HIGH PRESSURE INVESTIGATIONS OF CONDUCTING MATERIALS

Vladimir V. Shchennikov, Andrew Yu. Derevskov, Vladislav A. Smirnov

aInstitute of Metals Physics Ural Branch RAS, 620219 Ekaterinburg, GSP-170, Russia
bEcological Centre of National Academy of Sciences of Ukraine 314000 Poltava, Ukraine

ABSTRACT

The diamond-plungers apparatus for simultaneous measurements of resistance $\rho$, thermoelectric power $S$, volume $V$ of samples is described. The apparatus contains the microcontroller for the operation by the measurements and keeping the experimental data. The examples, comprised $S$, $\rho$, $V$ recording for semiconductors Ge, Si and HgTeS in pressure range 0–30 GPa are represented.

Keywords: pressure, diamond electrodes, thermoelectricity, component mixture, inclusion configuration, phase transition

A thermal, electrical, elastic etc. properties of composite materials (including IC structures) are a complex functions of the component concentrations and configurations. The effective values of resistivity $\rho$, thermal conductivity $\lambda$, and thermoelectric power $S$ of mixture may be thought as a normalized sum of the components contributions

$$
\rho = \frac{\sum \rho_i C_i f_i(\rho)}{\sum C_i f_i(\rho)}, \quad \lambda^{-1} = \frac{\sum \lambda_i^{-1} C_i f_i(\lambda)}{\sum C_i f_i(\lambda)},
$$

where $C_i = V_i/V$ – concentration of $i$-phase ($V_i$ – is a volume of $i$-phase, $\sum C_i = 1$), and factors

$$
f_i(\rho) = \frac{3\rho}{\rho + (3-A)\rho_i}, \quad f_i(\lambda) = \frac{3\lambda_i}{\lambda + (3-A)\lambda_i}
$$

– determine the thermal and electrical connections of phase inclusions in a sample. For the total $S$ one have to take into account the dependence of summarized thermoelectric voltages of phases contributions on factor $f_i(\rho)$, as for effective $\rho$, and the inversely proportional dependence of temperature gradients on $\lambda_i$ and factor $f_i(\lambda)$

$$
S = \frac{\sum S_i C_i f_i(\rho) \lambda_i^{-1} f_i(\lambda)}{\sum C_i f_i(\rho) \lambda_i^{-1} f_i(\lambda)}.
$$

When the constant $A$ is equal 0 and 3, the Eq.1, 2 exactly coincide with the cases of parallel and consequent electrical and thermal connections of phases, and at $A = 1$ – with the well known case of spherical inclusions. Thus, the various values $0 < A < 1$ and $1 < A < 3$ correspond to the intermediate electrical connections of phases, and the appropriate shape of inclusions, presumably, are "contracted" and "elongated" orientated ellipsoids. The sizes of inclusions are assumed to be larger than the mean free path of charge carriers. For a two-component mixture the Eq.1 transforms to a quadratic equation

$$
A\rho^2 + \rho_2 (3C_1 - A) + \rho_1 (3C_2 - A) = 0.
$$

The change of the above effective values for mixture according to Eq.3 ought to begin near the different concentration of the conducting components, depending on parameter $A$ and the relation between the values $\rho_i$, $\lambda_i$ etc. of phases. For example, when $\rho_2/\rho_1 >> 1$, the threshold concentration is $C=A/3$. The appropriate threshold values are rather different for various properties of mixture and their temperature, magnetic field and others derivatives. It's interesting to note, that...
certain relations between conjucted values are independent on configuration of mixture. From Eqs.1 and 2 such a relationship may be written for the $\rho$, $\lambda$, $S$ at arbitrary values of parameter $A$:

$$\frac{S - S_2}{S_1 - S_2} = \frac{\rho \lambda_1 - \rho_2 \lambda_2}{\rho_1 \lambda_1 - \rho_2 \lambda_2}$$

Formerly Eq.4 was deduced for the peculiar case of isotropic disordered mixture in$^8$.

The above consideration tends to a conclusion, that a rising of the accuracy of multi-component materials investigations may be achieved by a measurements of several properties of sample simultaneously. The substances, undergoing the pressure-induced phase transition, may be viewed in the vicinity of transition points as peculiar case of composite system$^2$. So, the phase transition investigations of materials ought to be performed in the suggested way.

2. EXPERIMENTAL DEVICE

2.1 High Pressure Apparatus

The suitable device for such investigations includes the pressure apparatus with the diamond plungers (Fig.1-3), and recording block (Fig.4). At the table 1 of the apparatus the lever mechanism 2 and pressure chamber 3 are established. The reduction gear 4 with the electromotor drive is due for the creation of stress $F$, transferred to the plungers, contained in the removable cassette 5.

High pressure plungers of Bridgman anvils type$^9$ made of steel, tungsten carbide and superhard materials were used for pressure generation up to 5, 10 and 30 Gpa, respectively$^{10,11}$. We used different versions of plungers by variation of superhard materials and the construction of plungers to enlarge the pressure range (Fig.2). The recent proper model includes two-layers plungers consisting of sintered diamond tips and tungsten carbide matrices, produced at high pressures and temperatures$^{10,11}$ (Fig.3). The values of $P$ are estimated from the acting stress $F$ and tabulated dependencies $P(F)$, recording for the any pair of pressure plungers$^{12,13}$.

The boron nitride and the synthetic diamond without metal impurities we've used as a tip of plungers have a high electrical resistivity, so the platinum-silver ribbons of $\sim$ 5 $\mu$m thick are used to get electrical outputs to a sample. The other synthetic diamonds used are high conducting materials due to a thickness. metal inclusions and so are good as an electrical probes to a sample for the electrical measurements$^{10,11}$. The usual sizes of samples are $\sim$0.2-05 mm in a diameter and $\sim$0.1 mm in thickness. The pressure transmitting medium is a lithographic stone$^{10,13}$.

Fig.1. High pressure apparatus. 1- table, 2 – lever mechanism, 3 – pressure chamber, 4 - reduction gear with the electromotor and handle drives, 5 – removable cassette with the pair of diamond plungers, 6 – parts of cassette.
The recording block (Fig. 4) contains the microprocessor 1, interfaces 8 – 11 for the connection of the outputs of standard digital voltmeters 14 – 17, communicated with the sensors of plunger displacement X, pressure P (stress F), temperature T, and electrical voltage U of sample. The experimental data are stored in the energy supply independent RAM, and may be read out from the display 13 or transferred to IBM-PC by serial interface 22.

Fig. 3. Version of high pressure apparatus. 1 - tungsten carbide matrixes, 2 - supporting rings, 3 - complex plungers, 4 - sintered diamond tips, 5 - lithographic stone container, 6 - sample.

The program of operation, measurements and testing is stored in ROM, the choice of ruling parameter (P, T, X, U) and step may be changed by keyboard 13. For the S-measurements the special block was constructed for operation by the heaters work in the pressure chamber and hence for producing the various thermal regimes during the testing. In a cases, when
diamond plungers are using as an electrical probes to a sample, the corrections have to be done to $S$-voltage, accounting the contribution of the plungers material. By using of noble metals as $S$-calibrates it's possible to specify the measured $S$ values and to take into account the necessary corrections, based on the results of computations, given below.

### 2.2. Temperature distribution computations

A temperature distribution in diamond plungers and a sample have been calculated for a substantiation of suitable $S(P)$-measurements. The approach used was similar to one, given in. For the computations the simplified scheme of high pressure apparatus was taken. We've took into account the thermal exchange between lateral surfaces of plungers and environment, the zero thermal resistance of borders and a constant temperatures at the upper and lower edges of plungers. The equation of thermal diffusion

$$
c\rho_0 \frac{\partial T}{\partial t} = \frac{1}{r} \frac{\partial}{\partial r} \left( r\lambda \frac{\partial T}{\partial r} \right) + \frac{\partial}{\partial z} \left( \lambda \frac{\partial T}{\partial z} \right)
$$

for a stationary thermal distribution was solved for numerous points of pressure apparatus by using of finite differences method.

In Eq.5 $\rho_0$ is a density, $r$ and $z$ are radial and axial coordinates, and $c$ is a specific heat capacity. The most of thermal parameters were varied at calculations. The thermoconductivity of synthetic diamond plungers $\lambda_0$ was taken to be equal to one for Cu (for native diamond it's much higher), and thermal parameters of real metals and semiconductors: Se, Te, Si, Pt, Cu, Au - were used for a samples. The parameters of real high pressure apparatus were taken in computations.

Calculated thermal gradients along the sample thickness $h$ (Fig.5) depending on the thermoconductivity $\lambda$ and $h$. At Fig.5 $\Delta T/\rho$ is a temperature difference between the upper and lower edges of diamond plungers. The intensification of heat flux density through the sample takes place due to a low $\lambda$ of lithographic stone medium around a sample, and so the sufficiently high gradient $\Delta T = qh/\lambda$ is produced along the sample thickness even for a high thermoconductive substances (Fig.5). The $T$-gradients arising along the plungers height tend to a errors in $S$-values.

### 2.3. Methods of $S$-measurements

The diamond plungers are used as the cooler and heater for producing the constant $T$-gradient in a sample at $S$-measurements. When $\lambda$ of substance is less, than $\lambda_0$ of synthetic diamond, the error in $\Delta T$ isn't large and it may be taken into account from the above calculations. Indeed, for the various materials the results of above $S$-measurements were in a good agreement with the analogous data, received by the current techniques.

For example, $S(P)$ - data for semiconductor compounds: HgSe up to 2 GPa, SmX (X = Te, Se, S), EuO, and Bi$_2$Te$_3$ up to 10 GPa, were in good agreement with the results, obtained in the described diamond plunges apparatus. For other semiconductors: Ge, Si, Se, Te, HgX, CdX, ZnX, CuO, etc. - the results of $\rho$ and $S$ measurements by the described technique correlate with the overall picture of electron structure transformation during the phase transitions, but there are no
published $S(P)$-data for this materials at pressure range up to 10-30 GPa. It's worth to note the similarity of $S(P)$ dependencies on $\text{YBa}_2\text{Cu}_3\text{O}_7$ crystals and ceramics, investigated by the present method up to 20 GPa\textsuperscript{21} and by the current one up to 6 GPa\textsuperscript{22}.

The $S(P)$ results for Iodine in paper\textsuperscript{23}, where the native diamond anvils were used and a very skillful technique of $S$ measurements was developed, up to 25 GPa are rather similar with ones obtained in present diamond chamber\textsuperscript{24} and correlate with the data of optics measurements and theoretical calculations of electron structure. A certain difference of $S$-values at $P = 20-25$ GPa may be reduced by a corrections mentioned\textsuperscript{7,24}.

For metals the results were also checked with the table data and the corrections to measured values of $S$ were estimated due to influence of plungers parts\textsuperscript{7,15,16}. In Bi the obtained data were equal to ones at hydrostatic conditions up to 10 GPa\textsuperscript{18}.

So, the above checking of $S(P)$-measurements method for various materials may be viewed as successful.

The non-stationary thermal investigations methods may be also developed by using of this apparatus, the data of $S$-measurements being in well accordance with the stationary ones\textsuperscript{31}. As one can see from Fig.5, the dependence of $\Delta T$ on the $\lambda$ and $h$ of sample allows to observe the phase transition points by recording the jumps of $\Delta T$. Below there are experimental data received by the described high pressure device, confirming this suggestion.

3. EXPERIMENTAL RESULTS

During the testing of the materials mentioned above the validity of relation (3) was established for Si, Ge, GaP, ZnX where $S(P)$-dependence during semiconductor-metal phase transition have leaved behind $\rho(P)$, one and vice versa - at the inverse transition\textsuperscript{2,7}. The similar effects were observed also at temperature-induced metal-semiconductor phase transitions\textsuperscript{25,2}. The treatment under pressure shows also that the changes of volume during structural phase transitions and the appropriate changes of properties ($\rho, S, \lambda$) occur at different values of $P$ (and $T$\textsuperscript{25}) according to Eq.1-3 12,2.

Fig.6. Dependence of thermoelectric voltage of n-Si (left picture, $P$ up to 30 GPa) and p-Ge (right one, $P$ up to 18 GPa) on the stress $F$, driving by the high pressure apparatus with synthetic diamond plungers.

At Fig.6 the recording of $S$-voltage drops (at $\Delta T = \text{constant}$) are shown in n-Si and p-Ge during the pressure induced phase transition into tetragonal $\beta$-Sn-structure at 12 and 9 GPa, respectively\textsuperscript{26-28}. Measurements were made by using synthetic diamond plungers with the platinum-silver ribbons to the samples. The values of $S$ for these high pressure metal phases of Si, Ge are positive: + (5 – 10) mK/V. The inverse transition tends to change the sign of $S$ for Si as the sphalerite structure didn't restore\textsuperscript{28}. The beginning of phase transition in these materials spreads on wide pressure interval due to the quasihydrostatic conditions and high hardness of Si and Ge, so in the vicinity of transition the samples are the mixture of phases.
At Fig. 7 the simultaneously recordings of resistance and plunger displacement are shown for HgTe$_{0.6}$S$_{0.4}$ sample. The plungers used were conducting synthetic diamonds, which served as the electrical outputs to sample. The abrupt jump of $\rho$ at $P > 1$ GPa and appropriate plunger displacement drop correspond to the sphalerite - cinnabar phase transition$^{22,13}$. The pure effect of sample contraction is smaller, than the total variation of $X$, including the contraction of lithographic stone container. The decreasing of $\rho$ at pressures $P < 10$ GPa and a weak dependence on $P > 10$ GPa relates with the transition into NaCl structure and metal state, occurring at HgTe$^{22,13}$. The replacement of Tellurium by Sulfur atoms in anion sublattice shifts the points of the both transitions$^{20}$.

The consequent cycles of pressure generation in this sample are recorded at Fig. 8. One can see the correlation of $\rho(P)$, $S(P)$, $X(P)$ and $\Delta T(P)$ behavior. The jump of $\Delta T$ at the first transition may be explained by the decreasing of the thermoconductivity in semiconductor phase with Selenium-like cinnabar structure$^{28}$. And vise versa, the latest drop of $\Delta T$ during the second transition relates to the increasing of $\lambda$ in the high pressure metal phase.

The examples described, where the samples contained a mixture of phases near the semiconductor-metal phase transitions, allow to modeling any
composite system. The value of $S$ is insufficient to a resistance error, so simultaneously measurements of $\rho$, $S$, $\Delta T$, and $X$ improves the interpretation of experimental data. The above techniques may be useful also for the materials control and trial of semiconductor devices, consisting of the layers and other discrete conducting elements.

ACKNOWLEDGEMENTS

Authors are grateful to Mr. V.N. Neverov for assistance in manuscript preparing.

REFERENCES

6. V.V. Shchennikov, "Magnetoresistance of metastable high pressure phases" *Fizika Tverdogo Tela* (St.-Peterburg) 37, N 4, pp. 1015-1021, 1995.

20. V.V.Shchennikov, N.N.Stepanov, I.A.Smirnov, A.V.Golubkov, "ThermoEMF and resistivity of Samarium monochalcogenides at ultrahigh pressure" Fizika Tverdogo Tela (St.-Peterburg) 30, N 10, pp. 3105-3110, 1988.


24. V.V.Shchennikov, "Magnetoresistance of Iodine at high pressure" Fizika Tverdogo Tela (St.-Peterburg) 38, N 9, pp. 2680-2685, 1996.


29. V.V.Shchennikov, N.P.Gauleshko, V.M.Frasunyak, "Phase transition in HgTeS crystals at high pressure" Fizika Tverdogo Tela (St.-Peterburg) 37, N 11, pp. 3532-3535, 1995.