

# Electrical Properties of CdTe Near the Melting Point

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A new experimental setup for the investigation of electrical conductivity ( $\sigma$ ) in liquid and solid CdTe was built for a better understanding of the properties near the melting point (MP). The temperature dependence of  $\sigma$  was studied, within the interval 1,050–1,130°C, at defined Cd-partial pressures 1.3–1.6 atm, with special attention to the liquid-solid phase transition. We found that the degree of supercooling decreases with increasing Cd overpressure and reaches the lowest value at 1.6 atm without change of the melting temperature during heating.

**Key words:** CdTe, high-temperature conductivity, van Doorn

## INTRODUCTION

Cadmium-telluride (CdTe) single crystals are widely used for fabrication of gamma-ray and x-ray detectors and as substrates for narrow-gap (HgCd)Te epitaxy. For increasing production efficiency of both detectors and substrates, the growth of large-diameter, inclusion and precipitate-free single crystals with low concentration of native and foreign defects is necessary. It is known from available growing experiments that the quality of CdTe single crystals is connected with the history of the melt. But so far, the knowledge about the properties of the CdTe melt and about the process of solidification is insufficient. The properties of CdTe melt differ extremely from other semiconductors. It was found that the dissociation of CdTe molecules to Cd and Te atoms is only 5%, slightly above the melting point (MP).<sup>1</sup> Strong cohesive forces remain after the breaking of the long-range ordered and the short-range ordered clusters were observed by neutron-diffraction measurements in the melt.<sup>2</sup> The weak dissociation and semiconductor-like character of the CdTe melt was also confirmed by electrical measurements, which show that the electrical conductivity of the liquid CdTe increases with increasing temperature similarly to solid-phase semiconductors.<sup>3–7</sup> The temperature limit where semiconducting behavior changes to the metallic one was not reached up to 1,500°C.<sup>8</sup> For deeper understanding of the properties of the CdTe melt, we have built a new experimental setup for the

investigation of  $\sigma$  in liquid and solid CdTe near the MP. First results of the temperature dependence of  $\sigma$  in the temperature interval 1,050–1,130°C at three different Cd-partial pressures ( $P_{\text{Cd}}$ ) are presented in this paper.

## EXPERIMENT

The undoped, stoichiometric CdTe used in this study was grown by the vertical-gradient freezing method from 6N-purity Cd and Te elements in the charge. Electrical conductivity was measured by the van der Pauw method in the temperature range 1,050–1,130°C at defined  $P_{\text{Cd}}$  1.3–1.6 atm. A special experimental configuration,<sup>9</sup> which allows the precise setting of  $P_{\text{Cd}}$  by means of argon overpressure, was used in our experiment. The diagram of the experimental setup is shown in Fig. 1. The measuring cell is a vertical half-open quartz tube with four contact pipes, which are located at the bottom of the cell. Graphite rods inside the pipes are used for contacts because only graphite is a suitable contact material because of the high reactivity of liquid CdTe with most metals. The cell is shielded by another closed quartz tube, which is filled by argon. At the beginning of the experiment, the measuring cell is filled by CdTe powder and excess Cd is added as a source of Cd overpressure. After heating up above the MP, the powder is molten, and liquid CdTe filled the whole volume of the cell above the graphite-contact rods. The defined  $P_{\text{Cd}}$  above the sample is established by evaporation of Cd from the added Cd source and its condensation on a wall of the cell at

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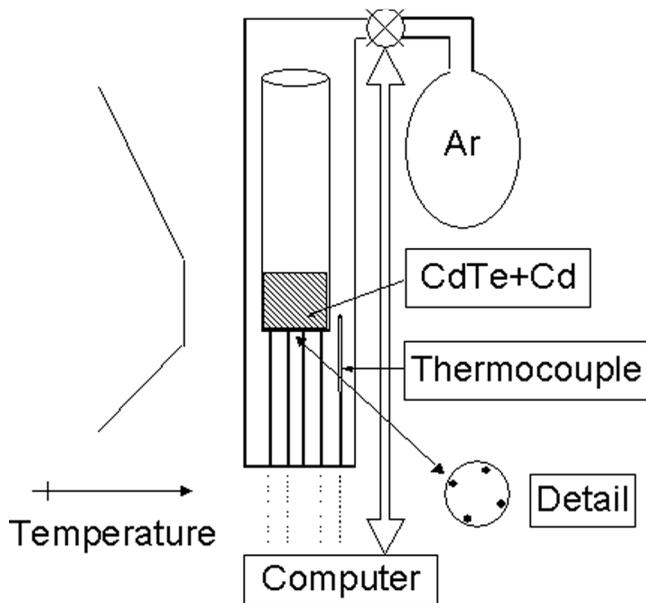


Fig. 1. The diagram of the measuring setup.

the place<sup>1</sup> where temperature decreases below the dew point of Cd. The liquid cadmium drops, consequently, along the wall to the place with higher temperature, where it evaporates again. This cycle is similar to the operation regime of the diffusion pump. The temperature of Cd condensation, which defines  $P_{Cd}$ , depends on the argon pressure, which is PC controlled by a pressure gauge. The total pressure in the measuring cell is the sum of Cd and Ar partial pressures. The Cd/Ar pressure ratio depends on the place in the cell, and it changes from the pure Cd pressure near the CdTe surface to the same value of Ar pressure at the top of the cell. During our experiment, several runs through the solid-liquid phase transition were carried out, the velocity of heating/cooling being  $15^\circ\text{C}/\text{h}$ . The experimental setup was designed to obtain the data from the liquid and solid CdTe in the temperature range near the MP. The precise electrical investigation of the solid CdTe far from the MP is difficult using this setup because of the microcracks between the CdTe and the graphite contacts in the measuring cell.

## RESULTS AND DISCUSSION

The temperature dependence of  $\sigma$  of CdTe near the MP for three different Cd pressures both in the heating and the cooling regime is shown in Fig. 2. As can be seen, the liquid CdTe remains semiconducting for all investigated  $P_{Cd}$  up to a temperature of  $1,130^\circ\text{C}$ , and the slope of the temperature dependence of  $\sigma$  in the liquid is practically independent of  $P_{Cd}$ . The solid line  $\sigma_L = 9.1 \times 10^4 \exp(-0.8 \text{ eV}/k_B T) (\Omega^{-1} \text{ cm}^{-1})$  represents the exponential fit of the conductivity of the liquid CdTe, and  $\sigma_S^i$  is the intrinsic conductivity of the solid CdTe calculated according to the theoretical model.<sup>10</sup> Detailed measurements with small temperature steps allowed us to distinguish a small

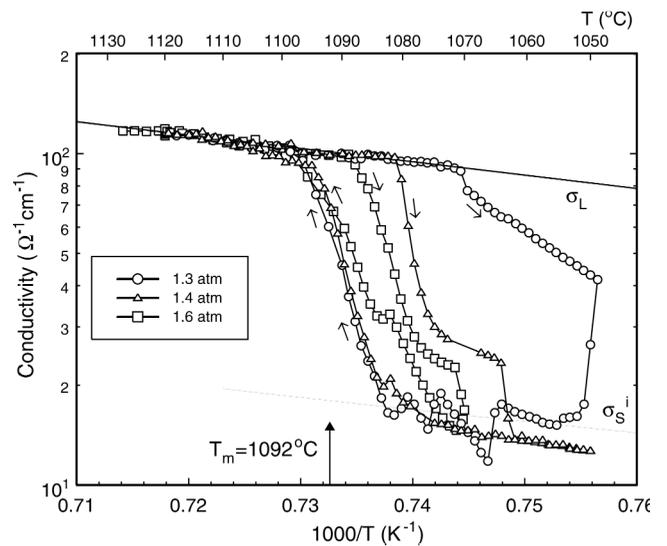


Fig. 2. The temperature dependence of the electrical conductivity  $\sigma$  at three different Cd pressures. The solid line  $\sigma_L$  shows the exponential fit of  $\sigma$  in the liquid, and  $\sigma_S^i$  represents the intrinsic conductivity of the solid calculated according to our theoretical model.<sup>10</sup> The term  $T_m$  marks the temperature of the congruent MP and arrows indicate the cooling/heating regime.

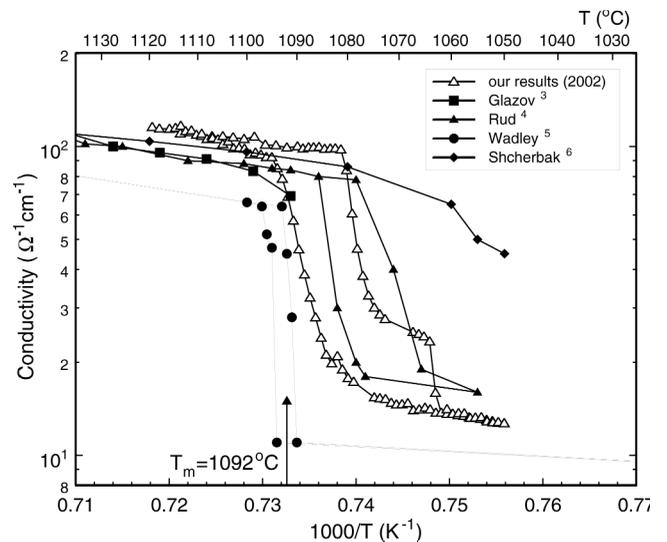


Fig. 3. The overview of temperature dependencies of  $\sigma$  of liquid and solid CdTe near the MP published by various authors. The term  $T_m$  marks the temperature of the congruent MP.

maximum in  $\sigma$  near  $1,085^\circ\text{C}$ , which appeared during heating at all  $P_{Cd}$ . Making a decision as to whether this effect corresponds to some special process in the material or whether it is related to the measuring conditions needs more extensive study in this field.

The comparison of our and other published results of the temperature dependence of  $\sigma$  in liquid and solid CdTe near the MP is presented in Fig. 3. In the case of Refs. 3 and 6, the measurements without defined  $P_{Cd}$  were done. The results, which are close to our presented data, were published in Ref. 4, where liquid-solid phase transition including

supercooling was studied at  $P_{\text{Cd}} = 1.42$  atm. Indirect investigation of  $\sigma$  in closed system by the eddy current method was presented in Ref. 5. This method seems to be optimal for determination of the temperature interval of phase transition, but absolute values of  $\sigma$  are systematically shifted, comparing the data from direct measurement. The measurements of  $\sigma$  presented in Ref. 7 deviate from our new data because of the large temperature gradient along the measuring cell.

The fully new result, which is also apparent from Fig. 2, is the dependence of the degree of supercooling  $\Delta T^-$  of the CdTe melt on  $P_{\text{Cd}}$ . The  $\Delta T^-$  was evaluated from the initial points of the sharp decreasing of  $\sigma$  during cooling. It was found, that the  $\Delta T^-$  decreases ( $\Delta T^- = 23^\circ\text{C}$ ,  $13^\circ\text{C}$ , and  $8^\circ\text{C}$ ) for increasing  $P_{\text{Cd}}$  ( $P_{\text{Cd}} = 1.3$  atm, 1.4 atm, and 1.6 atm, respectively). Simultaneously, the course of  $\sigma$  is independent of  $P_{\text{Cd}}$  during the heating. The observed dependence is a little surprising because one would expect an opposite behavior because of the segregation of Cd at the crystallization front. We correlate our results with Ref. 11, where the dependence of supercooling  $\Delta T^-$  on Te mole-fraction  $x$  in Te-rich CdTe is reported. For decreasing  $x$  ( $x = 0.55$ ,  $0.51$ , and  $0.5$ ) the  $\Delta T^-$  decreases ( $\Delta T^- = 100^\circ\text{C}$ ,  $75^\circ\text{C}$ , and  $38^\circ\text{C}$ , respectively). Summarizing, both in Te-rich and in Cd-rich material,  $\Delta T^-$  decreases when the content of Cd in CdTe increases. Based on our solidus model,<sup>12</sup> which allowed us to evaluate the T-x projection of the CdTe-phase diagram inclusive of the solidus-stability region and the experimental liquidus line,<sup>13</sup> we estimated the composition of the liquid and summarized our data together with those from Ref. 11 in Fig. 4. Because the course of the T-x diagram is known only approximately, the error of the estimated composition can be relatively large. Nevertheless, the decrease of  $\Delta T^-$  with the increased content of Cd in the liquid is apparent.

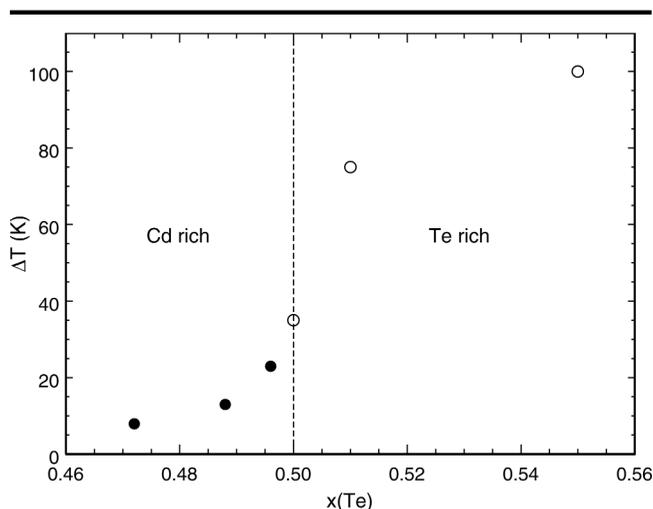


Fig. 4. The dependence of the supercooling  $\Delta T^-$  of the CdTe melt on Te mole-fraction  $x$ . The full circles show our results; the open circles are from Ref. 11.

The most credible, current theoretical models describing structural properties of liquids are based on large-scale, molecular-dynamics simulations, and the supercooled stoichiometric CdTe was also studied by this method.<sup>14,15</sup> However, the effect of stoichiometry deviations on the supercooling was not examined yet. Nevertheless, the results obtained for stoichiometric CdTe can be used for a qualitative explanation of the observed dependence of  $\Delta T^-$  on  $P_{\text{Cd}}$  or  $x$ . It was found that Te atoms form extended chainlike structures in the CdTe melt near the MP.<sup>2,15</sup> These structures must be rearranged and broken during crystallization to form Cd-Te pairs exclusively. In the case of increased  $x$  (decreased  $P_{\text{Cd}}$ ), the structures are more stable, and the rearrangement is complicated (increasing  $\Delta T^-$ ). On the other hand, Cd atoms do not form extended structures, being the less stable and more mobile species in the system. In addition, higher concentration of Cd atoms causes destruction of the Te chains more easily and promotes the phase transition. Therefore, the increased  $P_{\text{Cd}}$  (or content of Cd) results in decreasing  $\Delta T^-$ .

## CONCLUSIONS

A new experimental setup for the investigation of the electrical conductivity in the liquid and solid CdTe near the MP was presented. The temperature dependence of  $\sigma$  was studied during the phase transition from liquid to solid CdTe and back at defined Cd-partial pressures 1.3–1.6 atm. We investigated in detail the degree of the supercooling  $\Delta T^-$  of the CdTe melt depending on  $P_{\text{Cd}}$ . It was found that  $\Delta T^-$  decreases with increasing  $P_{\text{Cd}}$  both in Te-rich and in Cd-rich material. This result is important for the preparation of single crystals, where a minimum supercooling is one of the dominant requests. Because the density of Cd inclusions in the crystal increases at higher  $P_{\text{Cd}}$ , the determination of the optimal Cd overpressure during the crystal growth, which eliminates both higher supercooling and formation of inclusions, is necessary for production of high-quality, large-diameter CdTe single crystals.

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## REFERENCES

1. P. Rudolph, *Prog. Cryst. Growth Charact.* **29**, 275 (1994).
2. J.P. Gaspard, C. Bergman, C. Bichara, R. Bellissent, P. Chieux, and J. Goffart, *J. Non-Crystalline Solids* **97–98**, 1283 (1987).
3. V. Glazov, S. Chizhevskaya, and N. Glagoleva, *Liquid Semiconductors* (New York: Plenum Press, 1969).
4. V. Rud and K.V. Sanin, *Sov. Phys. Semicond.* **5**, 1385 (1972).

5. H.N.G. Wadley and B.W. Choi, *J. Cryst. Growth* **172**, 323 (1997).
6. L. Shcherbak, *J. Cryst. Growth* **197**, 397 (1999).
7. J. Franc, P. Höschl, R. Grill, L. Turjanska, E. Belas, and P. Moravec, *J. Electron. Mater.* **30**, 595 (2001).
8. L. Shcherbak, P. Feychuk, Y. Plevachuk, V. Sklyarchuk, O. Kopach, B.J. Suck, and O. Panchuk, *Phys. Status Solidi (b)* **229**, 165 (2002); P. Feychuk (2002, private communication).
9. C.Z. van Doorn, *Rev. Sci. Instr.* **32**, 755 (1961).
10. J. Franc, R. Grill, L. Turjanska, P. Höschl, E. Belas, and P. Moravec, *J. Appl. Phys.* **89**, 786 (2001).
11. P. Rudolph, in *Recent Development of Bulk Crystal Growth*, ed. M. Milssiki (Trivandrum, India: Research Signpost, 1998), p. 127.
12. R. Grill, J. Franc, P. Höschl, I. Turkevych, E. Belas, P. Moravec, M. Fiederle, and K.W. Benz, *IEEE Trans. Nucl. Sci.* **49**, 1275 (2002).
13. M.R. Lorenz, *J. Phys. Chem. Solids* **23**, 939 (1962).
14. V.M. Glazov and L.M. Pavlova, *J. Cryst. Growth* **184–185**, 1253 (1998).
15. V.V. Godlevsky, M. Jain, J.J. Derby, and J.R. Chelikowsky, *Phys. Rev. B* **60**, 8640 (1999).