Thermochimica Acta, 71 (1983) 323–336
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

THE ELECTRICAL CONDUCTIVITY AND MAGNETIC SUSCEPTIBILITY OF GERMANIUM(II) MONOSELENIDE IN THE SOLID AND LIQUID STATES

L. ROSS and M. BOURGON

Département de Chimie, Université de Montréal, Faculté des Arts et des Sciences, Case postale 6210, succursale A, Montréal, Que. H3C 3V1 (Canada)

J.J. HECHLER

Institut de Génie des Matériaux, Conseil National de Recherche du Canada, 75, Boul. de Mortagne, Boucherville, Que. J4B 5K5 (Canada)

(Received 6 July 1983)

ABSTRACT

The specific conductivity of germanium(II) monoselenide has been measured, under equilibrium pressure, from room temperature to 802°C. Interpretation of the results leads to the conclusion that the intrinsic conductivity is observed in the solid in the upper temperature range: the calculated energy gap is $E_{0g} = 1.222 \pm 0.027$ eV which coincides with the value of the optical gap. In liquid GeSe the calculated energy gap is 1.504 ± 0.016 eV. This increase of the energy gap in liquid GeSe is due, presumably, to the strengthening of the intralayer bonds of the structure. Electrical conductivity and magnetic susceptibility measurements confirm the existence of a polymorphic transformation in GeSe at 656°C.

INTRODUCTION

Germanium(II) monoselenide is known to be a semiconductor in the solid state. The electrical properties of several *p*-type polycrystalline samples were investigated by Vestrepen [1] and Asanabe and Okasaki [2] at temperatures below 525°C. From the conductivity curves the value of the thermal energy gap E_{0g} for intrinsic conduction was calculated to be 1.0 eV.

The optical properties of single crystals and very thin films of GeSe were studied by Kannewurf and Cashman [3]. At room temperature the value of the optical gap was found to be 1.10 ± 0.02 eV. By X-ray spectroscopy at 25°C, Mande et al [4] found a value of 1.2 eV for the energy gap of GeSe.

Ross and Bourgon [5] determined the phase diagram of the Ge–Se system. The reported diagram differs considerably from that obtained by Ch'un-Hua and Pashinkin [6] but is in substantial agreement with the diagrams reported by Karbanov et al. [7] and Ipser et al. [8]. Two peaks at 661°C and 667°C,

0040-6031/83/$03.00

which appear on the thermograms of all samples on the germanium-rich side of the diagram, were interpreted as being due, respectively, to a first-order solid state transition which occurs in GeSe (661°C) and to the incongruent melting (667°C) of GeSe according to the peritectic reaction

$$\mathrm{GeSe(s)} \rightleftarrows \mathrm{Ge}_{1-x}\mathrm{Se(l)} + x\,\mathrm{Ge(s)} \tag{1}$$

The aim of the present investigation was to study the electrical properties of GeSe over as wide a temperature range as possible in order to obtain as yet non-existent data on the specific conductivity of GeSe in the liquid state, and also to gain more insight into the solid state transition and the change in electrical properties that this compound undergoes on melting.

EXPERIMENTAL

Preparation of GeSe

Stoichiometric GeSe was prepared in 60 g quantities using a method described previously [5]. It is believed that the compositions were known to 0.03% or better.

The conductivity cell

The cell used for measuring the electrical conductivity of GeSe in the solid and liquid states is shown in Fig. 1. A closed cell must be used to prevent loss of GeSe, the vapour pressure of which increases somewhat rapidly with temperature, and also to prevent loss of selenium, which would change the stoichiometry of the alloy, should partial dissociation of the latter occur in the vapour phase. Furthermore, to prevent bubble formation in liquid GeSe, which would lead to difficulties during the measurements, it was found necessary to design a cell which can be operated under vacuum conditions.

The cell is made entirely of pure silica tubing (General Electric). Electrical contacts to the solid or liquid sample are assured by means of precisely machined high purity (AUC grade) graphite plugs (A in Fig. 1) fitted into female standard joints (7/25); threaded graphite rods B are fitted into the larger plugs. Their length is adjusted so that their narrow tip is located at the opening of the capillary (2 mm I.D.). The cell constant is determined by the length (6–7 cm) of the U-shaped capillary C at the bottom of the cell. A horizontal tube D connects the two cell compartments in order to equilibrate the cell pressure. The cell is loaded with the sample in powder form by way of tube E and then sealed at constriction F.

The graphite electrodes are connected to the measuring device by means of stainless steel screws G fitted into the graphite plugs and onto which are attached chromel wires. The potential probe wires and the current wires are

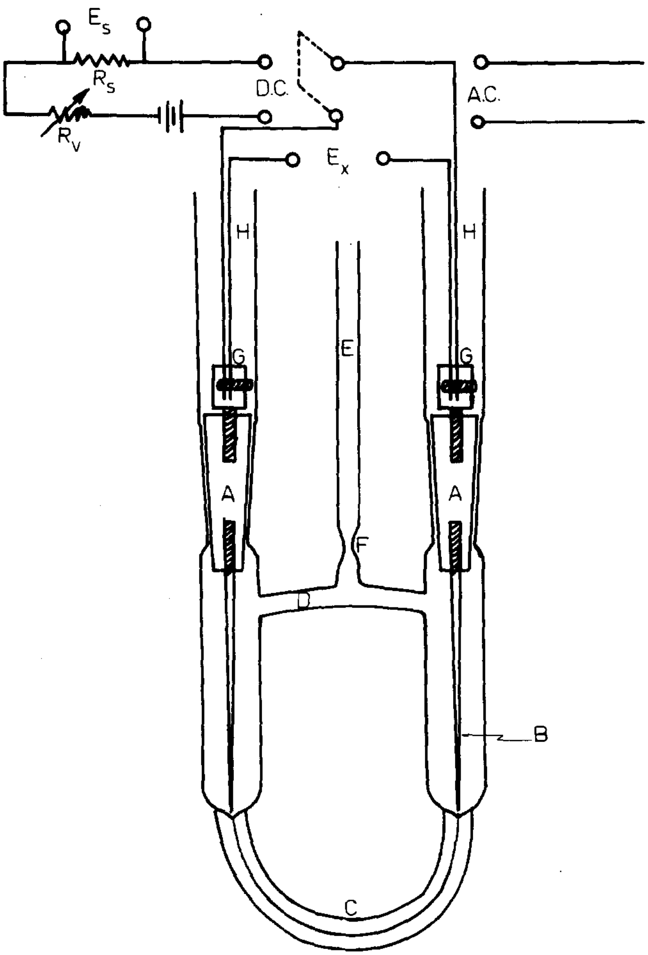

Fig. 1. Quartz cell for the measurement of the electrical conductivity of solid and molten GeSe.

protected by double-bore insulating alumina sheathing. Over each electrode a silica tube H is partially filled with boric oxide; the latter seals the cell on melting.

Preparation of the cell

Because of the high vapour pressure of GeSe, it was thought wise to reduce the porosity of the graphite plugs. The latter were coated with a suspension of graphite in toluene and left to dry at room temperature for 2 days under vacuum. The temperature was then raised slowly to 550°C, under vacuum, and kept at this temperature for a further 2 days. The electrodes were then fitted into the standard joints of the cell. To do so, each electrode was again coated with the graphite suspension and tightly adjusted (under suction) into each standard joint. The whole conductivity cell was then treated thermally as described above. Finally, the porosity was reduced to a minimum by vacuum filtering a suspension of graphite in toluene through the graphite electrodes. This operation was repeated and the whole cell left to dry under vacuum for 2 days. This treatment made it possible to maintain, by continuous pumping (through E), a vacuum of 0.25–0.30 mmHg in the conductivity cell under an external pressure of 1 atm. The conductivity cell was then filled with powdered GeSe, rubber stoppers were fitted in tubes H, and the cell was sealed under a vacuum of 10^{-3} mmHg at constriction F. Finally, the chromel wires attached to their stainless steel screws G coated with the graphite suspension in toluene were fitted into the graphite electrodes.

Cell calibration and principle of measurement

Prior to filling and sealing the cells, the latter were calibrated at 0°C by a conventional AC method using 1 N KCl. After calibration, the whole conductivity cell was cleaned several times in large quantities of boiling deionized water to eliminate any trace of KCl that might contaminate the graphite electrodes. The cell constants were determined at 0°C for convenience; because of the very small expansion coefficient of silica glass, the variation of the cell constant is negligible in the temperature range studied. Typical values of cell constants were between 250 and 270 cm^{-1}. The resistance of the potential probes and of the current wires, as well as that of the graphite electrodes, was measured by filling the cell with mercury.

In order to detect polarization effects in the cell, both DC and AC methods were used during measurements on GeSe. For the DC measurements a four-probe method was used. A potential difference of 3 V was applied to three resistors in series by means of a potentiostat (Tacussel, Type PRT 20): the first is a variable resistance R_v (0 to 11 110 ohms, Cambridge No. L-308952) used for coarse adjustment of the current; the second is a standard resistor R_s (0.01, 0.1, 1.0, 10, 1000 or 10 000 ohms, Guildline Multiple Standard Resistor type 9,300 No. 24,570) which was used to accurately measure the current in the circuit; the last resistor is the conductivity cell, whose resistance is determined by measuring the potential drop across the potential probes of the cell using a high precision potentiometer (Honeywell 2781). The value of the current was generally 0.2 mA. However, when the resistance of the cell became too low to be measured with good precision, the current was increased to 30 mA maximum.

The AC measurements were made by means of an AC universal bridge (Wayne Kerr B-221, 1592 Hz s^{-1}). The resistance of the leads and the graphite electrodes was duly accounted for.

Conductivity measurements

Ground anhydrous boric oxide was introduced into the upper tubing H over each electrode after the conductivity cell had been filled and sealed. Commercial boric oxide containing up to 3% water was dehydrated using a method described by Walton and Rosenbaum [9]. The cell was then enclosed

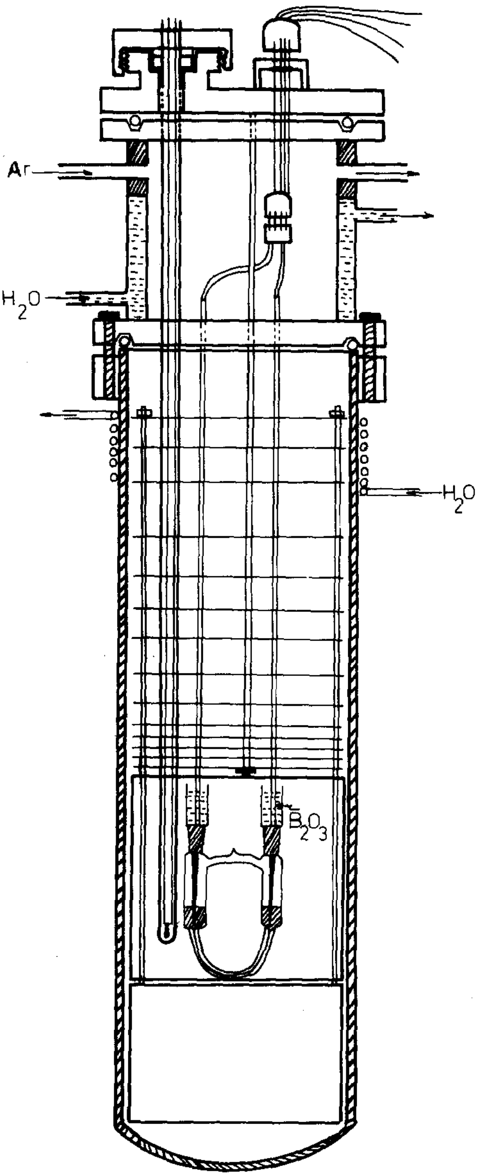

Fig. 2. Assemblage for the measurement of the electrical conductivity

in a grounded stainless steel housing fitted with several steel radiation shields (Fig. 2); the whole assembly was enclosed in a gas-tight quartz chamber closed with a water-cooled head sealed with an O-ring. This head allowed the passage of the necessary connections and also permitted the introduction of inert gas or the evacuation of the chamber. Temperature measurements were made with chromel–alumel thermocouples suitably protected by silica tubing and located at a distance of 1 cm from the cell capillary. The furnace used has been described by Handfield et al. [10].

The whole system was evacuated (10^{-3} mmHg) and then heated very slowly under vacuum to melt the boric oxide (m.p. 220°C). As an additional precaution, to overweigh the high vapour pressure of molten germanium selenide, purified argon was admitted into the furnace chamber at 500°C and above. This was a security measure only, since no trace of GeSe was detected at any moment in the graphite electrodes. Finally, the GeSe was melted with the furnace inclined to insure complete filling of the capillary.

At the beginning of a run, after melting of a fresh sample, 3 days were necessary to attain equilibrium conditions and thus obtain reproducible results. However, when a GeSe sample had been previously melted equilibrium was attained after only a few hours. No final readings were taken until consecutive measurements, after repeated mixing of the sample (rocking the furnace), gave identical results.

In the liquid state, after the initial equilibrium period, the technique of measurement adopted was to increase the temperature to a given value and to record readings until reproducibility indicated that thermal equilibrium had been established. A period of 20 min was necessary for the establishment of the equilibrium. The same technique was used for measurements during cooling of the liquid.

Magnetic susceptibility measurements

Magnetic susceptibility measurements were performed by the Faraday method, with a torsion balance constructed in Mr. Fruchart's laboratory at the Centre d'Etude de Chimie Métallurgique in Vitry, France. The magnetic susceptibility and the electrical conductivity data were obtained from two different samples of the same GeSe batch. All samples were vacuum sealed in quartz vials. The system was equipped with a completely automatic programming device. Since the magnetic susceptibility measurements were made after the conductivity measurements, the system was programmed for a stabilization period of 30 min in order to obtain equilibrium conditions, as determined during the conductivity measurements.

RESULTS

Electrical conductivity

The results are shown in Figs. 3, 4 and 5, where the natural logarithm of the specific conductivity σ is plotted against the reciprocal of the Kelvin temperature. During the measurements no polarization effects could be detected; AC and DC measurements agreed very well. For this reason the DC measurements, which are more accurate, are the only ones reported. Furthermore, after each DC measurement, the polarity was reversed and the measurements repeated in order to detect possible thermoelectric effects; the

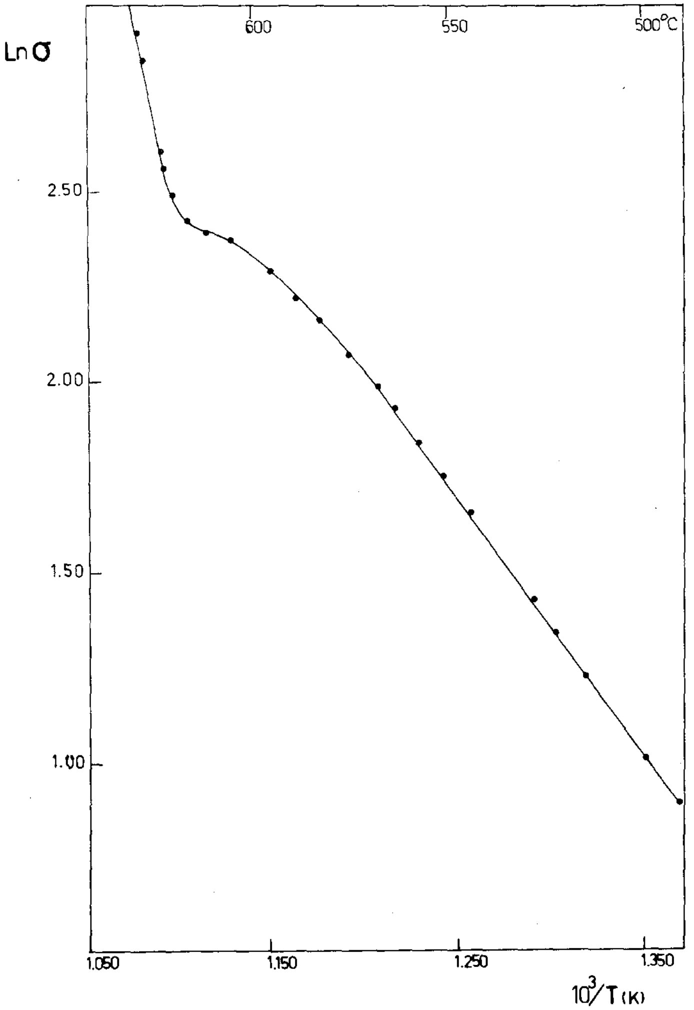

Fig. 3. Natural logarithm of the specific conductivity σ (ohm^{-1} cm^{-1}) as a function of the inverse of the absolute temperature (K) in solid GeSe.

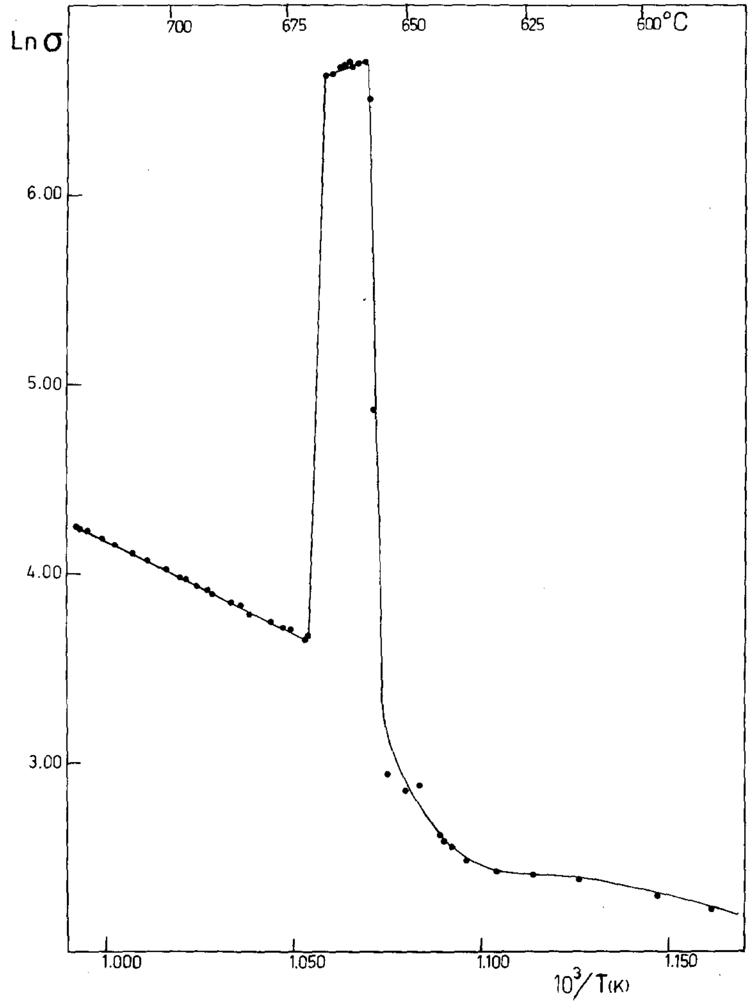

Fig. 4. Natural logarithm of the specific conductivity σ (ohm^{-1} cm^{-1}) as a function of the inverse of the absolute temperature (K) in the transition range of solid GeSe.

maximum difference observed between two such measurements was negligible. The data were analyzed by a least-squares method to obtain the energy gaps.

The specific conductivity curve of solid GeSe is shown in Fig. 3. The conductivity values were obtained from three different samples, under the equilibrium vapour pressure of GeSe, each sample having undergone several melting–freezing cycles. Each sample was studied during a period of 10–30 days and the reproducibility of the results indicates that no loss of selenium occurred during the measurements. The results obtained below 400°C are not reported. At these lower temperatures, the conductivity curve was not reproducible. The various curves obtained, however, were always lower in

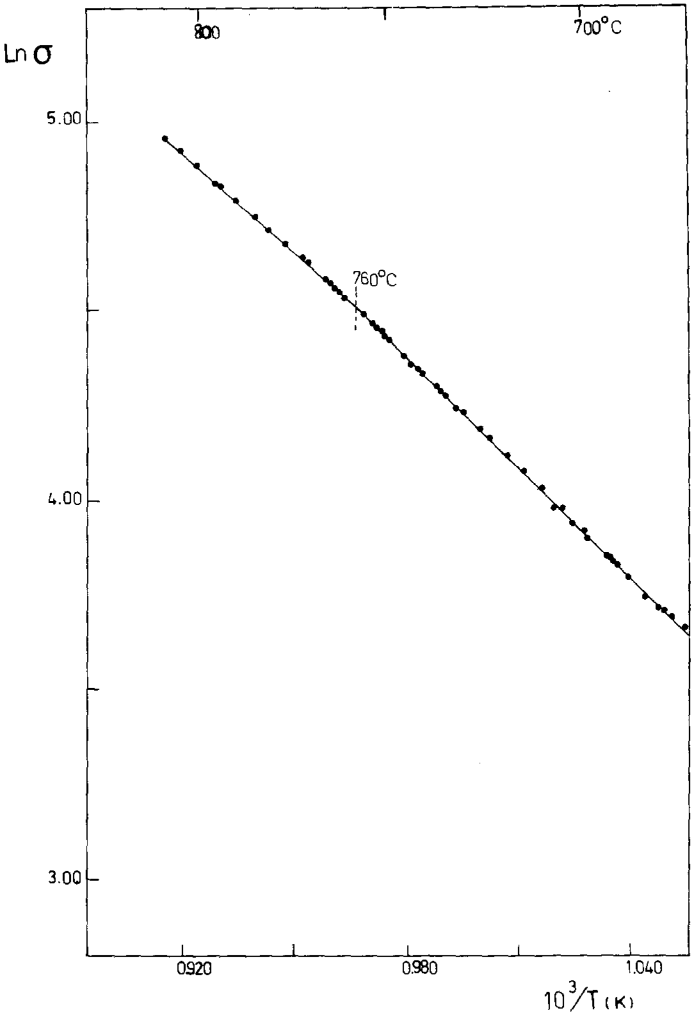

Fig. 5. Natural logarithm of the specific conductivity σ ($\text{ohm}^{-1}\ \text{cm}^{-1}$) as a function of the inverse of the absolute temperature in liquid GeSe.

slope than the curve at higher temperature (Fig. 3). It is assumed that in the lower temperature range the non-reproducible values are due to extrinsic conductivity.

The values of the specific conductivity of the solid are probably not the true values, since the measurements were taken on polycrystalline samples obtained after freezing of the melt. However, since reproducible values were obtained after several melting–freezing cycles, we believe that the values are very close to the true values. Since evaluation of the energy gap was the aim of the present work, true values were not essential. Between 430 and 570°C the logarithm of the electrical conductivity varies linearly with $1/T$ and this region seems to be the intrinsic region. Between 570 and 656°C there is a curvature in the log σ vs. $1/T$ curve followed by a jump of conductivity at 656°C.

Figure 4 shows, on a larger scale, the values of the specific conductivity between 596 and 726°C. At 656°C the conductivity jumps from 19.04 ohm^{-1} cm^{-1} to a maximum of 810.07 ohm^{-1} cm^{-1} at 666°C. From 664 to 672°C the temperature coefficient of conductivity is negative. Around 672°C there is a sudden fall of the specific conductivity which returns to a value comparable to that in the solid state, i.e., 39.370 ohm^{-1} cm^{-1} at 672°C.

The conductivity curve of GeSe in the liquid state is shown in Fig. 5. The high value of the conductivity and the positive temperature coefficient of conductivity indicate, as is the case for other IV–VI compounds, that GeSe remains a semiconductor in the liquid state. Two straight lines which intersect at 760°C are observed; the change in slope is due to crossing of the liquidus. Thus homogeneous liquid GeSe exists at temperatures above 760°C. Without taking into account the sudden conductivity jump at the transition temperature there is a conductivity difference of 20 ohm^{-1} cm^{-1} between the solid and the liquid.

Magnetic susceptibility

Figure 6 gives the magnetic susceptibility χ as a function of temperature

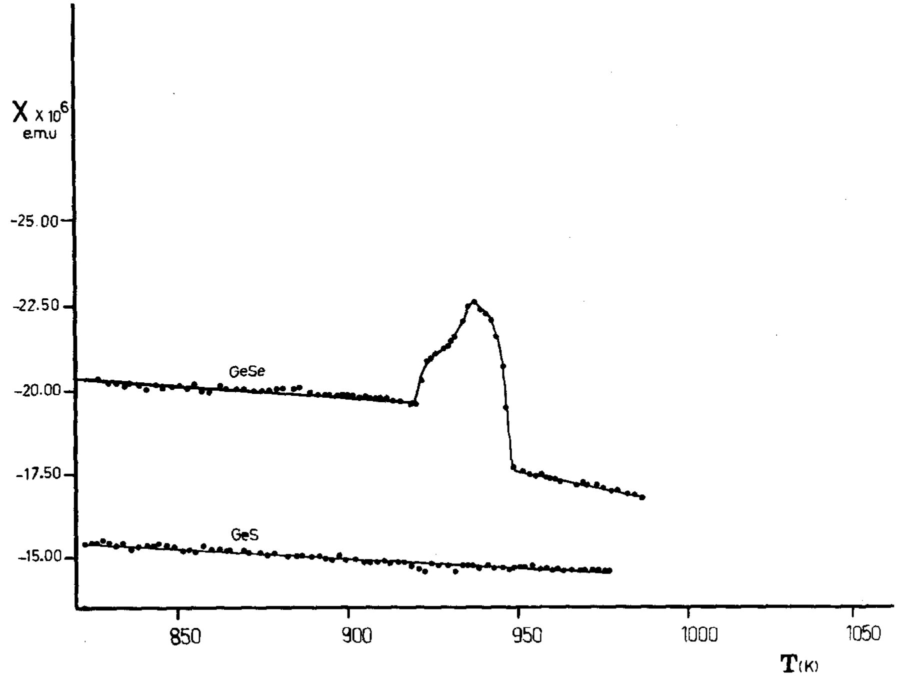

Fig. 6. Magnetic susceptibility χ (e.m.u.) of GeSe as a function of the absolute temperature T(K) in the solid and liquid states.

for GeS and GeSe in the solid (polycrystalline) and liquid states. The diamagnetic component of both compounds is larger than the paramagnetic one.

The aim of these magnetic susceptibility measurements was to confirm, by a different method, the existence of the transition in GeSe observed by electrical conductivity and by thermal analysis at 656°C, and also to observe the change in the magnetic susceptibility at the melting point to see if it could be reconciled with the conductivity measurements.

In solid GeSe the paramagnetic susceptibility component seems to increase with temperature. A sudden increase of χ occurs around 650°C towards higher diamagnetic values with a maximum of -22.50×10^{-6} e.m.u. at 664°C. After the melting point around 677°C there is a sudden fall of the magnetic susceptibility. In the liquid state the paramagnetic component seems to increase. Without taking into account the susceptibility jump there is a change in magnetic susceptibility at the melting point of $\Delta\chi$ fusion $= 2 \times 10^{-6}$ e.m.u.

DISCUSSION

Solid state

A straight line in the conductivity curve in the 430–570°C temperature range does not necessarily indicate that intrinsic conductivity is being observed. The value of the slope could be related to the energy of formation of defects (vacancies or interstitials). We believe that at high temperature the electrical conductivity of GeSe which varies with temperature according to the relation

$$\sigma = A \exp(-E_{0g}/2RT) \tag{2}$$

is intrinsic because the value of $E_{0g} = 1.222 \pm 0.027$ eV, calculated from the slope of the conductivity curve in Fig. 3, is identical with the optical gap E_g. A value of $E_g = 1.16$ eV at 300 K was obtained from optical measurements with unpolarized light on single crystals and very thin films by Kannewurf and Cashman [3]; they observed, qualitatively, that this E_g increases as the temperature decreases. A similar behaviour has been observed for GeS [11] and SnS [12,13] where the variation of the optical gap is approximately -4.8×10^{-4} eV K^{-1}.

The optical E_g is a linear function of the temperature in a certain temperature range; as 0 K is approached the variation becomes non-linear. The linear part of the curve can be represented by the equation

$$E_{g(\text{solid})} = E_{0(\text{solid})} + \alpha T$$

where $E_{0(\text{solid})}$ is the optical energy gap extrapolated to 0 K (and not the true value at 0 K) and $E_{g(\text{solid})}$ is the optical energy gap of the solid at T. It can be easily shown that E_0 is identical with E_{0g}. GeSe, being isostructural with GeS and SnS, must have an α value near -4.8×10^{-4} eV K^{-1}. This has been confirmed by El-Korashy [14] who calculated the optical energy gap of GeSe from the absorption coefficient on single crystals with polarized light. At room temperature the E_g is 1.075 ± 0.017 eV $\perp$ to the a axis and 1.080 ± 0.016 eV $\perp$ to the b axis. It is to be noted that axis $a = 4.403 \pm 0.005$ Å and axis $b = 3.852 \pm 0.005$ Å both lie in the plane of cleavage [15], i.e., parallel to the layers in the GeSe structure. Also, the dependence of the energy gap on temperature is linear in the range 96–250 K, with a negative coefficient equal to -4.3×10^{-4} and -4.9×10^{-4} eV K^{-1} for the a and b axes, respectively. These values give $E_0 = 1.203$ eV and 1.226 eV for axes a and b, respectively. Kannewurf and Cashman [3] reported an $E_g = 1.16$ eV from optical measurements on a single crystal with unpolarized light along the c axis at 300 K. This value gives 1.29 eV and 1.31 eV for E_0 using the two El-Korashy α values. Thus the value of $E_{0g} = 1.222 \pm 0.27$ eV obtained in the present work from the electrical conductivity of polycrystalline samples is in very good agreement with the value of the optical energy gap E_0.

Liquid state

In liquid GeSe the following equation was used to calculate the activation energy in the homogeneous region

$$\sigma = B \exp(-E_{g(l)}/2RT)$$

where $E_{g(l)}$ is the thermal energy gap in the liquid state.

A value of $E_{g(l)} = 1.504 \pm 0.016$ eV is found. As no optical measurements have been reported for liquid IVA-chalcogenides, the value of the activation energy measured by electrical conductivity cannot be compared, as in the solid state, with the optical activation energy.

Thus upon melting, the activation energy of GeSe increases from 1.222 eV to 1.504 eV. Germanium monoselenide has a black phosphorous-type structure [15] with intralayer bonds different from the interlayer bonds, the latter being considerably weaker than the former. It seems that the activation energy is directly associated with the stronger intralayer bonds. Thus the increase in the energy gap upon melting appears to be due to a strengthening of these intralayer bonds and by consequence to a weakening of interlayer bonds which leads to the separation of the layers. A similar explanation was suggested in the case of GeS [10] where the interlayer bonds are weaker than in GeSe. A more detailed discussion on the IVA-monochalcogenides will be given in a future paper.

Polymorphic transformation in GeSe

From Fig. 4 the jump (nearly 100-fold) in conductivity at 656°C seems to be associated with the first-order transition in GeSe. Further evidence for the existence of a first-order transition in GeSe is given by the magnetic susceptibility measurements given in Fig. 6. The same behaviour as with conductivity measurements is observed around 650°C; there is a jump towards more diamagnetic values. Uemura et al. [16] have studied the magnetic susceptibility of amorphous GeSe in the solid and in the liquid state and found neither a sudden change at 656°C nor any jump upon melting. This fact strengthens the evidence that the sudden change must be associated with a transition in crystalline GeSe.

As can be seen by the DTA technique [5] the thermal effect associated with the first-order transition in GeSe occurs around 661°C while, by electrical conductivity and magnetic susceptibility measurements, the same effect is detected between 650 and 656°C. The difference in temperature must be attributed essentially to the fact that DTA is a dynamic method while σ and χ were measured under equilibrium conditions.

Wiedemeier and Siemers [17] found that at 656 ± 5°C germanium monoselenide transforms from an orthorhombic to a NaCl structure; no X-ray diffraction pattern of GeSe could be indexed on the basis of a hexagonal unit cell reported previously by Karbanov et al. [18]. Furthermore, Karbanov reported that above 590°C the structure of GeSe is hexagonal. No evidence of this transition at 590°C could be detected by electrical conductivity or magnetic susceptibility in the present work.

It will be observed from Fig. 4 that in the range 664–672°C the specific conductivity is quite high and the temperature coefficient of conductivity is negative which is indicative of a metallic-type conduction. This is consistent with the NaCl structure reported by Wiedemeier, since strong delocalization of the electrons must be assumed in the cubic structure to account for the bonding of any particular atom to six nearest neighbours.

CONCLUSION

It is instructive to compare the behaviour of GeSe with that of other IVA–VIA compounds. GeS, which is isostructural with GeSe and which undergoes a similar peritectic disproportionation upon melting, does not show a solid state transition before melting [19,20]; the DTA curve of GeS only presents one endothermal peak at 667°C, the melting point. From conductivity measurements Handfield et al. [10] did not observe a jump in conductivity before melting in GeS. The peritectic reaction in GeS leads to a conductivity change of only 2 $\text{ohm}^{-1}\ \text{cm}^{-1}$, whereas in GeSe it produces a conductivity jump of 20 $\text{ohm}^{-1}\ \text{cm}^{-1}$. Also, as shown in Fig. 6, there is no sudden jump of magnetic susceptibility for GeS that could be associated with a solid state transition; there is also no change of slope of the straight line or any jump at the melting point. These facts suggest that upon melting the structure of GeS is perturbed to a smaller degree than the structure of GeSe.

Other IVA–VIA compounds like PbS, PbSe and PbTe which have the NaCl structure in the solid state have high conductivity values of the order of 300–500 $\text{ohm}^{-1}\ \text{cm}^{-1}$. On melting, the conductivity increases to values of 500–1500 $\text{ohm}^{-1}\ \text{cm}^{-1}$. In the case of GeSe, however, which undergoes a transition to a NaCl structure before melting, with conductivity values in the 800 $\text{ohm}^{-1}\ \text{cm}^{-1}$ range, the conductivity on melting decreases to a value comparable to the value of the conductivity before transition. This behaviour is most probably related to the melting mechanism which is different from that of the above mentioned IVA–VIA compounds with the NaCl structure. This point will be discussed more fully in forthcoming papers on the electrical properties of GeSe as a function of composition.

ACKNOWLEDGEMENTS

The financial support of the National Research Council of Canada is gratefully acknowledged. One of us (L.R.) wishes to thank the association "France-Québec" for a travelling grant. We are also grateful to Mr. R. Fruchart at the Centre d'Etude de Chimie Métallurgique in Vitry-sur-Seine, France, for his invitation to work in his laboratory.

REFERENCES

1 J.V. Vestrepen, C.R. Acad. Sci., 251 (1960) 1273.
2 S. Asanabe and A. Okasaki, J. Phys. Soc. Jpn., 15 (1960) 989.
3 C.R. Kannewurf and R.J. Cashman, J. Phys. Chem. Solids, 22 (1961) 293.
4 C. Mande, R.N. Patil and A.S. Niganekar, Indian J. Pure Appl. Phys., 3 (1965) 761.
5 L. Ross and M. Bourgon, Can. J. Chem., 47 (1969) 255.
6 L. Ch'un-Hua and A.S. Pashinkin, Dokl. Akad. Nauk S.S.S.R., 146 (5) (1962) 1092.
7 S.G. Karbanov, V.P. Zlomanov and A.V. Novoselova, Vestn. Mosk. Univ., Khim., 23 (1968) 96.
8 H. Ipser, M. Gambino and W. Schuster, Monatsh. Chem., 113 (1982) 389.
9 J.H. Walton and C.K. Rosenbaum, J. Am. Chem. Soc., 50 (1928) 1648.
10 G. Handfield, M. D'Amboise and M. Bourgon, Can. J. Chem., 44 (1966) 853.
11 C.R. Betz, Thesis, Northwestern University, 1958.
12 K.F. Lider and L.E. Solov'ev, Sov. Phys.—Solid State, 4 (6) (1962) 1102 (English Translation).
13 H. Rau, J. Phys. Chem. Solids. 27 (1966) 761.
14 A.M. El-Korashy, Inst. Phys. Conf. Ser., 43 (1979) 817.
15 S.N. Dutta and G.A. Jeffrey, Inorg. Chem., 4, 9 (1965) 1363.
16 O. Uemura, Y. Sagara and Tsunev Satow, J. Inst. Met. Trans., 17, 7 (1976) 457.
17 H. Wiedemeier and P.A. Siemers, Z. Anorg. Allg. Chem., 411, 1 (1975) 90.
18 S.G. Karbanov, V.P. Zlomanov and Yu. M. Ukrainskii, Izv. Akad. Nauk S.S.S.R., Neorg. Mater., 1 (1970) 6.
19 L. Ross and M. Bourgon, Can. J. Chem., 46 (1968) 2464.
20 W. Viaene and G.H. Moh, Neues Jahrb. Mineral., Abh., 119, 2 (1963) 113.