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Abstract
High-temperature measurements of the electrical conductivity $\sigma(T)$, thermo-emf $S(T)$ (in a range from the vicinity of the melting temperature, $T_m = 1371$ to 1600 K), and viscosity $\eta(T)$ (from T_m to 1420 K) were performed for equiatomic liquid CdTe alloys and with admixtures of In, Ge, Sn. It was shown that all the compositions kept their semiconducting properties during transition from a solid to a liquid state. A gradual melt metallization has been observed in the course of further heating. The results obtained are interpreted in the framework of the two-structure model suggesting coexistence of two areas: a densely packed metallic one and an area with the crystalline CdTe clusters. Transition to metal conductivity is considered as a gradual increasing of the densely packed metallic fraction. The influence of admixture on the electrical conductivity and thermo-emf is explained by the s–p hybridization phenomenon.

1. Introduction

Investigations of II–VI systems in a liquid state are few in number due to the difficulties of high-temperature measurements and the high pressure of the component saturated streams. Nevertheless, these systems, especially the tellurium-based alloys, are of interest because of their practical applications. CdTe-based alloys are known as important materials for gamma-ray detector production due to their large atomic number and high band gap at room temperatures. The phase diagram of the CdTe system containing one compound, CdTe, and strongly degenerate eutectics closer to the pure components is the most extensively studied [1]. Melting of the semiconducting compound CdTe follows a pattern of the 'semiconductor–semiconductor' type [2]; it was shown earlier that a structural heterogeneity connected with

the crystalline structure elements (clusters) held out in similar semiconducting materials upon melting [3]. Another type, a structure–heterogeneous melt, is considered as a two-structure one. This is due to the fact that structural changes accompanying the phase transition from a solid to a liquid state are not over at the phase transition point, but extend to some higher-temperature region. Such phenomena most often show up in semiconducting melts, changing upon melting their interatomic bonds, from prevailingly covalent in the solid to metallic ones in the liquid state. Transformation of microheterogeneities or clusters into a homogeneous liquid during heating is known as a post-melting phenomenon. The melting process is accompanied with establishment of a new short-range order, peculiar to liquids. According to diffraction experiments, remnants of the crystalline order persist in the liquid [4]. Thus, existence of dynamic atom groups with a quasicrystalline structure seems quite possible and suggestions of cluster formation are not unreasonable.

2. Experimental details

The electrical conductivity and thermo-emf measurements were performed under argon gas with pressures up to 25 MPa to avoid intensive melt evaporation and provide a constant chemical composition of the samples. A contact four-point method has been employed. Ceramic measuring cells manufactured from BN in the form of vertical cylindrical containers with graphite electrodes placed in their wall along the vertical axis were used. The cell construction permits one to carry out the electrical conductivity and thermo-emf measurements simultaneously in one run. A high-temperature heater with three independently controlled heating elements enables one to create a temperature field homogeneous within ± 0.3 K or maintain temperature gradients of 15–20 K along the cell. The apparatus and the measurement procedure were identical to those described earlier in [5]. The errors of the electrical conductivity and thermo-emf determinations did not exceed ± 1.5 and $\pm 5\%$, respectively.

Viscosity measurements were carried out using a computer-controlled oscillating-cup viscometer, where a cylindrical quartz crucible with a liquid sample undergoes rotational oscillations. The friction between the cylindrical neighbouring layers of the liquid causes a damping torque or drag. This damping is a function of the viscosity of the liquid. Using a modified Roscoe equation, the viscosity has been calculated from the logarithmic decrement and the period of oscillations. The experiments were performed in a helium atmosphere after initially pumping out the working volume of the furnace to 10 Pa.

The measuring cell was made of quartz in the form of a cylindrical container with an internal diameter of 21 mm. A homogeneous temperature field, ± 0.3 K in the range of absolute values up to 1420 K, was created inside a furnace. The molten alloys were gradually cooled at a rate of 20 K h^{-1}. The temperature was measured with a Pt/Rh–Pt thermocouple arranged just below the crucible. The viscometer and the measurement procedure were described in [6]. The viscosity values were obtained with an accuracy of $\pm 3\%$.

High-purity elements (all 99.999 wt%) weighed to within 10^{-4} g were employed in this study.

3. Results and discussion

Experimental viscosity data are presented in figure 1. We suggest that a microheterogeneous structure persists in the liquid state; the clusters have spherical symmetry and the well-known Einstein equation can be applied:
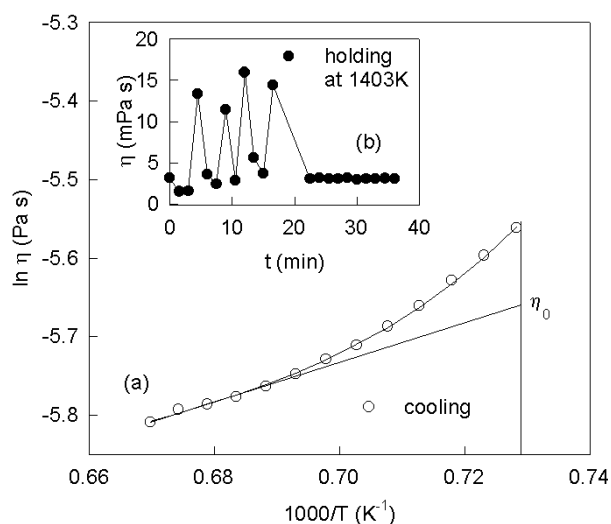
$$\eta = \eta_0(1 + 2.5\varphi + 7\varphi^2) \tag{1}$$

Figure 1. Viscosity, η, as a function of reciprocal temperature (a) and of time at 1403 K (b) for the CdTe liquid alloy.

where φ is the volume fraction of microregions remaining to some extent a solid-state structure, η is the experimental viscosity value, η_0 is the ideal viscosity of 'pure' liquid. The φ-value, thus defined, is about 4.2% at a melting temperature T_m and decreases to 0.4% in the course of further heating up to $T_m + 30$ K. But actually it is unlikely that clusters of the liquid CdTe are really of spherical symmetry [2]. Moreover, a rather narrow temperature range of clusters destruction (about 30 K) does not correlate with electrical conductivity results (see figure 3).

We fell back on a model proposed in [7], where a cluster portion for liquid tellurium having its chain structure had been estimated. Assuming similar chain structure for the CdTe melt, we performed the same calculations with corresponding structural parameters taken from [4]. The volume fraction of the chain structure was estimated as 13% at T_m with further decrease upon heating. Different φ-values favour the chain structure of liquid CdTe.

Considering the general run of the $\ln \eta = f(1000/T)$ dependence in its non-linear part as well as the absolute viscosity values, it is believed that at least two complicated processes occur during heating: restructuring from spatial homopolar to linear bonds and dissociation. Excess atoms of tellurium occurred owing to dissociation combined with CdTe forming chain molecules; other Te–Te bonds form due to thermal dissociation of the Cd–(Te)$_n$-type clusters yielding holes in the valence band. On this assumption, the experimental data obtained on the viscosity, electrical conductivity, and thermo-emf are in good agreement.

Temperature dependences of the electrical conductivity, $\sigma(T)$, and thermo-emf, $S(T)$, are presented in figures 2–7. Our results on $\sigma(T)$ and $S(T)$ for the equiatomic undoped CdTe are in agreement with resistivity and thermo-emf data reported recently in [8]. The conductivity data also agree well with those presented in [9]. The low $\sigma(T)$ values in the solid state increase upon melting and saturate at higher temperatures for some melts.

To our knowledge, the influence of In, Sn, and Ge admixtures on electronic properties of equiatomic CdTe is being studied here for the first time. Additions of In and Sn increase the electrical conductivity, while addition of Ge reduces the $\sigma(T)$ values. As is seen from figures 2–7, the admixtures affect the melting and crystallization temperatures. The occurrence of hysteresis upon melting and crystallization suggests the possibility of melt undercooling,
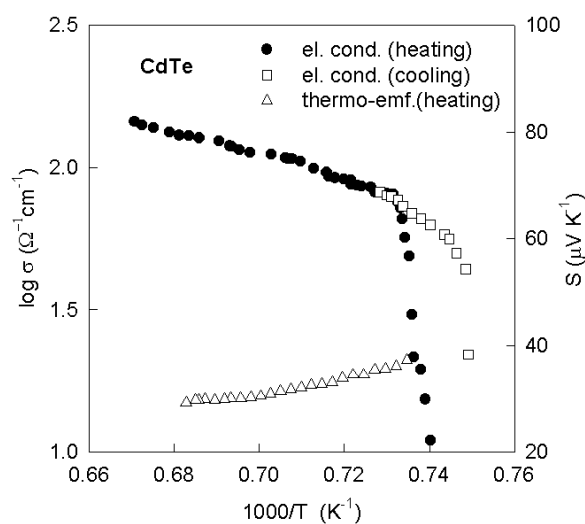
Figure 2. Electrical conductivity, $\log \sigma$, and thermo-emf, S, as a function of reciprocal temperature for the CdTe liquid alloy.
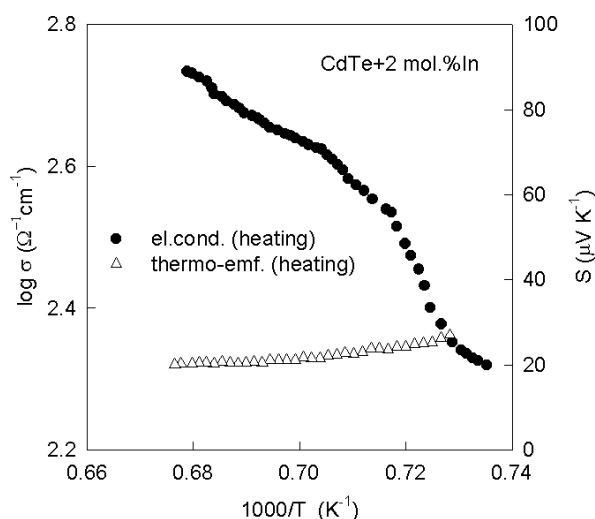

Figure 3. Electrical conductivity, $\log \sigma$, and thermo-emf, S, as a function of reciprocal temperature for the CdTe + 2 mol% In liquid alloy.

which could reach about 45 K. This insignificant value supports the view that these melts are not homogeneous but have at least two structures. The presence of clusters maintaining a solid-state structure facilitates crystal nucleus formation and significantly affects the crystallization process. Thus, a tendency to undercooling in semiconducting melts with clusters should show considerable dependence on thermal conditions and cooling kinetics. Different slopes of the $\log \sigma (1000/T)$ dependences, which determine the conductivity activation energy during melting and crystallization, also favour this assumption. A smaller slope during cooling relative to that obtained in the course of the previous heating indicates that the melt became more metallic.
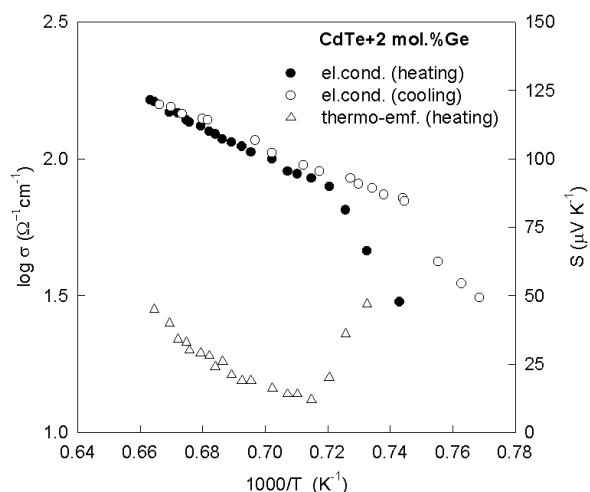
Figure 4. Electrical conductivity, $\log \sigma$, and thermo-emf, S, as a function of reciprocal temperature for the CdTe + 2 mol% Ge liquid alloy.
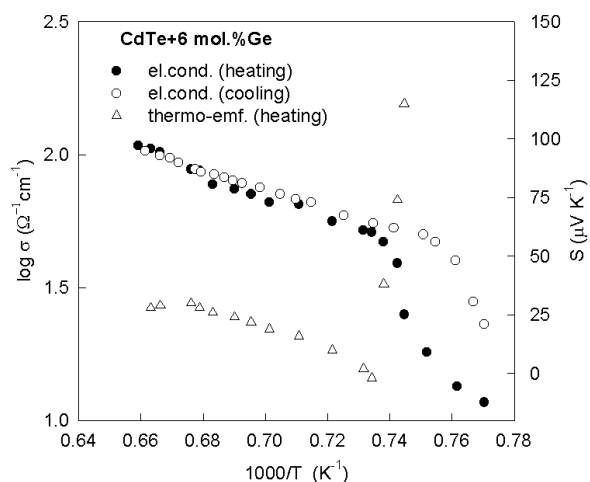

Figure 5. Electrical conductivity, $\log \sigma$, and thermo-emf, S, as a function of reciprocal temperature for the CdTe + 6 mol% Ge liquid alloy.

The thermo-emf decreases on melting from 130–150 μV K^{-1} to metallic values in the temperature range of $T_m + 100$ K. The regularities revealed are general for all the liquid alloys investigated and suggest that a post-melting phenomenon is inherent to the systems which melt in a 'semiconductor–semiconductor' manner.

According to the $\sigma(T)$ and $S(T)$ results, the increase of the metallic fraction on temperature increase can be considered as a semiconductor–metal transition. Considering results for pure tellurium [10], it is suggested that a liquid with a chain-like structure forms during melting, and current carriers occur at the chain ends. This leads in turn to an increase of the content of current carriers and the conductivity. Further increase in σ is obviously caused by increase of the density of states in a pseudogap.

An influence of admixtures makes itself evident in the mechanism of the cluster thermal decay. It was shown in [10] that such admixtures can lead to cluster structural
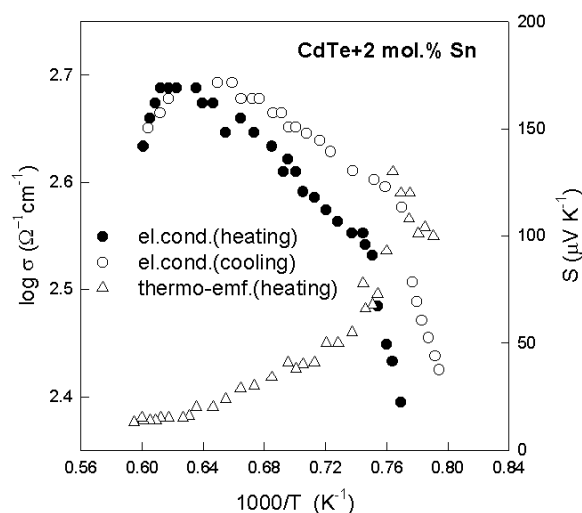
Figure 6. Electrical conductivity, $\log \sigma$, and thermo-emf, S, as a function of reciprocal temperature for the CdTe + 2 mol% Sn liquid alloy.
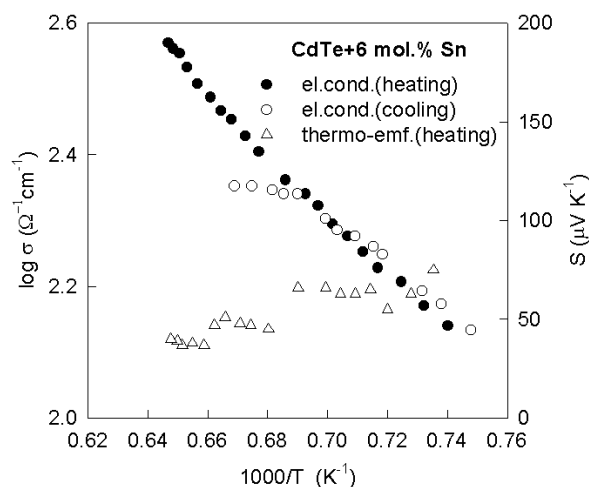

Figure 7. Electrical conductivity, $\log \sigma$, and thermo-emf, S, as a function of reciprocal temperature for the CdTe + 6 mol% Sn liquid alloy.

defects and cluster decay either by the customary dissolution or by fragmentation. The dissolution and fragmentation mechanisms can dominate alternately while a liquid remains inhomogeneous. Such alternating prevalence of different mechanisms manifests itself in the viscosity dependences in the form of oscillations [11] (see figure 1(b)).

The two-structure cluster model allows us to explain semiquantitatively the $\sigma(T)$, $S(T)$, and $\eta(T)$ dependences obtained. A mechanism of change of the electron properties with the local electron and semiconductor spectra was proposed for similar melts in [12]. It was suggested that a local Fermi level lies within the pseudogap of a semiconductor and that the depth of penetration of a 'metal' electron into the cluster is so small that the tunnelling effect can be neglected.

Table 1. Electrical conductivity increments of equiatomic CdTe and with In, Ge, and Sn additions.

T (K)	CdTe (Ω^{-1} cm^{-1}) σ	CdTe+ addition (Ω^{-1} cm^{-1})									
		2 mol.% In		2 mol.% Sn		6 mol.% Sn		2 mol.% Ge		6 mol.% Ge	
		σ	$\Delta\sigma$	σ	$\Delta\sigma$	σ	$\Delta\sigma$	σ	$\Delta\sigma$	σ	$\Delta\sigma$
1393	95	330	+235	420	+325	175	+80	90	−5	65	−30
1473	135	540	+405	460	+325	225	+90	125	−10	85	−50

The density of states can be expressed as

$$N(E_f) = N_0(E_f)C(E_f) \tag{2}$$

where $N_0(E_f)$ is a real density of states in the metallic phase, $C(E_f)$ is the volume fraction of the metallic phase.

For $C(E_f) = C_{cr}$ an endless metallic cluster occurs, i.e. the electrons localized on the separated clusters become delocalized. It should be noted that we are dealing with two types of delocalized state. The first type are responsible for clusters stabilization. The second type include some states in the metallic area, which could become localized if $C(E_f) < C_{cr}$. Thus, this model is well suited to explain the mechanism of cluster thermal dissociation.

Another model based on special energy dependence of kinetic coefficients was proposed in [13] and applied later in [14] to explain the concentration dependences of the electrical conductivity and thermo-emf of CdTe melts. In this model, the Fermi level lies closer to the valence band. Upon admixture concentration changes as well as temperature increase, the Fermi level shifts towards the centre of the pseudogap. Thus, both the conduction and valence bands can contribute to the electrical conductivity. In this case low values of $\sigma(T)$ could be accompanied by low values of $S(T)$, as is observed in our experimental dependences.

Of particular interest is the influence of the admixtures on the electronic properties of the basic CdTe matrix. Some electrical conductivity values for equiatomic CdTe, as well as with the In, Ge, and Sn additions, are presented in table 1. The increase of σ occurs in both the vertical Ge $\rightarrow$ Sn and horizontal In $\rightarrow$ Sn ranges. The maximum conductivity increment, $\Delta\sigma$, was observed in the case of admixture concentrations up to 2 mol%, while for those of 6 mol% this increment was lower.

Such peculiarities can be considered as experimental evidence for the spin–orbit interaction in the admixture field being responsible for the electron scattering in the matrix. The role of the spin–orbit interaction increases with increase of the atomic number of the admixture. The electrical conductivity values obtained depend on the p-electron content at the exterior admixture level as well as on the admixture p-orbital number. The results suggest the occurrence of virtual p states, similar to the Friedel virtual d states at admixture atoms in transition metals [15]. Considering the s–p resonance scattering, we suggest that all exterior p electrons of the admixture are included in this scattering mechanism.

For small concentrations of admixtures, each new electron falling into the virtual p level simply changes the sum of resonance shifts to $\pi/3$, which leads to $\Delta\sigma$ increasing. For high concentrations of admixtures, their contribution to the electrical conductivity becomes smaller or even negative, as in the case of germanium. This means that for the common scattering cross-section determining the electrical conductivity, the contributions of the non-resonance phase shifts should also not be neglected. Supposing that for the diffusion mechanism of charge transfer, $S \sim \mathrm{d}\ln\sigma/\mathrm{d}E$, similar reasoning could also be applied to the thermo-emf behaviour.

4. Conclusions

The electrical conductivity, thermo-emf, and viscosity studies performed for liquid CdTe-based alloys revealed that all the melts kept their semiconducting properties during transition from a solid to a liquid state, with gradual metallization during further heating. The two-structure model suggesting coexistence of two areas—a densely packed metallic one and an area with the crystalline CdTe clusters—was applicable. The ambipolar contribution of carriers to the charge transfer mechanism suggests a gradual electrical conductivity increase on heating, while the thermo-emf is metallic from the outset in all the liquid regions investigated. The electrical conductivity of liquid CdTe with various admixtures depends on a number of outer admixture's p-shell and on the p electron's quantity at this shell.

Acknowledgment

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