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lücke; sie beschränken sich jedoch meistens auf das Ginzburg-Landau-Gebiet in der Nähe von T_c . Darüber hinaus ist üblicherweise die freie Weglänge nicht bekannt. Experimente, welche das in dieser Arbeit beschriebene Verhalten untersuchen, wurden in Nijmegen begonnen.

Wir möchten dem Rechenzentrum der Universität Nijmegen, insbesondere Direktor C. J. M. AARTS und H. J. BEIJNVOORT, für die grosse Unterstützung und Hilfe danken.

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Optical Properties of Some Molten Semiconductors

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(29. IV. 68)

Abstract. On the basis of measurements of optical reflectivity or thermal emissivity of molten Bi_2Te_3 , CdSb and CdTe in the photon energy range 0.5 to 4 eV conclusions are drawn on the changes of their electronic structure occurring during melting. With the exception of CdTe the liquids were found to have optical properties typical of metals.

1. Introduction

One of the many fields to which Prof. G. BUSCH and his collaborators have significantly contributed is the investigation of the electronic transport properties of liquids. The present paper deals with a study of their optical properties and has the same aim – a clarification of the changes in the electronic properties which occur during melting.

The optical properties in the low energy range are sensitive to the change of the short-range order. A typical example are germanium-like semiconductors in which the coordination number changes from 4 to 8 on melting. The electrical conductivity and the optical constants undergo a change corresponding to the transition from the semiconducting into the metallic state. The change is clearly seen in the reflection spectrum in the low energy range as shown in Reference [1]: in a semiconductor the reflectivity increases with photon energy, in a metal it decreases from unity to smaller values. This is due to the fact that in a semiconductor the interband transitions determine the optical properties in this range, while in a metal the free carriers. We determined the reflection spectra in the range 0.5 to 4 eV of some molten semiconductors to see whether they correspond to the semiconducting or the metallic state. We obtained in this way an additional experimental evidence on the nature of the change of the electronic structure of these materials during melting.

2. Theoretical Considerations

The results obtained are only of a qualitative nature and for the understanding of the influence of free carriers a simple theory due to DRUDE (cf. e.g. [2]) is adequate. Using it, we shall discuss the question under what conditions free carriers are negligible or dominate the optical constants of a solid or liquid. The real and imaginary parts of the dielectric constant ϵ_1 , ϵ_2 and the optical constants n , k are determined by the equations

$$\epsilon_1 = n^2 - k^2 = \epsilon_{10} - \frac{\omega_p^2 \tau^2}{\omega^2 \tau^2 + 1} \quad (1)$$

$$\epsilon_2 = 2 n k = \epsilon_{20} + \frac{\omega_p^2 \tau}{\omega (\omega^2 \tau^2 + 1)} \quad (2)$$

where ϵ_{10} , ϵ_{20} correspond to the material without free carriers (which we assume to be of one kind only), ω_p is the plasma frequency ($\omega_p^2 = 4 \pi N e^2/m^*$), N is the concentration of carriers, m^* their effective mass, τ their relaxation time. At high enough frequencies, the free carrier parts in Equations (1) and (2) are negligible compared with ϵ_{10} , ϵ_{20} . The critical frequency is

$$\omega_{crit} = \sqrt{\omega_p^2 / \epsilon_{10} - 1 / \tau^2} . \quad (3)$$

At frequencies $\omega \gg \omega_{crit}$ the reflectivity

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (4)$$

will be negligibly influenced by free carriers (even if $\epsilon_{20} = 0$, because then $\epsilon_2 \ll \epsilon_1$ and k^2 is small compared with $(n-1)^2$). For $\omega < \omega_{crit}$, free carriers will have an influence and at sufficiently low frequencies, they will finally dominate the spectrum. We shall therefore speak about the semiconductor case if in the range considered $\omega \gg \omega_{crit}$ and the metallic case if $\omega \ll \omega_{crit}$.

To quote concrete numbers, let us consider Ge. In solid pure Ge just before melting N is of the order 10^{19} cm^{-3} , $\hbar \omega_p / \sqrt{\epsilon_{10}} \approx 0.1 \text{ eV}$, $\epsilon_{10} = 16$, $\hbar/\tau \approx 3 \times 10^{-3} \text{ eV}$, $\hbar \omega_{crit} \approx$

0.1 eV; indeed at photon energies above 2 eV no influence of carriers on reflectivity is seen (cf. [1]). In molten Ge, $N \approx 2 \times 10^{23} \text{ cm}^{-3}$, $\hbar \omega_p \approx 16 \text{ eV}$, $\epsilon_{10} = 1$, $\hbar/\tau \approx 2.7 \text{ eV}$, $\hbar \omega_{crit} \approx 16 \text{ eV}$: the reflection spectrum in the low energy range is dominated by free carriers as it was actually observed [1].

It can be easily seen that in the part of the spectrum which is dominated by free carriers, interband transitions decrease the reflectivity; without free carriers, interband transitions generally increase the reflectivity.

3. Experimental Methods

For the determination of the reflectivity, we used two methods which did not give us directly R after Equation (4) but the reflectivity of the molten material against quartz

$$R_q = \frac{(n - n_q)^2 + k^2}{(n + n_q)^2 + k^2} \quad (5)$$

where n_q is the index of refraction of quartz. The methods were applicable in the spectral range in which fused quartz is transparent; suprasil was used which is practically transparent in the range 0.4 to 4 eV even at high temperatures [4].

A. Direct Measurement of Reflectivity

The material was inside an evacuated vessel shown in Figure 1. It was surrounded with an oven and the reflectivity was measured by the same method as used for solids [3]. This arrangement was applicable for semiconductors with relatively low melting points (Bi_2Te_3 , CdSb).

B. Measurement of Emissivity

When higher temperatures were required (in particular for CdTe) we measured the thermal emissivity ϵ which is related to R_q by the relation

$$\epsilon = 1 - R_q \quad (6)$$

valid for opaque materials. The emission from quartz was neglected. The emissivity is defined as the ratio of the energy emitted from the material E to that emitted from the black body E_{bb} at the same temperature. As the emitted energy is very sensitive to temperature it is essential to realize the equality of temperatures with a high precision. We used the arrangement shown in Figure 2. The material was placed into an evacuated quartz vessel and the radiated energy E was compared with that of molten Ge in a similar vessel E_{Ge} . As R_q for molten Ge is known from Reference [1], we calculated

$$\epsilon_{Ge} = \frac{E_{Ge}}{E_{bb}} = 1 - R_{q, Ge} \quad (7)$$

and determined ϵ from the relation

$$\epsilon = \frac{E}{E_{bb}} = \frac{E}{E_{Ge}} \epsilon_{Ge} \quad (8)$$

The shape of the curve ϵ vs. $\hbar \omega$ was found to be reliably reproducible but the absolute value may be subject to a systematic error which it was difficult to evaluate.

As we are interested only in the qualitative features we plot ϵ in arbitrary units. Having the relation (6) in mind, we obtain in this way an information only on the general shape of the curve R_q vs. $\hbar\omega$; this is sufficient for our aim stated in Section 1. It is believed that this method may be elaborated into a truly quantitative method useful for the more detailed investigations at high temperatures.

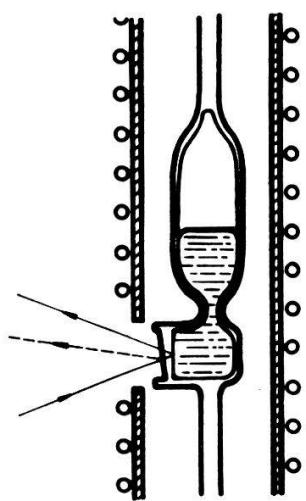


Figure 1

Arrangement for the measurement of the reflectivity of liquids.

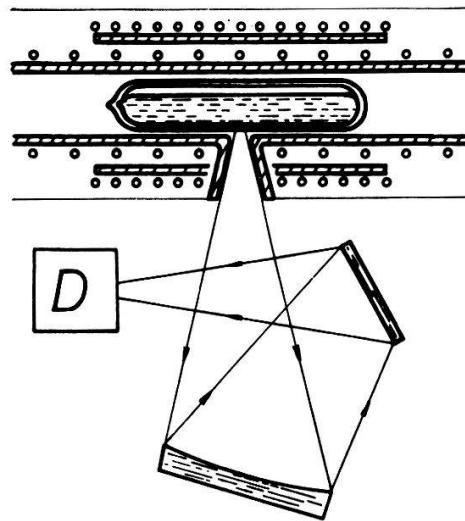


Figure 2

Arrangement for the measurement of thermal emissivity.

4. Results and Discussion

Bi₂Te₃ and CdSb

These materials are interesting because their electrical conductivity increases with temperature even in the liquid state [5]; this was considered to be an evidence that the covalent bands were maintained across the melting point. However, ENDERBY and WALSH [6, 7] found on the basis of their studies of the Hall effect and thermoelectric power of these liquids that the carrier concentration remains constant or even slightly decreases with temperature and that therefore the increase of conductivity must be ascribed to the increase of mobility with temperature.

The reflection spectra shown in Figure 3 are in accord with this interpretation; free carriers clearly determine the optical properties.

The spectrum of Bi₂Te₃ measured at 670°C can be described by Drude formulas with ω_p and τ determined by ENDERBY and WALSH [7] from the Hall constant and d.c. electric conductivity (m^* was put equal to m): $N = 5.5 \times 10^{22} \text{ cm}^{-3}$, $\sigma = 3500 \Omega^{-1} \text{ cm}^{-1}$, $\hbar\omega_p = 8.65 \text{ eV}$, $\tau/\hbar = 0.35 \text{ (eV)}^{-1}$. It was not possible to describe the spectrum of CdSb observed at 540°C using the values found in Reference [7] ($N = 6.3 \times 10^{22} \text{ cm}^{-3}$, $\sigma = 5600 \Omega^{-1} \text{ cm}^{-1}$, $\hbar\omega_p = 9.25 \text{ eV}$, $\tau/\hbar = 0.49 \text{ (eV)}^{-1}$); a better fit shown in Figure 3 was obtained with $\hbar\omega_p = 9.25 \text{ eV}$, $\tau/\hbar = 0.28 \text{ (eV)}^{-1}$.

The experimental determination of the shape of the spectra is much more precise than the absolute values which may be subject to an uncertainty as high as 10% of R_q . We used this circumstance to multiply the reflection spectra with an appropriate

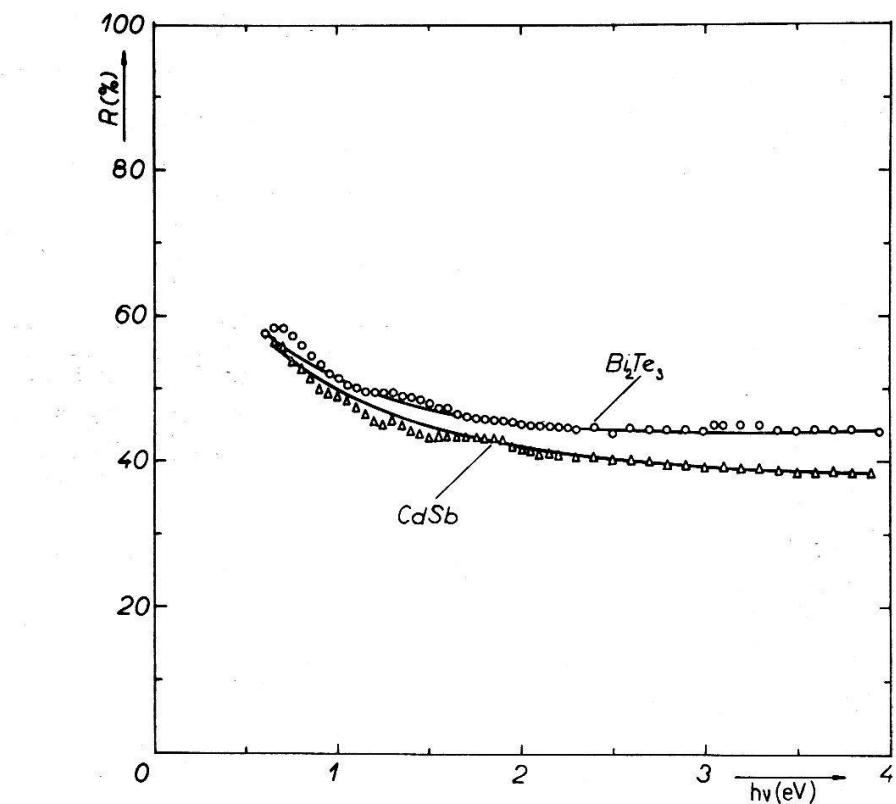


Figure 3

Reflectivity R_d of liquid Bi_2Te_3 and liquid CdSb . The full lines were calculated from Drude formulas with the parameters given in the text.

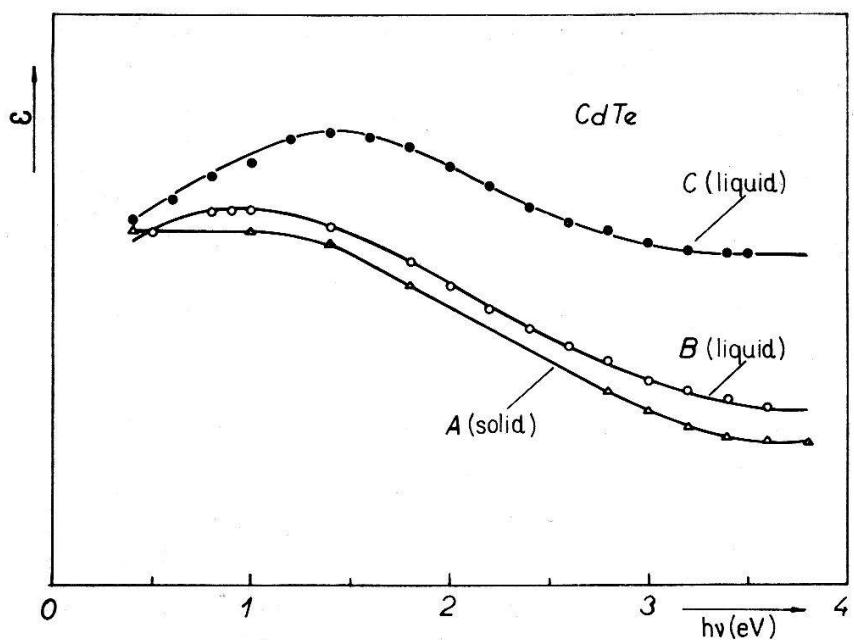


Figure 4

Thermal emissivity ϵ (in arbitrary units) of CdTe . Curve A: solid CdTe at a temperature somewhat lower than the melting point B: liquid CdTe at a temperature somewhat higher than the melting point C: liquid CdTe at a temperature about 150°C above the melting point.

factor to make the coincidence with the calculated curves as good as possible. We do therefore not consider our results as a quantitative check of Enderby and Walsh's results. However, they are a convincing evidence that the free carrier concentrations must be of the order 10^{22} cm^{-3} and the relaxation times $10^{-1} \text{ (eV)}^{-1}$ because it can be shown that a change of the order of magnitude of these quantities makes any reasonable agreement with the measured spectra impossible.

The measurements of magnetic susceptibility of molten CdSb by MATYÁŠ [8] are consistent with the picture obtained from the transport and optical data.

CdTe

The situation with CdTe is different. The emission spectra (Fig. 4) show that this material remains semiconducting even in the molten state. This is consistent with the conclusion obtained from the study of the electric conductivity [9, 10] that the covalent bonds are for a large part conserved through the melting point. The increase of carrier concentration during melting which causes an increase of electric conductivity is seen also in the optical data: before melting, R_q in the low energy range is constant, after melting it decreases down to a certain minimum. This is what one would expect on the basis of the picture suggested in References [9, 10].

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The Development of Knowledge and Understanding of the Anomalous Resistivity of Diluted Metallic Solutions of Transition Metals

by **G. J. van den Berg** and **C. J. Gorter**

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(14. V. 68)

In 1930 [1] MEISSNER and VOIGT (Berlin) published a long series of data on electrical resistance of several metals as a function of temperature. In the region of liquid helium the resistance at the lowest of 2 or 3 temperatures was higher by 0.5–2% for