Thermoelectric power of sulphur at high pressure up to 40 GPa

Vladimir V. Shchennikov* and Sergey V. Ovsyannikov
Institute of Metal Physics, Urals Division of Russian Academy of Sciences, 620219 Yekaterinburg, GSP-170, Russia

Received 5 August 2002, revised 3 March 2003, accepted 15 April 2003
Published online 29 July 2003

PACS 71.30.+h, 72.20.My, 72.20.Pa, 72.80.Cw

From the thermoelectric power $S$ measurements on sulphur at high pressure $P$, a hole-type electrical conductivity has been established above 25 GPa. A correlation of the pressure dependence of $S$ with the previously published optical reflectance data has been found. The positive value of $S$ and its decrease with pressure have shown the similarity of the electron structure of sulphur and its neighbours from Group VI – Te and Se. However, a negative magnetoresistance (MR) established at $P \approx 30$ GPa points to low mobility of holes and implies an indirect semiconductor gap for sulphur in contrast to the direct gap for Te and Se in the vicinity of the semiconductor–metal phase transition.

1 Introduction

At ambient pressure sulphur is a molecular crystal; it is an insulator with forbidden gap $E_g \approx 2.9$ eV [1]. Under high pressure $P$, a sequence of phase transitions in sulphur has been observed: at $\sim 5.3$ GPa from orthorhombic to monoclinic phase, at $\sim 25$ GPa to amorphous phase, at $\sim 34$ GPa to an undetermined phase with chain structure, at $\sim 100$ GPa to body-centred orthorhombic phase, and at $\sim 162$ GPa to $\beta$-Po phase [2–4]. At $P \sim 50–90$ GPa the semiconductor–metal phase transition and superconductivity with high critical temperature $T_c > 10$ K have been established [3, 5–7]. Thus, the structural transformation of sulphur has been studied in a large pressure range up to 212 GPa. But the variations of electron structure with $P$, especially in the vicinity of the semiconductor–metal boundary, have been studied in a few works only [1–7], where the investigations of electrical resistivity and optical reflectance were performed. Note that resistivity data do not give sufficient information for analysis of electron structure of high-pressure phases, and sometimes contradictions arise between optical and resistivity measurements [8, 9].

Thermoelectric and galvanomagnetic investigations are known to be effective methods for studying conductivity type and parameters of electron structure of high-pressure phases [9–13]. So, the purpose of the present paper was to investigate the thermoelectric power and magnetoresistance of sulphur in the semiconductor region at high pressure.

2 Experimental technique

Measurements of electrical resistance $R$ and thermoelectric power of sulphur samples were performed using a high-pressure chambers with sintered diamond anvils [14]. Three chambers with working diameters of diamond anvils $\sim 0.6–1$ mm were used [14]. Pressure in quasi-hydrostatic medium (catlinite) was

* Corresponding author: e-mail: vladimir.v@imp.uran.ru, Phone: +7 3432 783545, Fax: +7 3432 745244

© 2003 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim
determined with ∼10% error from fixed-point calibration dependences obtained from the resistivity jumps of certain materials with known transition pressures: Bi (2.5, 7.7 GPa), ZnS (15 GPa), GaP (22 GPa), etc. [12, 13]. Note that, even in a case when no transmitting medium was used, the direct measurements of $P$ by ruby fluorescence technique showed acceptable uniformity of quasi-hydrostatic pressure during recent superconductivity measurements at sulphur up to 230 GPa [15]. For creation of a temperature gradient, one of the anvils was warmed by a heater; the temperatures at fixed points of the anvils were measured by thermocouples [12, 13, 16]. Thermoelectric measurements $S$ were started when the resistance of samples decreased under pressure below $\sim 10^8\ldots10^7$ ohm. The technique of thermoelectric power measurements corresponded to that in [12, 13, 16, 17]. The error of $S$ values above 30 GPa was about 20% and much worse (∼30%) in the high-resistance region (below 30 GPa).

Crystals of pure rhombic sulphur have been taken for investigations. Samples of ∼0.1 mm in thickness and ∼0.2–0.4 mm in width were placed into the central hole ∼0.3–0.5 mm in diameter drilled in a catlinite gasket. To obtain signals from a sample and to supply electrical current, pressed silver–platinum ribbons of 5 µm in width or conducting diamond anvils were used [12, 13].

Measurements of transverse magneto-resistance (MR) were carried out at a fixed pressure of ∼30 GPa for two directions of magnetic induction $B$ at both increasing and decreasing cycles. All measurements were performed by an automated setup allowing several environmental parameters and signals from a sample to be simultaneously recorded and stored in the memory of a recording block [17]. After measurements the experimental data were transferred to a computer.

### 3 Results and discussion

In accordance with previous works [5, 7] the electrical resistance of sulphur samples decreased with pressure (Fig. 1). Above $P \approx 25$ GPa where the structural transformations were established [1, 2] the slope of the $R(P)$ relation decreased (Fig. 1).

The thermoelectric power of sulphur decreases with pressure; the sign of $S$ corresponded to hole-type conductivity (Fig. 2). Analysis of experimental dependences were performed by using the basic equations for electrical conductivity $\sigma$ and $S$ [18]:

$$
\sigma = \int \sigma(E) \left( -\frac{\partial f}{\partial E} \right) dE, \quad S = \frac{k}{e} \int \frac{\sigma(E)}{\sigma} \left[ \frac{E - E_F}{kT} \right] \left( -\frac{\partial f}{\partial E} \right) dE,
$$

where $E$ is the electron energy, $E_F$ the Fermi energy, $f$ the Fermi–Dirac distribution function, $k$ the Boltzmann constant, and $e$ the electron charge. For a non-degenerate semiconductor with one type of

![Fig. 1](image)

Dependence of electrical resistance $R$ of sulphur sample on pressure $P$ at $T = 295$ K.
charge carrier, $f$ transforms to the Maxwell–Boltzmann distribution function, and Eqs. (1) tend to

$$S = -\frac{k}{e} \left( r + \frac{5}{2} + \frac{E_g}{kT} \right), \tag{2}$$

where $E_g$ is counted from the edge of the conduction (valence) band [19], and $r$ is the scattering parameter determining the dependence of the relaxation time $\tau$ on $E$: $\tau \sim E^{-(1/2 < r < 3/2)}$ [19]. For liquid systems [18] as well as for disordered ones [20] a similar equation is valid with constant $A \approx 1$ instead of the ‘scattering term’ $(r + 5/2)$. For intrinsic semiconductors [19]

$$S = -\frac{k}{e} \left[ b - 1 \right] \frac{E_g}{2kT} + \left( r_e + \frac{5}{2} \right) \frac{b - 1}{b + 1} \left( r_h + \frac{5}{2} \right) \frac{1}{b + 1} - \frac{3}{4} \ln \frac{m_e}{m_h}, \tag{3}$$

where $b = \sigma_e/\sigma_h$ is the ratio of partial conductivities of electrons and holes, $r_e$ and $r_h$ are the scattering parameters, $m_n$ and $m_p$ are the effective masses of density of states of electrons and holes, and $m_{n,p} = N_s^{1/3}(m_1m_2m_3)^{1/3}$, where $m_1$, $m_2$, $m_3$ are the electron (hole) effective masses of isoeenergetic surfaces (ellipsoids) along the principal axes and $N_s$ is the number of equivalent extrema in the electron (hole) band (for example, $N_s = 4$ and 6 for Ge and Si) [19]. The main dependence of $S$ on $P$ for sulphur in the pressure interval 0–40 GPa is due to the large first term in Eq. (3) ($E_g/2kT \gg 10$). The variations with $P$ of the other terms in Eq. (3) containing $r_{n,p}$, $m_{n,p}$ and $m_{n,p}$ entitles is much weaker [21]. The experimental pressure dependence of the thermoelectric power of sulphur was indeed close to the approximate theoretical one $S \approx (k/e)(E_g/2kT)$ (Eq. 3, for case $\sigma_n = 0$) with $E_g(P)$ values taken from optical reflectance [1] (Fig. 2). The difference of measured and calculated values of $S$ could probably arise due to both neglected ‘scattering terms’ in Eq. (3) and to the ignored electron contribution to the conductivity.

Substituting the value of $E_g$ from the equation for the electrical resistance $R = R_0 \exp (E_g/2kT)$, one can obtain the relation between $S$ and $R$: $S \approx -(k_e/|e|)((b - 1)/(b + 1) (\ln R - \ln R_0))$ to estimate the contribution of electron conductivity ($R_0$ is the pre-exponential factor having weak pressure dependence [21]). When electron (hole) mobility has an activation character (hopping conductivity) a similar relation $\ln R \sim -e/kTd$ is valid, the parameter $d$ being equal to the ratio of the full activation energy of conductivity to the value of the semiconductor gap $E_g$. The activation energy of mobility according to Eq. (1) makes no contribution to $S$ [18]. From the above parametric dependence between $S$ and $R$ (Fig. 3, values of $P$ are excepted), the dominant hole conductivity has been established ($\sigma = 0$) and no sign of mobility activation was observed. The variation of $E_g$ estimated from $S(P)$ data in the pressure range ~30–40 GPa (Fig. 2) was ~0.8–0.4 eV. In general, the thermoelectric properties of sulphur under pressure are similar to those for its neighbours from Groups VI and VII: Te, Se and I [8–10, 12].
The magnetoresistance of sulphur at $P \approx 30$ GPa was found to be negative – electrical resistance decreased with magnetic field (Fig. 4). The magnetic field dependence of negative MR for most mechanisms known – ‘warm’ charge carriers, splitting of impurity levels, ‘quantum corrections’ to conductivity, etc. [9–11, 22] – usually has near-parabolic behaviour at low $B$, and tends to saturation at large $B$. So, to fit experimental MR curves the approximate equation $MR = -aB^2/(1 + cB^2)$ was used, where the constants $a$ and $c$ are fitting parameters. From the results obtained it is difficult to determine the mechanisms responsible for negative MR in sulphur. Note, however, that negative MR was previously observed for high-pressure phases with low mobility $\mu$ of charge carriers [9–11, 23], and reversible inversions of MR sign were established under phase transitions to a high-mobility phases [9]. So, it is reasonable to suppose a low mobility of holes $\mu_p$ for sulphur at ~30 GPa.

![Diagram](image1)

**Fig. 3** Relation between thermoelectric power $S$ and electrical resistance $R$ for sulphur sample at $T = 305$ K in the pressure range 33–42 GPa. Points are experimental data and the dashed line represents the theoretical slope of the dependence for pure hole conductivity (Eq. (3), $b = 0$).

![Diagram](image2)

**Fig. 4** Dependence of electrical resistance $R$ on a) magnetic field $B$ at $T = 295$ K and b) temperature at fixed pressure $P \approx 30$ GPa for sulphur sample. Points are from experiment and the lines show theoretical fitting by the equations $MR = -aB^2/[1 + b(B)^2]$ and $R(T) = R_0 \exp(E_g/2kT)$, where $a$ and $b$ are fitting constants.
The variations of mobility under pressure depend on the relation between $\mu$ and $E_g$ and so there are two opposite cases: for direct-gap semiconductors the ratio $\mu \sim 1/n_{h,p} \sim 1/E_g$ is valid [23], which tends to strong dependence on $P$; while for indirect-gap semiconductors $\mu(P)$ dependences are usually weak [9–11, 19, 21]. The first case corresponds to Te and Se where the exponential rising of $\mu$ with $P$ was observed near the semiconductor–metal phase transition [9–11]. According to optical data [1] the forbidden gap of sulphur near $\sim 30$ GPa is probably indirect and hence lowering of $E_g$ with pressure did not increase the mobility of holes, contrary to Te and Se [9, 10]. Accounting for the MR and $S(P)$ properties investigated, sulphur seems to be similar to amorphous Se and molecular iodine, which also have negative MR at high pressure [9, 10, 23].

The electron structure of sulphur is not known well for the initial orthorhombic phase [24] and also for high-pressure semiconductor phases [15]. However, the variation of electron structure of sulphur under pressure may be qualitatively described by the model of Peierls distortion of simple cubic lattice, as suggested in [25, 26] for Group V, VI and VII elements. This approach is based on the fact that $p$ electrons play a dominant role in the formation of lattice bonds in these materials having incomplete $p$ band (in crystalline, liquid and amorphous states) [25, 26]. This allows us to understand the crystal structure, the origin of the semiconductor gap, the tendency to metallization and the similarity of various substances within Group VI and also for elements of Groups VI and VII [25, 26]. Real structures of Group VI elements indeed may be obtained by a slight shift $u$ of atoms of simple cubic lattice: $wA = (q' - Q')/(3 \sqrt{2} \cdot A')$, where $Q$ is the distance between the nearest neighbour atoms, $q$ the distance between the next neighbours, and $A$ the translation period of the lattice [25]. On increasing the atomic number from Se to polonium the above distortion $u$ as well as the semiconductor gap $E_g$ decrease, so that for metallic polonium they are both equal to zero [25]. In a simple cubic structure sulphur also has to be a metal because the $p$ band is only $\frac{2}{3}$ filled by electrons [25, 26]. The orthorhombic crystal structure of sulphur may be considered as a Peierls distorted simple cubic lattice, where six equivalent $p$ bonds are transformed into two strong covalent and four weak (Van der Waals) ones [25, 26]. This leads to a chain (or ring) structure with two nearest neighbours for each atom [24, 25]. The corresponding three-fold splitting of the $p$ band lowers the system energy due to opening of the semiconductor gap at the Fermi level [25, 26]. Peierls structures have lower density than initial undistorted phases, so, at a certain pressure, the distortion becomes energetically disadvantageous [26]. This is a reason for the reduction of $E_g$ [2] and $S$ (present data) with pressure for both the amorphous and the unidentified chains phase of sulphur above $\sim 25$ GPa and $\sim 34$ GPa, respectively [1]. These phases probably conserve the chain or ring structure (like amorphous Se [24]) with two neighbours for each $S$.

Owing to the formation of $S_n$ rings, the lattice parameter of sulphur in comparison with trigonal Te and Se has additional enlargement [1, 2], which has to cause an additional splitting and hence a narrowing of the $p$ bands. As the effective mass $m$ depends on the band width $\Delta E$, $m^\star \sim A^2/(6\hbar^2 \Delta E)$ [20], where $A$ is the lattice parameter and $\hbar$ the Planck constant, so the narrowing of bands at high pressure phases is responsible for the large effective mass and low mobility $\mu \sim 1/m$ of holes for the orthorhombic and especially the amorphous high-pressure phases near $\sim 30$ GPa [1].

At further transitions into the high-pressure metallic phase having a body-centred orthorhombic (layered) structure, the coordination of the sulphur atom increases from 2 up to 4, and in the next phase with $\beta$-Po structure up to 6 [1, 2], which may indeed be interpreted as removal of Peierls distortion. Thus, the measurements performed have revealed a difference of metallization process under pressure for sulphur on the one hand and for its analogues from Group VI (Te and Se) on the other, which remain direct-gap semiconductors until the phase transitions [9, 10]. However, the thermoelectric and galvanomagnetic measurements in the vicinity of $E_g \rightarrow 0$ near 90 GPa are still desirable to clarify the type of semiconductor gap close to the semiconductor–metal phase transition.

Acknowledgements This work was partly supported by the Russian Foundation for Basic Research, Grant No. 01-02-17203 and CRDF (TGP-599).
References

[14] V. V. Shchennikov and V. A. Smirnov, Russian patent No. 2050180.