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X-ray Ge K bands of Bi–Ge–S and Sb–Ge–S glasses

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Abstract. The x-ray Ge K emission and absorption bands were measured in the stoichiometric glass systems $(\text{GeS}_2)_x(\text{Bi}_2\text{S}_3)_{1-x}$ and $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$; $x = 0$ to $x = 0.5$. The results do not confirm the existence of the Ge–Bi or Ge–Sb bonds and they imply that the GeS_2 clusters are formed in both systems studied.

1. Introduction

Ternary alloy glasses Ge–Bi–X ($X = \text{Se}$ or S) prepared by quenching from the melt have been intensively studied [1–4] because, contrary to almost all other chalcogenide glasses, they reveal n-type conductivity at higher concentrations of Bi. A series of experiments and models [5, 6] was presented which were compatible with the idea of percolation-controlled conductivity in the two-phase system GeS_2 – Bi_2S_3 ; lately, a connection with the Ge–Bi bond has been put forward: its existence is supposed in the Ge–Bi–S(Se) system [7–9]. The authors in [9] conclude from their x-ray absorption near edge structure (XANES) measurements that at higher concentrations of Bi the Ge–Bi bond is favoured in the Ge–Bi–Se glass, but no bond Ge–Sb is ascertained in the Ge–Sb–Se system. On the contrary, the interpretation of the extended x-ray absorption fine structure (EXAFS) measurements in [10] supports the existence of the Ge–Sb bond in the Ge–Sb–S system. In a recent paper [11] the far infrared spectra of Ge–Bi–S(Se) glasses were analysed and it was shown that the IR feature at 160 cm^{-1} assigned by Sharma and co-workers [8] to the IR activity of the Bi–Ge bond could be assigned rather to the Bi–Se stretching mode. Also Elliott and Steel [12], who studied the Ge–Bi–S and Ge–Sb–S systems by EXAFS, exclude the existence of the Ge–Bi (Ge–Sb) bond. These contradictory results reopen the question of the short-range order in Ge–Bi(Sb)–S glasses. We therefore decided to examine these ideas by means of the x-ray emission and absorption K bands of germanium in the stoichiometric glass systems $(\text{GeS}_2)_x(\text{Bi}_2\text{S}_3)_{1-x}$ and $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$. The K emission bands correspond to the transition of the 1s hole to the valence-band p states and the K absorption bands (represented by the absorption coefficient $\mu(E)$) correspond to the transition of the 1s electron to the conduction-band p states. In both cases the symmetry is related to the Ge centre. Due to the localization of the 1s state the x-ray emission and absorption bands very sensitively reflect the changes in the first coordination sphere of the studied atom as to its symmetry and/or the kind of atoms: we can report, for example, the application of Si K and $L_{2,3}$ emission bands to the study of the SiO_x system [13], the Ge and Se K absorption bands to the study of the

GeSe_x system [14] and the Ge K emission and absorption bands to the study of the system GeS_x [15]. In figure 1 we give our measurements of the x-ray Ge K bands which reveal the sensitivity of x-ray bands to the change in the neighbourhood of the Ge atom. (i) Ge, GeO₂ and GeS₂: an important change of the Ge K emission band caused by the exchange of the elements in the first coordination sphere preserving the symmetry. (ii) K₂GeF₆: both symmetry and elements are changed; see figure 1(a) [15]; the Ge K absorption bands of amorphous Ge, amorphous and crystalline GeS where both the symmetry and elements are changed (c-GeS: Ge has three nearest S-neighbours; a-GeS: the nearest neighbours form a tetrahedron occupied by both S and Ge); see figure 1(b) [15].

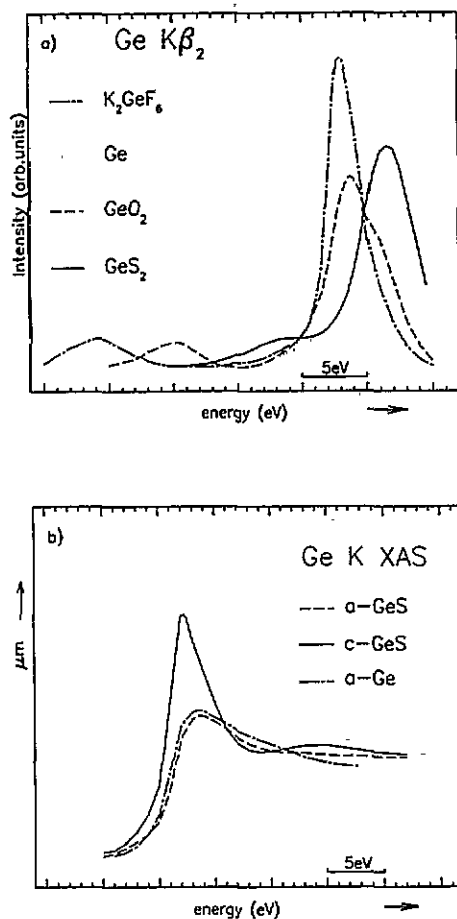


Figure 1. Influence of changes (elements and/or symmetry) in the first coordination sphere on the Ge K bands [15]: (a) Ge Kβ₂ emission bands; (b) Ge K absorption bands. c-GeS has three nearest S-neighbours; in a-GeS the nearest neighbours form a tetrahedron occupied by both S and Ge.

2. Experiment

The glasses under study were prepared by direct synthesis from germanium, bismuth and antimony (5N purity). Sulphur (Mark DAB-6) was purified in the way described in [16]. For each composition the mixture of elements (total weight of 5 g) was sealed in an evacuated quartz ampoule ($p \sim 10^{-3}$ Pa). The ampoules were heated in a rotary furnace at

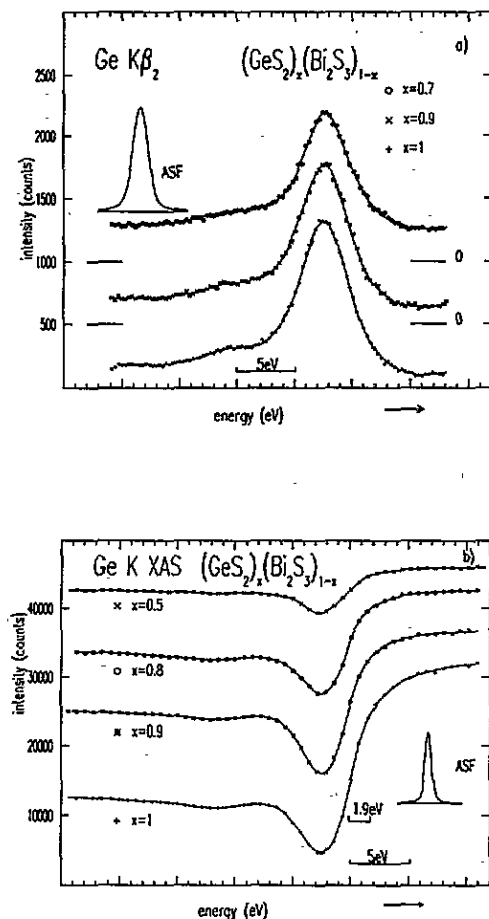


Figure 2. The measured x-ray Ge K spectra of the Ge-Bi-S system; the intensity scales are valid only for $x = 1$, the other curves are shifted vertically. (a) The uncorrected Ge $K\beta_2$ emission band; counts at the maximum for $x = 0.9$ are 1271 and for $x = 0.7$ are 1192; (b) the measured absorption curves $N(E)$ monitored to $N_0 = 50\,000$ counts; counts at the minimum for $x = 0.9$ are 16\,155 (36\,800), for $x = 0.8$ are 7661 (23\,300), for $x = 0.5$ are 9344 (16\,200); the maximum values are given in parentheses. The abscissa in (b) (1.9 eV) shows the shift of the Ge K edge found by Agnihotri and co-workers [9].

a temperature $\sim 1100\text{K}$ for eight hours. Before cooling the ampoule in ice water the melt was mixed rigorously for at least one hour. The glassy nature of the prepared samples was tested by x-ray diffraction measurements, infrared microscopy ($100\times$ magnification) and differential thermal analysis.

The x-ray bands were measured on two crystal spectrometers with perfect Si single crystals as follows. The x-ray Ge K-absorption band: position (n, m) , crystals Si (220) and Si (111); the x-ray Ge $K\beta_2$ emission bands of a Ge-Bi-S system: position $(n, -m)$, crystals Si (220) and Si (400); Ge-Sb-S: position (n, n) , both crystals Si (220).

The measurements of the Ge $K\beta_2$ emission bands were carried out stepwise using the fluorescence method [17]. A small plane crystal spectrometer of a very low resolving power was used as a monitor; it counted the Ge $K\alpha$ radiation N_M taken from the sample (for a single measurement $N_M = 100\,000$ counts).

Absorption measurements carried out stepwise were monitored in the following way: the sample swung in and out of the beam; the direct beam, I_0 , and the beam passing through the sample, I , were alternately measured, each during two seconds. This function was controlled by a mechanical device coupled with the electronic switch, which successively directed the pulses I_0 and I to two separate counters, N_0 and N respectively. When N_0 reached 50\,000 counts the single measurement was terminated (the total time amounted to about 600 s).

The samples used in the absorption measurements were in the form of pressed tablets; the pulverized material was mixed with the powdered polystyrene.

All angular position measurements were made to a precision of one second of arc.

Each point of the uncorrected curves (figure 2(a) and (b)) represents an average of repeated measurements (5–10) because of the low intensity of the spectra. Tails were measured with lower precision. As reference energies, the Ge $K\beta_{1,3}$ line of pure germanium and the W $L\gamma_1$ line of the primary radiation were used for emission and absorption respectively; both were checked daily.

3. Results

The averaged measured curves of the Ge–Bi–S system are given in figure 2; the absorption curves (figure 2(b)) present counts of the transmitted beam. The results of the Ge–Sb–S system are similar. The measured curves were corrected, which means that they were deconvoluted by the apparatus smearing function (ASF). The ASF are given in all figures. The absolute energy scale is not given because it is not important for the interpretation; furthermore, the precision of the tabulated reference lines is of the order of eV. Nevertheless, it seems informative to know the energy region of the measured spectra; the tabulated values [18] of pure germanium are 11 100.8 eV for Ge $K\beta_2$ and 11 103.6 eV for the Ge K-absorption edge.

The x-ray Ge $K\beta_2$ emission bands are shown in figure 3 for both systems. The energy and shape of the bands in practice do not depend on the Bi or Sb content (to stress this fact a vertical line is drawn in figure 3). Relatively small changes of the shape at the band maximum are due to the limited accuracy of the measurements and to the different widths of the ASF for both systems.

In figure 4 the x-ray Ge K-absorption bands are given for both Bi and Sb systems. They represent the energy dependence of the absorption coefficient $\mu(E)m = \ln(N_0(E)/N(E))$ (μ is the absorption coefficient, m is the mass of the sample per cm^2 , N and N_0 are the corrected counts of the monochromatic radiation transmitted by, and falling on, the sample respectively). Again, we see practically no changes in the energy of the absorption edge or of the band shape.

The studied non-stoichiometric glasses are more often specified as $\text{Ge}_x\text{Bi}_y\text{S}_{1-x-y}$; using this notation we give the composition of our samples in table 1 for comparison.

Table 1. The $\text{Ge}_x\text{M}_y\text{S}_{1-x-y}$ notation for the measured samples ($M = \text{Bi}$ or Sb).

$(\text{GeS}_2)_{0.9}(\text{M}_2\text{S}_3)_{0.1}$	$\text{Ge}_{0.28}\text{M}_{0.06}\text{S}_{0.66}$
$(\text{GeS}_2)_{0.8}(\text{M}_2\text{S}_3)_{0.2}$	$\text{Ge}_{0.23}\text{M}_{0.12}\text{S}_{0.65}$
$(\text{GeS}_2)_{0.7}(\text{M}_2\text{S}_3)_{0.3}$	$\text{Ge}_{0.19}\text{M}_{0.17}\text{S}_{0.64}$
$(\text{GeS}_2)_{0.5}(\text{M}_2\text{S}_3)_{0.5}$	$\text{Ge}_{0.12}\text{M}_{0.25}\text{S}_{0.63}$

4. Discussion

Our results show no changes in the x-ray bands dependent on the Bi or Sb concentration in the glasses studied, nor any difference between the systems Ge–Bi–S and Ge–Sb–S. This means that in all the materials studied the coordination of Ge atoms does not differ from

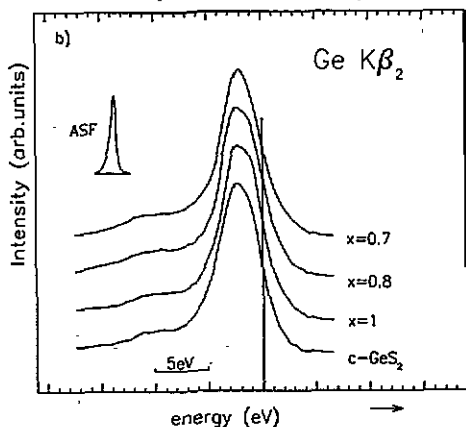
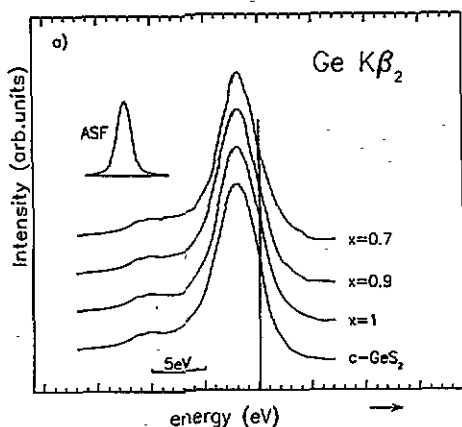


Figure 3. (a) x-ray Ge $K\beta_2$ -emission bands of $(\text{GeS}_2)_x(\text{Bi}_2\text{S}_3)_{1-x}$ glasses and GeS_2 crystals; (b) x-ray Ge $K\beta_2$ -emission bands of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses and GeS_2 crystals. ASF is the apparatus smearing function.

that in amorphous GeS_2 . The formation of a Ge-Bi (or Sb) bond would bring about a more significant change in the x-ray bands because the Bi (or Sb) atoms are unlike in valency and in requirements for the symmetry of neighbours, in comparison with sulphur. Therefore, in agreement with Tichý and co-workers [11], we doubt the existence of a Ge-Bi bond in the systems measured.

Our results do not confirm those presented by Agnihotri and co-workers [9]. The system they studied, rich in Se, can be expected to form fewer Ge-Bi bonds than the stoichiometric one. Yet they found a shift of the Ge K-absorption edge of 1.91 eV for the $\text{Ge}_{22}\text{Bi}_{10}\text{Se}_{68}$ glass in comparison with the $\text{Ge}_{22}\text{Se}_{78}$ glass; for glasses of the same composition, where Bi was substituted by Sb, they found practically no shift. For the glass $\text{Ge}_{22}\text{Bi}_2\text{S}_{66}$ of low Bi content they obtained no shift either; thus the existence of the Ge-Bi bond seems to depend on the Bi concentration. Despite the fact that the system of glasses measured by us comprised samples of Bi concentration considerably higher than that investigated by Agnihotri and co-workers no change was ascertained (the accuracy of our measurements, roughly 0.1 eV per second of arc, is an order of magnitude better than the value 1.91 eV; see also figure 2(b)). It is very improbable that the glasses containing Se would behave so differently compared to those containing S [6]. However, it is necessary to consider that Agnihotri and co-workers used a spectrometer with a very low dispersion and photographic registration of spectra; using the photometer measurements the spectra were magnified

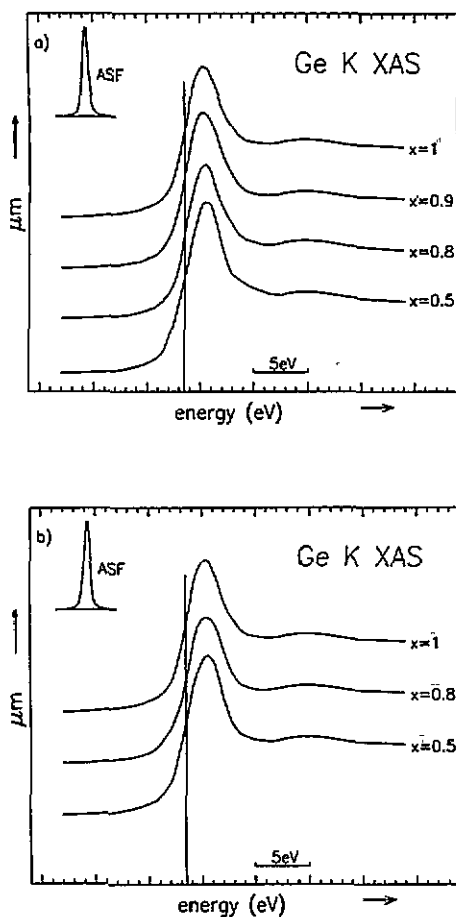


Figure 4. (a) x-ray Ge K absorption bands of $(\text{GeS}_2)_x(\text{Bi}_2\text{S}_3)_{1-x}$ glasses; (b) x-ray Ge K absorption bands of $(\text{GeS}_2)_x(\text{Sb}_2\text{S}_3)_{1-x}$ glasses. ASF is the apparatus smearing function.

by a factor of 100; apparatus smearing was not discussed. According to the data about their spectrometer we can estimate the linear dispersion to be about 8 eV per 0.01 mm (photographic registration!)

Furthermore, our measurements of the Ge K bands of the amorphous system do not confirm the interpretation of the EXAFS measurements in [10] from which the existence of the Ge–Sb bond follows. However, the interpretation uses the model assumption that germanium is coordinated by S, Ge or Sb, and in fact the existence of the bond Ge–Sb results from the minimizing process of more than ten parameters. The authors in [10] also give a value of the resulting Debye–Waller factor of the Ge–Sb bond which is two times greater than that of the Ge–S or Ge–Ge bond.

It should be mentioned that the glasses are prepared by quick cooling and thus, accidentally, Bi (or Sb) may be found in the first coordination sphere of Ge. Yet the authors of [8,9] conclude from their measurements that the Ge–Bi bond is created and that its concentration increases with increasing Bi concentration; however, the lowest Bi concentration at which they observed the Ge–Bi bond was high enough to be revealed by the x-ray Ge K bands. This is also supported by our measurements of the amorphous system Ge_xS_2 ($1 \leq x \leq 2$) [15], where it was demonstrated that the x-ray Ge K bands sensitively react to the progressive exchange of S atoms for the Ge atoms in the GeX_4 tetrahedron ($X = \text{Ge}, \text{S}$). The x-ray absorption measurements of the Ge_xSe_2 system made by Zhou and

co-workers [14] give analogous results.

In [5, 19] the measured dependence of the optical gap on the Bi and Sb content in the stoichiometric Ge-Bi-S and Ge-Sb-S glasses respectively is given; in the concentration range of the glasses measured by us the mentioned changes of the gap width are up to 2 eV (in Ge-Bi-S glass). We found no shifts of the x-ray emission or absorption band edge and thus we can infer that the gap width (see figure 5) in all studied glasses corresponds to that of amorphous GeS₂. In fact, the x-ray K bands yield information of the p-partial density of states (PPDOS) only; but it is extremely improbable that the changes of the gap width given above would not be accompanied by a change of the PPDOS (neither occupied nor unoccupied) detectable by our measurements. The Ge 4p electrons always participate in the bond! Recently Šipr [20] thoroughly analysed the question of the size of the cluster around the studied atom to calculate the real shape of the absorption band (XANES). It turns out that several coordination spheres must be taken into account to get the approximate shape of the band.

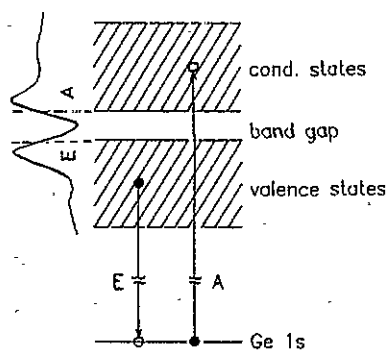


Figure 5. Schematic diagram of the x-ray K-emission (E) and K-absorption (A) bands and their linkage to the gap.

Our measurements therefore support the idea that the glasses studied are built of GeS₂ clusters. Contrary to the measurements of the x-ray bands the optical measurements of the width of the gap [5, 19] can only indirectly distinguish if the material is composed of two sorts of microclusters or if the atoms of sulphur are bonded (in some order) to both Ge and Bi(Sb), respectively.

A detailed inspection of figure 4 reveals small changes of the main peak[†]. Similar changes were found in the intensity of Ge K β_2 -bands if they are related to the constant intensity of the Ge K $\beta_{1,3}$ -line (core transition Ge(1s) \rightarrow Ge(3p) in the hole notation). These small changes are probably connected with the size of the clusters.

5. Conclusions

The x-ray K emission and absorption bands of germanium were measured in two stoichiometric glass systems: Ge-Bi-S and Ge-Sb-S. In discussion it was shown that our results for both studied systems (i) support the idea of forming clusters of GeS₂ and (ii) do not confirm the existence of the Ge-Bi or Ge-Sb bonds, in particular the dependence of such bonds on the concentration of Bi or Sb.

[†] The Ge K-absorption bands are related to a constant absorption jump.

Acknowledgments

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References

- [1] Tohge N, Yonesaki Y and Minami T 1985 *J. Appl. Phys.* **58** 4225-9
- [2] Elliot S R and Steel A T 1987 *J. Phys. C: Solid State Phys.* **20** 4335-57
- [3] Frumar M and Tichý L 1987 *J. Non-Cryst. Solids* **97/98** 1139-46
- [4] Bhatia K L, Gosain D P and Bhatnagar V K 1987 *Phys. Rev.* **35** 4503-6
- [5] Tichý L, Tichá H, Beneš L and Málek J 1990 *J. Non-Cryst. Solids* **116** 206-18
- [6] Phillips J C 1987 *Phys. Rev. B* **36** 4265-70
- [7] Bhatia K L 1983 *J. Non-Cryst. Solids* **54** 173-7; **58** 151
- [8] Sharma A K, Bhatia K L, Bhatnagar V K, Malik S K and Kratschmer W 1989 *J. Non-Cryst. Solids* **108** 309-14
- [9] Agnihotri A K, Kumar A and Nigam A N 1987 *J. Non-Cryst. Solids* **93** 267-72; 1988 *Phil. Mag. B* **57** 319-24
- [10] Červinka L, Smotlacha O, Bergerová J and Tichý L 1991 *J. Non-Cryst. Solids* **137**, **138** 123-6
- [11] Tichý L, Tichá H, Pačesová A and Petzelt S 1991 *J. Non-Cryst. Solids* **128** 191-6
- [12] Elliott S R and Steel A T 1986 *Phys. Rev. Lett.* **57** 1316-9
- [13] Šimůnek A and Wiech G 1991 *J. Non-Cryst. Solids* **137**, **138** 903-6
- [14] Zhou W, Paesler M and Sayers D E 1991 *Phys. Rev. B* **43** 2315-21
- [15] Drahokoupil J, Smotlacha O, Fendrych F, Klokočnicková H and Kozlov M A 1986 *J. Non-Cryst. Solids* **88** 43-54
Drahokoupil J, Klokočnicková H and Šimůnek A 1981 *Inner-Shell and X-ray Physics of Atoms and Solids* ed. D J Fabian, H Kleinpoppen and L M Watson (New York: Plenum) p 749-52
- [16] Tichý L, Tichá H, Frumar M, Klikorka J, Tříska A, Barta Č and Němečková A 1982 *Czech. J. Phys. B* **32** 1363-3
- [17] Drahokoupil J and Fingerland A 1968 *Czech. J. Phys. B* **18** 1190
Drahokoupil J and Fingerland A 1982 *Advances in X-ray spectroscopy—Contributions in Honour of Professor Cauchois* ed. C Bonnelle and C Mande (Oxford: Pergamon) p 167-201
- [18] Bearden J A 1964 *X-ray Wavelengths* (Oak Ridge: US Atomic Energy Commission)
- [19] Nagels P, Tichý L, Tichá H and Tříska A 1985 *Physics of Disordered Materials* ed. D Adler, H Fritzsche and S R Ovshinsky (New York: Plenum) p 645-62
- [20] Šipr O 1992 *J. Phys.: Condens. Matter* **4** 9389