singularities of the magnetic properties should be different. Recently, for example, the question of the ferromagnetism in narrow-band semiconductors[12,13] has been discussed in the literature. It is possible that a similar situation can take place also in Mo_5GaS_6. It is still impossible to say to what extent the structural transition can be connected with the magnetic order. It should be noted, however, that the theory of "excitonic ferromagnetism," proposed in[12,13], presupposes the presence of a structural transition that precedes the magnetic transition. As follows from our measurements of $\chi(T)$, structural transitions take place also in other magnetic chalcogenides, such as Mo_5AlS_6 and Mo_5GaSe_6.

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1) In hexagonal axes we have for superconducting Chevrel phases $c/a \approx 1.2$, while for Mo_5GaS_6 we have $c/a \approx 0.8$.

2) One cannot exclude the possibility that the higher value of the Curie point, given by us in[7] is due to the fact that in that paper we extrapolated the function $\chi^{-1}(T)$, the values of which were obtained at points occurring in the region of the structural transition.

3) The absolute values of resistance at 4.2 °K, as well as the value of Δ in the expression for the temperature dependence of the resistance, varied from sample to sample and were probably determined by the conditions under which the samples were prepared.

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