Effect of pressure on the magnetic and structural transitions in $GaMo_5S_6$

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The effect of pressure on the magnetic-transition temperature T_m and on the structural-transition temperature T_s of molybdenum-gallium sulfide $GaMo_5S_6$ is investigated in the pressure range 0–6 kbar. It is shown that T_m and T_s increase with pressure, and that their ratio ($T_s/T_m = 2.5$) is practically independent of pressure.

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1. INTRODUCTION

The great interest in ternary sulfides of molybdenum is due to the unusual properties of these compounds. The composition of ternary sulfides can, as is well known, be represented in the form $M_xMo_6S_8$. A rather large number of ternary sulfides have by now been obtained, with a variety of elements as the third component.[1–5] Many of these compounds are superconductors; some, e.g., $PbMo_6S_8$, have unprecedented values of the critical magnetic field.[4,6] As shown in a number of papers,[7] superconducting sulfides have a rhombohedral structure (space group $R\bar{3}$) and consist of Mo_6S_8 octahedra between which the atoms of the third components are located.

We have previously[9] investigated the influence of pressure on the superconducting properties of ternary molybdenum sulfide with tin as the third component, and have shown that the superconducting transition temperature decreases with pressure, and that $\partial T_c/\partial p$ greatly exceeds the corresponding value for ordinary metallic superconductors (see also[10]).

If the superconducting compounds are made up mainly of elements of groups I, II, and IV of the periodic system then, as shown in[11], magnetic compounds are produced with group-III elements such as Ga and Al. We have investigated in greater detail the ternary sulfide $GaMo_5S_6$. The resistivity of this compound, in contrast to most superconducting sulfides, has temperature dependence of the semiconducting type. The dependence of the resistivity on the temperature is approximated well for most samples at $T > 30$ K by an exponential law. The energy gap for different sample batches lies in the range 100–800 K. An estimate of the carrier density on the basis of the Hall effect for samples of one batch shows that the conductivity is of the n-type and that $n \approx 4 \cdot 10^{20}$ cm^{-3}.

We have carried out[12] x-ray diffraction investigations of $GaMo_5S_6$ powders at temperatures from 4.2 to 300 K. It was shown that at room temperatures the $GaMo_5S_6$ diffraction pattern can be indexed in a rhombohedral syngony with $a = 6.17$ Å and $\alpha = 104°17'$, i.e., unlike superconducting sulfides, for which $\alpha \lesssim 90°$, the rhombohedral angle for $GaMo_5S_6$ is much larger than 90°. In the same study, a structural transition was observed at $T = 48$ K, manifest by a splitting and broadening of certain diffraction maxima when the temperature was lowered. A structural transition was observed also in the measurement of the magnetic properties. Thus, a break appeared on the plot of the reciprocal susceptibility $\chi^{-1}(T)$ against temperature in the region of the structural-transition temperatures. A weak anomaly was observed also, at the structural-transition point, on the plot of the resistivity against temperature. The magnetic-transition temperature, determined more accurately from the temperature dependences of the magnetic moment in different magnetic fields, turned to be approximately 20 K.[12] The latest measurements of the heat capacity[13] have shown that the $C_p(T)$ plot has a maximum at 20 K. The heat capacity has also an anomaly in the region of the structural-transition temperature.

The presence of structural and magnetic transitions in a semiconducting compound (which contains no magnetic ions) gives grounds for assuming that this compound may be an "excitonic ferromagnet." The theory of "excitonic ferromagnetism" was considered by Volkov, Kopaev, and Rusinov.[14,15] According to this theory, if the form of the carrier energy spectrum satisfies certain conditions, the onset of magnetic order is the result of simultaneous formation of a charge density wave (CDW) and a spin density wave (SDW).

Since the pressure changes greatly the properties of superconducting ternary sulfides of molybdenum, it was of interest to investigate the influence of the pressure on the magnetic and structural properties of the compound $GaMo_5S_6$. In view of the relatively weak magnetism of this system (the absolute values of the saturation moment at low temperatures are of the order of 5 G-cm^3/g, and the initial susceptibility is of the order of 3×10^{-4}), it was necessary to choose a sufficiently convenient and sensitive measurement procedure.

2. MEASUREMENT PROCEDURE

String magnetometer and experimental setup

The magnetic moment at various fields and temperatures was measured as a function of the pressure with a string magnetometer similar to that described in[16]. A similar magnetometer was already used by us in measurements of the magnetic properties of ternary sulfides.[3,11,13] A block diagram of the setup is shown in

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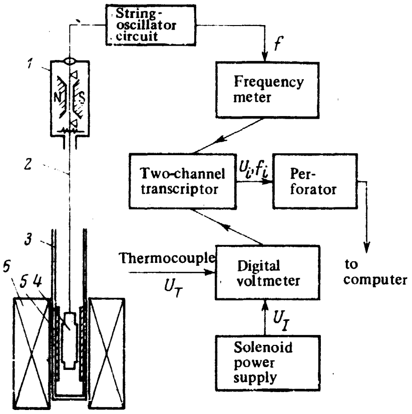

FIG. 1. Block diagram of installation: 1—measuring head of string magnetometer, 2—quartz suspension, 3—internal dewar, 4—pressure vessel, 5—copper block with thermocouple and heater, 6—superconducting solenoid.

Fig. 1. The operating principle of the string magnetometer is based on the measurement of the magnetic force acting on a sample placed in a solenoid at an operating point with a known magnetic-field gradient. The sensitive element of the instrument is a thin tungsten string that vibrates in the gap of a permanent magnet. The magnet force is directly proportional to the square of the string-vibration frequency: $F_m = a(f^2 - f_0^2)$; here a is the constant of the instrument and f_0 is the initial frequency. The initial tension in the string, determined in the usual case by the weight of the sample and of the quartz suspension, is of the order of several grams. This makes it possible to use a thin (20 μm dia) tungsten string, thereby increasing appreciably the sensitivity of the instrument.

In our case (see Fig. 1), the sample together with pressure vessel 4 was attached through a quartz suspension 2 to a tungsten string located in the measurement head 1. To prevent the thin string from breaking during the installation, an electromagnetic locking device was placed in magnetometer head 1.

The magnetic field was produced by superconducting solenoid 6. The magnetometer was placed in an internal dewar for measurements at high temperatures. A bulky copper block 5 with a bifilarly wound heater was placed at the lower end of the magnetometer, where the heat-exchange helium gas was admitted. The temperature was measured with an Au(Fe)-chromel thermocouple whose cold junction was in thermal contact with the copper block, and the hot junction was in the dewar with melting ice. Special calibration has shown that a magnetic field up to 65 kOe does not influence, accurate to 0.05 K, the thermocouple readings in the entire investigated temperature range from 4.2 to 70 K. We have investigated for the most part the temperature dependences of the magnetic moment in constant magnetic fields at various pressures. To this end, after cooling the dewar to helium temperature, the required thermal conditions for the pressure vessel with the sample is established in the copper block by adjusting the current through the heater. The heating rate was usually from 0.25 to 0.5 K/min.

The pressure vessel

To produce pressures up to 6 kbar we used a vessel of specially selected nonmagnetic beryllium bronze. A section through it is shown in Fig. 2. In contrast to the standard designs, the vessel was made without an obturator, and the nut of the plunger was screwed directly on the vessel housing (I), making it possible to decrease significantly the dimensions and weight of the vessel. The outside diameter was 15 mm, the inner channel diameter was 4 mm, and the vessel mass about 50 g. The working liquid was a mixture of transformer oil and kerosene.

The pressure in the vessel was determined by the shift of the superconducting transition point of a tin plate (II) placed under the sample (III). The superconducting transition was measured with low-frequency alternating current using a separate system of compensated coils.

Samples

We used in the investigation polycrystalline $GaMo_5S_6$ samples whose principal magnetic and structural characteristics were reported earlier.[11,12] The samples were prepared by direct fusion of the original components in quartz ampoules filled with a small amount of helium gas. The powdered reaction products were pressed in cylindrical matrices and annealed at ~1000 °C for several days. The samples used for measurement under pressure were 3.5 mm in diameter and 4 mm high.

Registration and reduction of the data

Owing to the relatively large mass of the pressure vessel we customarily used a thicker tungsten string (of ~50 μm dia), thereby decreasing the sensitivity. In addition, the magnetic force produced by the pressure vessel itself turned out to be quite large and comparable with the magnetic force acting on the sample. We therefore used computer reduction of the data to obtain the final values of the magnetic moment as a function of the temperature or of the magnetic field. To this end, the output data from the frequency meter connected to the string generator and from the voltmeter that measured either the temperature or the magnetic field were fed in perforated form into the computer for primary reduction. The magnetic field in the measurements of $M(H)$ or the temperature in the measurement of $M(T)$

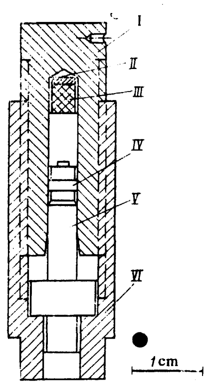

FIG. 2. Pressure vessel: I—shell, II—tin manometer, III—sample, IV—gasket of oil-resistant rubber, V—plunger, VI—sleeve nut.

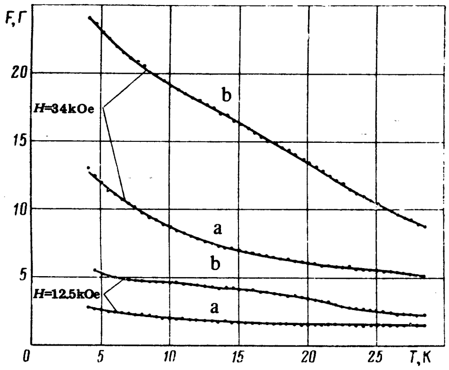

FIG. 3. Typical temperature dependences of the forces acting on the pressure vessel with the sample (b) and on the empty pressure vessel (a), obtained in magnetic fields 12.5 and 34 kOe. The points show the forces obtained after primary data reduction, and the smooth are the approximation results (see the text).

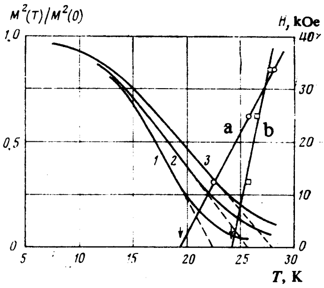

FIG. 5. Determination of the temperature of the magnetic transition from the plots of $M^2(T)/M^2(0)$. The extrapolation of $T^*(H)$ to zero field is shown at $p=0$ (a) and at $p=2.8$ kbar (b). The plots of $M^2(T)/M^2(0)$ at $p=0$ were obtained in fields 12.5 kOe (1), 25 kOe (2) and 34 kOe (3) and pertain to curve *a*. The arrows indicate the values of the magnetic-transition temperature at $p=0$ and $p=2.8$ kbar.

were subdivided into intervals and the primary reduction consisted of calculating the mean value of the force and referring it to the corresponding interval. In the measurements of the temperature dependences, for example, each interval was 0.5 K wide and corresponded to as many as 10 experimental points. The error in the determination of the force in the interval ranged from 10 to 50 mG. The error was calculated for each interval with allowance for the number of points in the interval.

The subsequent computer reduction consisted of approximating the obtained average force by a smooth curve. The results of the application of the described procedure to one of the measurements is illustrated in Fig. 3, where the points represent the values of the force after the primary reduction, and the smooth curves are the results of the approximation. This procedure was always employed both for the empty vessel (curves a) and for the vessel with the sample (curves b), and the magnetic moment was determined from the difference of the forces acting on the vessel with and without the sample. The values of the magnetic moment M obtained in control measurements at $p=0$ coincided with the values of M measured without the vessel.

3. RESULTS

The measurements have shown that the magnetic moment in the $GaMo_5S_6$ system increases with increasing pressure. Figure 4 shows plots of $M(H)$ at $T=4.2$ K and plots of $M(T)$ at $H=25$ kOe, obtained at $p=0$ (curves a) and at $p=2.8$ kbar (curves b). It is seen that at the low temperatures the saturation moment increases by approximately 12% when the pressure is increased to 2.8 kbar.

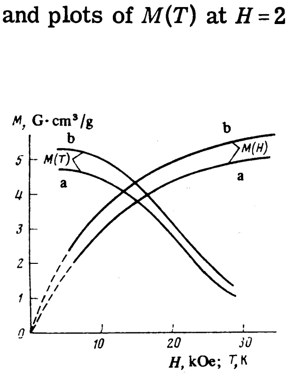

FIG. 4. Plots of the magnetic moment vs field at $T=4.2$ K and vs temperature at $H=25$ kOe for $p=0$ (a) and $p=2.8$ kbar (b).

Change of magnetic-transition temperature

The shift of the magnetic-transition temperature T_m under pressure was determined in the following manner: The linear section, in the region of T_m, on the temperature dependences of $M^2(T)/M^2(0)$ at constant H were extrapolated to their intercepts with the temperature axis at the points $T^*(H)$. The magnetic-transition temperature was determined by extrapolating the obtained values of $T^*(H)$ to $H=0$.

As seen from Fig. 5, at zero pressure we have $T_m = 19.5 \pm 0.5$ K.[1)] At $p=2.8$ kbar, the procedure described above yielded $T_m = 24 \pm 0.5$ K (see line b on Fig. 5). The average derivative of the change of the magnetic-transition temperature with respect to pressure is $\partial T_m/\partial p = +1.6 \pm 0.3$ K/kbar.

Effect of pressure on the structural-transition temperatures

As already mentioned, a structural transition was observed[12] in the system $GaMo_5S_6$ and it was shown that the splitting observed in the x-ray diffraction maxima with decreasing temperature is accompanied by a change of the magnetic properties. In particular, a break is observed on the $M(T)$ curves in the region of the structural-transition temperature T_s and starts at 48 K.

In the present study we investigated the temperature dependences of the magnetic susceptibility in the paramagnetic region under pressure. Figure 6 shows the temperature dependences of the force acting on the pressure vessel with the sample (curve 1) and on the empty vessel (curve 2). The measurements were made in a magnetic field of 25 kOe and a pressure of 6 kbar. The dashed line shows the temperature dependence of the reciprocal susceptibility. The arrow indicates the region of the structural transition at the given pressure. Thus, if we assume that the structural transition is accompanied by a singularity on the $M(T)$ curve, then it follows

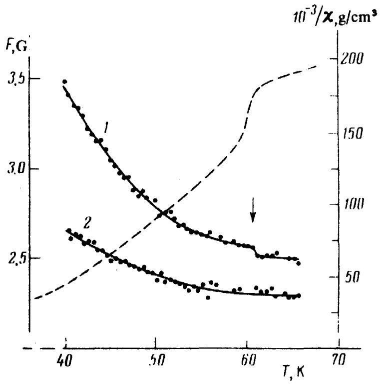

FIG. 6. Temperature dependence of the force acting on the empty pressure vessel (2) and on the vessel with the sample (1) in the region of the structural-transition temperature at a pressure 6 kbar. The dashed curve is the plot of the reciprocal susceptibility against temperature.

from our data that at 6 kbar the temperature T_s of the structural transition has increased by approximately 13 K. This corresponds to $\partial T_s/\partial p = 2.2$ K/kbar.

It must be noted that the effect of pressure on the saturation moment M_s and on the structural and magnetic transition temperatures was in practice reversible. The magnetic-transition point T_m was reproducible in repeated measurements under pressure, with accuracy not worse than 5%.

4. DISCUSSION OF RESULTS

It was noted earlier that the magnetic properties of $GaMo_5S_6$ and of $ZrZn_2$ are similar to a certain degree.[11,12] However, the magnetic order is apparently produced in these systems by different mechanisms, inasmuch as in intermetallic magnetic compounds such as $ZrZn_2$ an important role is played in the establishment of the magnetic order by indirect exchange via the conduction electrons, while $GaMo_5S_6$ is a semiconductor.

The main properties of $GaMo_5S_6$ are qualitatively described by the recently developed theory of excitonic ferromagnetism.[14,15] Thus, the presence of a structural transition and the onset of magnetic order in $GaMo_5S_6$ [12] agrees well with the phase diagrams constructed by Volkov, Rusinov, and Timerov[15] for an excitonic ferromagnet.

From the ratios of the experimental structural-transition temperature T_s to the magnetic transition points T_m we can determine, with the aid of the phase diagram, the ratio Δ_{t0}/Δ_{s0} of the triplet and singlet order parameters. For $T_s/T_m \sim 2.5$, an estimate yields $\Delta_{t0}/\Delta_{s0} = 0.9$. The dependence of the reciprocal susceptibility $\chi^{-1}(T)$ for $\Delta_{t0}/\Delta_{s0} = 0.9$, given in[15], agrees qualitatively with the experimental $\chi^{-1}(T)$ dependence obtained by us earlier.[12] The qualitative agreement of the theory with the experimental data can be regarded as an indication that the ordering mechanism proposed in[14,15] can be realized in $GaMo_5S_6$.

Thus, our experiments on the effect of pressure show that the saturation moment and the Curie point increase with pressure. The structural-transition temperature also increases with increasing pressure. The ratio of the structural-transition temperature to the magnetic-transition temperature is equal to 2.5 and hardly changes with increasing pressure. The derivatives of T_m and of T_s with respect to pressure are positive and are large, i.e., just as for superconducting ternary chalcogenides, relatively small pressures lead to rather large changes of the properties of such systems.

[1)] This value of T_m agrees well with the value of T_m obtained by us in measurements of the temperature dependence of the magnetic moment of a small sample with a magnetometer using a superconducting quantum interferometer in a magnetic field on the order of 1 G. In addition, it agrees with the temperature at which a maximum is observed on the plot of the heat capacity against temperature.[13]

[1] R. Chevrel, M. Sergent, and J. Prigent, J. Solid State Chem. **3**, 515 (1971); Mater. Res. Bull. **9**, 1487 (1974).
[2] B. T. Matthias, M. Marezio, E. Corenzwit, A. S. Cooper, H. Barz, Science **175**, 1465 (1972).
[3] N. E. Alekseevskiĭ, N. M. Dobrovol'skiĭ, and V. I. Tsebro, Pis'ma Zh. Eksp. Teor. Fiz. **20**, 59 (1974); **23**, 694 (1976) [JETP Lett. **20**, 25 (1974); **23**, 639 (1976)].
[4] Ø. Fischer, Proc. Fourteenth Intern. Conf. on Low Temp. Phys., Finland, 1975, **5**, North-Holland Publ. Co., Amsterdam, 1973, p. 172.
[5] Ø. Fischer, A. Treyvaud, R. Chevrel, and M. Sergent, Solid State Commun. **17**, 721 (1975).
[6] S. Foner, E. J. McNiff, Jr., and E. J. Alexander, Phys. Lett. A **49**, 269 (1974).
[7] M. Marezio, P. D. Dernier, J. P. Remeika, E. Corenzwit, and B. T. Matthias, Mater. Res. Bull. **8**, 657 (1973).
[8] O. Bars, J. Guillevic, and D. Grandjean, J. Solid State Chem. **6**, 48 (1973); **7**, 158 (1973).
[9] N. E. Alekseevskiĭ, N. M. Dobrovol'skiĭ, V. I. Nizhankovskiĭ and V. I. Tsebro, Zh. Eksp. Teor. Fiz. **69**, 662 (1975) [Sov. Phys. JETP **42**, 336 (1975)].
[10] R. N. Shelton, A. S. Lawson, and D. C. Johnston, Mater. Res. Bull. **10**, 297 (1975).
[11] N. E. Alekseevskiĭ, C. Bazan, N. M. Dobrovol'skiĭ, V. I. Nizhankovskiĭ, V. I. Tsebro, and V. M. Zakosarenko, Phys. Lett. A **54**, 375 (1975).
[12] N. E. Alekseevskiĭ, N. M. Dobrovol'skiĭ, V. I. Tsebro, and V. F. Shamraĭ, Pis'ma Zh. Eksp. Teor. Fiz. **24**, 417 (1976) [JETP Lett. **24**, 382 (1976)].
[13] N. E. Alekseevskiĭ, G. Vol'f, N. M. Dobrovol'skiĭ, E. I. Leyarovskiĭ, L. N. Leyarovskaya, and V. I. Tsebro, J. Phys. F (1977), in press.
[14] B. A. Volkov, Yu. V. Kopaev, A. I. Rusinov, Zh. Eksp. Teor. Fiz. **68**, 1899 (1975) [Sov. Phys. JETP **41**, 952 (1975)].
[15] B. A. Volkov, A. I. Rusinov, and R. Kh. Timerov, Zh. Eksp. Teor. Fiz. **70**, 1130 (1976) [Sov. Phys. JETP **43**, 589 (1976)].
[16] N. E. Alekseevskiĭ, E. P. Krasnoperov, and V. G. Nazin, Dokl. Akad. Nauk SSSR **197**, 814 (1971) [Sov. Phys. Dokl. **16**, 313 (1971)].

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