JOURNAL OF MATERIALS SCIENCE 4 (1969) 410-415

Some Electrical Transport Studies on Compounds of the Tl-Te System

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Received 24 October 1968

Galvanomagnetic, thermoelectric and electrical conductivity measurements were made on single crystal specimens of Tl_2Te_3, TlTe and γ-phase in the temperature range from 77° K up to 500 to 700° K. All crystals were found to be of p-type conductivity. Measurements of the electrical conductivity versus composition have revealed that γ-phase represents solid solutions of Tl and Te in the compound with formula Tl_5Te_3. Also, it has been found that both TlTe and γ-phase samples exhibit a metallic behaviour in contrast to Tl_2Te_3, which has semiconducting properties. In the intrinsic conduction region a thermal energy gap of a 0.68 ± 0.03 eV was found, which was compared with that obtained from optical transmission measurements. The electrical properties of Tl-Te compounds are discussed on the basis of the general valence rule.

1. Introduction

Studies undertaken for the establishment of the equilibrium diagram of the thallium-tellurium system proved the existence of the equiatomic compound TlTe which is formed by a peritectic reaction at 300° C, as well as of a congruently melting phase which, according to [1] and [2] is claimed to correspond to compounds with the formulas Tl_3Te_2 or Tl_5Te_3, respectively. More recently, Rabenau *et al* [3] have demonstrated that the equilibrium diagram contains an additional compound, Tl_2Te_3, which occurs following the peritectic reaction:

$$\text{TlTe} + \text{melt} \overset{238^\circ\text{ C}}{\rightleftarrows} Tl_2Te_3$$

and which, having a very high energy of seed formation has not been identified in previous investigations.

In recent years the Tl-Te system was given growing attention especially in connection with the study of the transport properties of liquid Tl-Te solutions within a wide range of compositions. It has been found that the thermoelectric figure of merit has large values at some ranges of temperature and composition [4]. Also, the applicability of the conventional theory for the semiconductor behaviour of solids to liquid semiconductors [5] was shown. Thallium-tellurium liquid solutions behave like a binary semiconductor subject to nonstoichiometric doping with deviations from an intrinsic composition close to the alloy with the formula Tl_2Te.

The solid state Tl-Te compounds have been studied less thoroughly. Not only are systematic data lacking for these compounds regarding their various properties, but also there does not even exist a uniform point of view concerning the nature of their conductivity. Characteristic from this viewpoint are the papers [3, 6] which report semiconductor behaviour only for Tl_2Te_3 while in other investigations it is demonstrated that TlTe [7] and Tl_5Te_3 [22] are semiconductors too.

In a paper published at the moment of the drafting of the present work Juodakis and Kannewurf [8], investigating the electrical properties of the alloy with 62.5 at. % of thallium showed at temperatures below 2.23° K the existence of a transition to the superconducting state which, of course, renders the Tl-Te system still more interesting.

The primary purpose of this work is to investigate the electronic transport properties of Tl-Te compounds by means of standard electrical measurements. Measurements were made on single-phase and single crystal specimens in the temperature range from 77° K up to 500 to 700° K. The investigation included electrical conductivity, Hall effect and thermoelectric power measurements as a function of temperature.

Although the results on the crystal structure of Tl-Te compounds will be published later elsewhere, we feel it is of use to present here some X-ray diffraction data referring to the identification of Tl_2Te_3, TlTe and Tl_5Te_3 by this method. We consider it important to present these data because the ASTM index [10] and [9] does not give information on Tl-Te compounds and different papers [3, 11, 12] contain only line diagrams (Strichdiagramm).

2. Experimental

The thallium-tellurium compounds were prepared by direct synthesis of stoichiometric proportions of Tl and Te (supplied by Johnson Matthey and Co Ltd) in silica tubes evacuated to a pressure of 10^{-3} torr. In order to prevent oxidation of Tl, it was handled and weighed in a tight glove-box, in a current of purified argon.

Large single crystals of Tl_2Te_3, and TlTe were obtained from tellurium rich melts. In order to determine the homogeneity range at room temperature of the phase identified in [3] as the γ-phase, crystals or various compositions between 62 and 64 at. % Tl, as well as a crystal with formula Tl_2Te, were grown by the Bridgman-Stockbarger method. Since only the crystals with compositions between 62 and 64 at. % Tl proved to be single-phase, in the following only the results for these compositions are presented.

The identification of the compounds was carried out and the single-phase character of the samples was checked by X-ray and metallographic studies, as well as by chemical and microhardness determinations.

Electrical conductivity and Hall effect measurements were performed on $9 \times 2.5 \times 1$ mm³ specimens using the conventional DC potentiometer method. Hall measurements were made in magnetic fields up to 8500 g; for thermoelectric measurements as a function of temperature, temperature gradients of 10° C were used. Immediately before the measurements, in order to remove the oxides from their surfaces the samples were etched in an HNO_3–HCl–H_2O mixture and then washed with concentrated NaOH solution. This treatment led to highly reproducible results, especially in the case of high Tl content samples (γ-phase) which exhibit a more pronounced instability in common atmosphere. At temperatures above 0° C the measurements were carried out in an atmosphere of high purity argon.

3. Results and Analysis

3.1. Structural Properties

Table I presents the diffraction data obtained from powder samples that were prepared from Tl_2Te_3, TlTe and Tl_5Te_3 single crystals. In table I the interplanar spacings and the relative intensities of the principal diffraction lines are given, which may serve for the identification of Tl-Te compounds. These data were obtained in a ϕ 114 mm camera using V-filtered chrome radiation.

TABLE I Interplanar spacings and relative intensities of the lines from powder diffraction pattern of Tl_2Te_3, TlTe and Tl_5Te_3 ($T = 298°$ K)

	Tl_2Te_3		TlTe		Tl_5Te_3	
No.	dÅ	I/I_1 %	dÅ	I/I_1 %	dÅ	I/I_1 %
1	3.74	60	3.08	90	3.15	50
2	3.26	20	2.88	90	3.08	60
3	3.22	20	2.78	100	2.87	100
4	3.14	25	2.55	20	2.82	95
5	3.10	30	2.46	20	2.55	20
6	2.99	60	2.23	50	2.22	50
7	2.95	80	2.16	40	2.18	25
8	2.88	90	2.07	50	2.12	40
9	2.84	100	2.04	15	2.09	80
10	2.66	15	1.84	30	1.99	75
11	2.60	30	1.83	30	1.92	80
12	2.44	60	1.781	30	1.84	30
13	2.37	50	1.766	20	1.814	75
14	1.833	60	1.722	50	1.729	60
15	1.818	60	1.712	25	1.690	25
16	1.654	80	1.572	100	1.680	75
17	1.638	50	1.551	25	1.537	90
18	1.535	40	1.536	25	1.529	70
19	1.471	30	1.525	50	1.485	85
20	1.457	50	1.476	80	1.384	40
21	1.340	50	1.378	75	1.374	40
22	1.219	90	1.360	75	1.325	60
23	1.173	50	1.221	50	1.318	60
24					1.287	50
25					1.262	60
26					1.214	65
27					1.155	90

The crystal system of TlTe was found to be body-centred tetragonal with $a = 12.950$ Å and $C = 6.175$ Å. Our data listed in table I fit in with this structural model of TlTe. It has been reported [3] that Tl_2Te_3 crystallises in the fc monoclinic system with the parameters $a = 13.5$ Å, $b = 6.5$ Å, $c = 7.9$ Å and $\beta = 73°$. Man [14] has reported a rhombohedral thallium telluride with the dimensions (in hexagonal description): $a = 9.00 \pm 3$ Å and $c = 21.90 \pm 8$ Å, space group $D^5{}_{3d}$.

In identifying Tl_5Te_3 as the γ-phase, Rabenau *et al* [3] determined the crystal system to be body-centred tetragonal with $a = 8.92$ Å and $c = 12.63$ Å. Recently [8] the diffraction data obtained from powder samples of Tl_5Te_3 were considered as belonging to a fcc crystal system with $a = 12.620 \pm 0.005$ Å at 300° K.

Though not being clearly different the microhardness of the Tl-Te compounds differs sufficiently to permit the identification of the phases in the microscope not only by the various shades caused by the chemical etching, but also by the microhardness values. Thus, the microhardness of Tl_2Te_3, TlTe and Tl_5Te_3 are 125 ± 2 kg/mm^2, 85 ± 3 kg/mm^2 and 137 ± 3 kg/mm^2, respectively.

3.2. Electrical Properties

Fig. 1 presents the results of electrical conductivity measurements as a function of temperature for a series of γ-phase samples of various compositions. It has to be mentioned that the alloy with 62.5 at. % Tl has the highest conductivity and that for all the samples the Hall effect has an extremely low constant value, corresponding to a high concentration of charge carriers ($p > 10^{21}$ cm^{-3}).

Fig. 1 also shows the variation of electrical conductivity of TlTe as a function of temperature. One can observe a decrease of electrical conductivity with temperature increase and approximately the same values as in the case of other semimetallic compounds (as for instance HgSe). In the case of both temperature increase and decrease the measured values of the conductivity were reproducible. The Hall coefficient, (as for γ-phase), has an extremely low value ($< 1.10^{-3}$ cm^3 C^{-1}) independent of temperature.

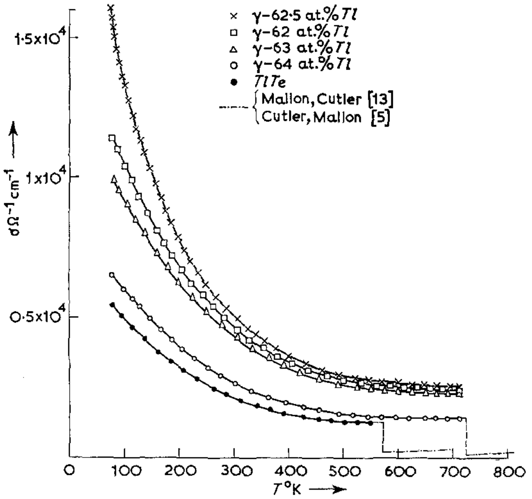

Figure 1 The electrical conductivity versus absolute temperature for some samples of γ-phase and TlTe.

Table II presents the values of the temperature coefficient of resistivity λ in the equation $\rho = \rho_0(1 + \lambda T)$ for some γ-phase and TlTe samples. Since the dependence of electrical conductivity on temperature is not linear, the values of λ in table II are presented at low temperatures (100° K), as well as at higher temperatures (400° K).

It appears that at both low and high temperatures, the alloy with 62.5 at. % Tl, corresponding to the Tl_5Te_3 compound, displays the highest values for the temperature coefficient of resistivity.

Fig. 2 shows the variation of the thermoelectric power (versus copper) as a function of temperature for Tl_5Te_3 and TlTe. In both cases the Seebeck coefficient remains positive within the whole temperature range, increasing monotonously with temperature. Such a linear variation of the thermoelectric power with the temperature together with the decrease of electrical conductivity with increasing temperature (the concentration of charge carriers remaining constant) is an

TABLE II Electrical conductivity and temperature coefficients of resistivity for various Tl-Te alloys

		σ, Ωcm^{-1}		Temp. coef. of resist. λ° K^{-1}	
	Material	100° K	400° K	100° K	400° K
	62 at. % Tl	1.04×10^4	0.340×10^4	4.37×10^{-3}	2.90×10^{-3}
	62.5 at. % Tl	1.32×10^4	0.367×10^4	5.66×10^{-3}	2.98×10^{-3}
γ-phase	63 at. % Tl	0.92×10^4	0.320×10^4	4.32×10^{-3}	2.50×10^{-3}
	64 at. % Tl	0.59×10^4	0.195×10^4	4.16×10^{-3}	2.32×10^{-3}
TlTe	50 at. % Tl	0.50×10^4	0.160×10^4	4.07×10^{-3}	2.24×10^{-3}

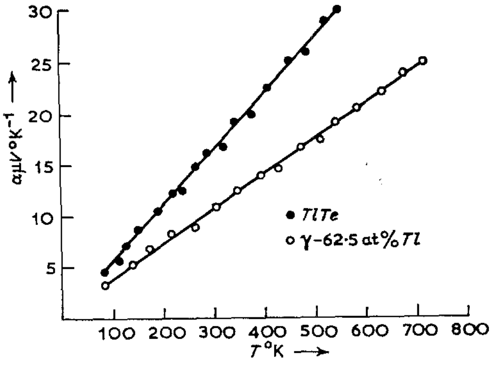

Figure 2 The thermoelectric power versus absolute temperature for Tl_5Te_3 and TlTe.

indication of the metallic behaviour of these materials.

Fig. 3 presents the temperature dependence of electrical conductivity for some Tl_2Te_3 samples, obtained from elements of differing purities. The temperature dependence of the Hall coefficient of the same samples as in fig. 3 is shown in fig. 4. The temperature dependence of thermoelectric power is given in fig. 5 for the sample number 2, which displaying a higher hole mobility (μ_p = 800 cm^2/v sec at 290° K) has been considered the purest.

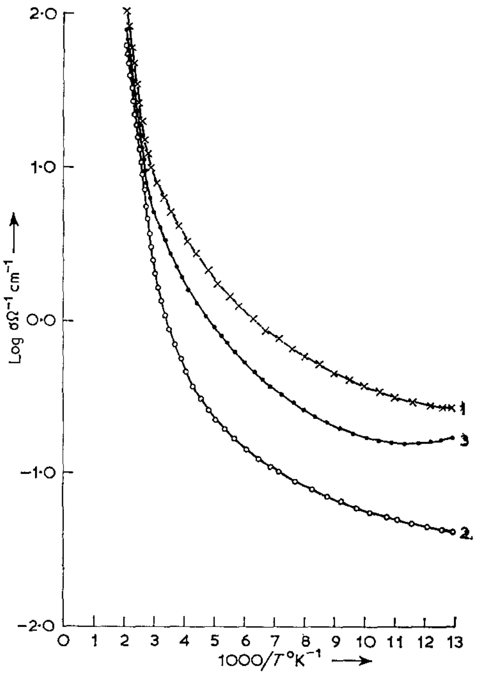

Figure 3 The electrical conductivity versus reciprocal absolute temperature for some samples of Tl_2Te_3.

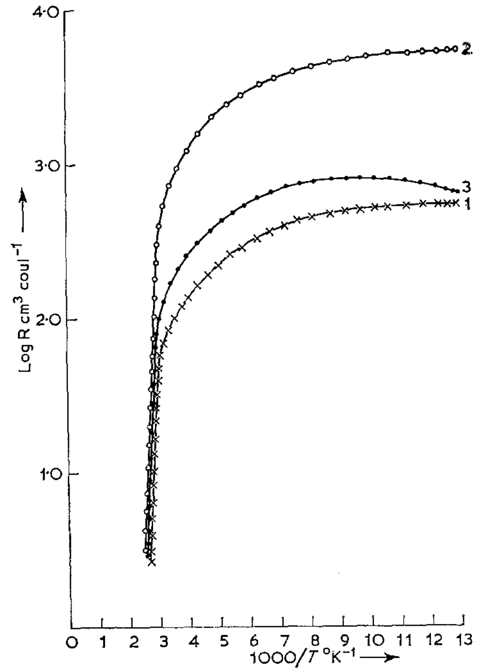

Figure 4 Hall coefficients versus reciprocal absolute temperature for Tl_2Te_3 samples.

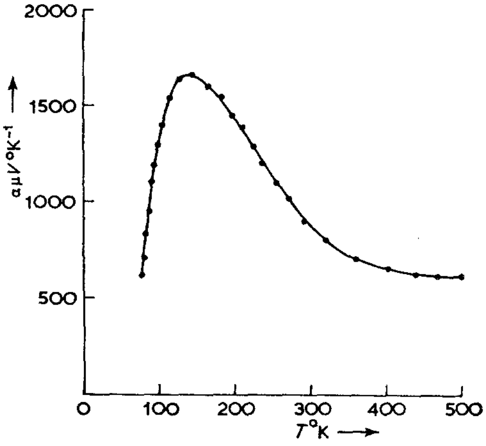

Figure 5 The thermoelectric power versus absolute temperature for the purest sample of Tl_2Te_3.

Both the sign of the Hall effect and that of the Seebeck coefficient show that from 77° K up to the temperature of the peritectic transformation Tl_2Te_3 behaves as a p-type semiconductor, with the mobility of the electrons being either equal or smaller than that of the holes.

The interpretation of experimental results regarding the semiconductor properties of Tl_2Te_3 is rendered difficult by the almost complete lack of data on the crystal and band structure of this compound. Consequently, the analysis of experimental data will be done admitting some simplifying assumptions: (a) that the constant energy surfaces are spherical; (b) the energy bands exhibit a quadratic dependence of energy on wave vector; (c) the ratio of the Hall mobility to the drift mobility is unity; (d) the mobility of both the electrons and the holes varies with temperature as $T^{-3/2}$; (e) the variation of energy gap with temperature is linear; (f) in the high temperatures range there is no additional carrier generation by processes other than intrinsic electron hole formation.

In view of our present stage of knowledge it is difficult to assess to what extent these assumptions are true to reality, especially as Tl_2Te_3 has less than the full cubic symmetry. However, taking into account the relatively low temperatures (below 220° C) at which the measurements were performed as well as the properties of the elements which form the compound we consider that the condition (f) is fulfilled. Consequently, the rapid increase of conductivity at temperatures above 250° K may be taken as intrinsic conduction range and the value $\Delta E_0 = 0.69 \pm 0.03$ eV determined from the plot of $\ln\sigma$ versus $1/T$ as thermal energy gap of Tl_2Te_3. This value satisfactorily agrees with $E_0 = 0.68 \pm 0.02$ eV determined from the plot $\ln RT^{3/2}$ versus $1/T$ in the rapid decrease range of the Hall coefficient. In both cases it has been considered that degeneration is absent in the whole temperature range. This assumption is plausible if we take into account the low concentration of holes in our samples ($p_{ex} = 1/eR_{ex} = 1.1 \times 10^{15} - 1.5 \times 10^{16}/cm^3$ at 77° K). The value of the thermal energy gap satisfactorily agrees with the optical energy gap obtained from transmission data. Thus, optical transmission measurements performed through a platelet of Tl_2Te_3, 200 μm thick throughout the wavelength range 0.6 to 12 μm give an energy gap of 0.70 ± 0.01 eV at 303° K and a temperature coefficient of the band gap of -2.68×10^{-4} eV/° K in the 103° to 303° K range [21].

4. Discussion

The determination of the main semiconductor parameters of Tl_2Te_3 was carried out in the present work with the hypothesis of the validity of some relations which permit the utilisation of the standard theory of semiconductors. As a basis for this we may use the results obtained in the study of the transport properties of liquid Tl-Te solutions [5] which proved that the conventional theory of semiconductors may be applied also in the case of disordered semiconductor systems. Consequently we may presume that they can be applied so much the more in the case of crystals of the same system, even if they have a low-symmetry structure.

Our measurements on the temperature dependence of the electrical conductivity of Tl_2Te_3 enable us to conclude that the "hysteresis" mentioned in [14] is not so much due to a phase transformation that would occur in this temperature range as, probably, to the individual characteristics of the specimens measured. The method used in [14] for the preparation of Tl_2Te_3 samples supports this assumption, it being a known fact that a complete peritectic transformation is only possible under the unrealistic conditions of complete equilibrium [15].

The energy gap of Tl_2Te_3 $\Delta E = 0.68$ eV determined in the present work fits correctly into the series of compounds of group III with tellurium: Al_2Te_3, Ga_2Te_3, In_2Te_3, Tl_2Te_3 whose energy gaps [16] are 2.5 eV, 1.09 eV, 1.0 eV and 0.68 eV, respectively.

From fig. 1 it appears that in the homogeneity range of γ-phase (62 to 64 at. % Tl) the alloy with 62.5 at. % Tl, corresponding to compound Tl_5Te_3, has the highest conductivity. This fact proves that γ-phase is formed on the basis of the intermetallic compound Tl_5Te_3 which can form solid solutions with both Tl and Te. This conclusion is also sustained by the variation with composition of the temperature coefficient of resistivity (see table II). For the alloy with 62.5 at. % Tl this coefficient has maxima values throughout the temperature range investigated.

Similarly as in the case of γ-phase the electrical conductivity of TlTe has a metallic behaviour with lower values than those for γ-phase and a good reproducibility throughout the temperature range.

The existence in the Tl-Te system of some compounds with anomalous conduction behaviour may be explained on the basis of the general valence rule of Pearson [17], according to which the compounds with semiconductor properties obey the rule:

$$\frac{n_e + b_a - b_c}{n_a} = 8$$

where n_e is the total number of valence electrons; n_a is the number of anions; b_a is the number of electrons involved in forming anion–anion bonds, and b_c the number of electrons involved in forming cation–cation bonds, including any "unshared" valence electrons on the cations, all of these values being calculated per formula unit of the compound.

As can be seen in table III only Tl_2Te_3 has an even number of valence electrons n_e per formula unit and only this compound satisfies the general valence rule. TlTe and Tl_5Te_3 are polycationic compounds with n_e/n_a equal to 9 and 11, respectively. The values of b_a and b_c are unknown because detailed information concerning the crystal structure of TlTe and Tl_5Te_3 is not available in the literature.

TABLE III Correlation between the conductivity behaviour of Tl-Te compounds and their ratio n_e/n_a

Compound	n_e	n_e/n_a	Conductivity behaviour
Tl_2Te_3	24	8	semiconductor
TlTe	9	9	metallic
Tl_5Te_3	33	11	metallic

The metallic character of the conductivity of Tl_5Te_3 might *a priori* be assumed, on the basis of the presence in the Tl-Te equilibrium diagram of a wide solubility range of thallium and tellurium in Tl_5Te_3. A more difficult problem was to predict the nature of the conductivity in the case of TlTe, particularly because the analogous compounds (e.g. TlSe, GaTe) exhibit semiconducting properties [18].

Although our measurements did not cover the decomposition or the melting point of the investigated compounds we can nevertheless conclude (using the results given in [19]), that, similarly to HgSe [20], the melting of the Tl-Te alloys is associated with a relatively sharp drop of electrical conductivity, followed by a variation with temperature, characteristic for semiconductors. This can be seen in fig. 1, where in the continuation of the curves referring to the temperature dependence of the electrical conductivity of TlTe and of the alloy with 64 at. % Tl, there are presented also data from [4, 19].

Acknowledgement

We would like to thank Mrs Didona Niculescu for numerous discussions, Mr J. Jaklovszky for preparation of samples and Mrs Olga Ivanciu and Mr N. Nistor for assistance with the chemical and X-ray diffraction analyses.

References

1. M. CHIKASHIGE, *Z. anorg. Chem.* **78** (1912) 68.
2. A. P. OBUHOV and N. S. BUBYREVA, *Izvest. Sekt. fiz. khim. Anal.* **17** (1949) 276.
3. A. RABENAU, A. STEGHERR, and P. ECKERLIN, *Z. Metalk.* **51** (1960) 295.
4. M. CUTLER and C. E. MALLON, *J. Appl. Phys.* **36** (1965) 201.
5. *Idem, Phys. Rev.* **144** (1966) 642.
6. L. A. BORISOVA, M. V. EFREMOVA, and V. V. VLASOV, *Dokl. Akad. Nauk SSSR* **149** (1963) 117.
7. P. FLICKER and F. GRASS, *Z. Metalk,* **57** (1966) 641.
8. A. JUODAKIS and C. R. KANNEWURF, *J. Appl. Phys,* **39** (1968) 3003.
9. R. W. G. WYCKOFF "Crystal Structures", Vol. II (John Wiley & Sons, New York, 1963).
10. Index to X-ray powder data file (ASTM, Baltimore, 1962).
11. A. RABENAU, US 3096 **151** (Cl 23-50) 2(1963).
12. H. HAHN and W. KLINGLER, *Z. anorg. Chem.* **260** (1949) 110.
13. L. I. MAN, VIIth Intern. Congr. IUC, Moscow 1966.
14. F. I. AHMEDOVA and L-E. PIRAGAS, *Izvestia BY3, Fizika* **9** (1966) 167.
15. B. CHALMERS, "Principles of Solidification" (John Wiley & Sons, New York, 1964).
16. M. RODOT, "Les Matériaux semi-conducteurs" (Dunod, Paris, 1965).
17. W. B. PEARSON, *Acta Cryst.* **17** (1964) 1.
18. G. A. AKHUNDOV, G. B. ABDULLAYEV, G. D. GUSEINOV, R. F. MEKHTIEV, and M. K. ALIYEVA, Proc. 7th Intern. Conf. Semic, (Dunod, Paris 1964).
19. C. E. MALLON and M. CUTLER, *Phil. Mag.* **11** (1965) 667.
20. A. F. IOFFE and A. R. REGEL, *Progr. in Semic.* **4** (Heywood Comp. Ltd, 1960).
21. E. CRUCEANU, ST. SLĂDARU, and T. BOTILĂ, *Phys. Stat. Solidi* **30** (1968) K149.
22. K. P. LIPS and W. NAHLIK, *Ann. Physik* **21** (1968) 402.