

## CsOH: LOW-TEMPERATURE HEAT CAPACITY AND HIGH-TEMPERATURE ENTHALPY INCREMENT

R. J. M. KONINGS,† E. H. P. CORDFUNKE,† E. F. WESTRUM, JR‡ and R. SHAVIV‡

†Netherlands Energy Research Foundation ECN, P.O. Box 1, 1755 ZG Petten, The Netherlands

‡Department of Chemistry, University of Michigan, Ann Arbor, MI 48104, U.S.A.

(Received 26 April 1989; accepted in revised form 3 January 1990)

**Abstract**—Heat capacities of CsOH(*s*) have been measured by adiabatic calorimetry from 5 to 350 K, and a reversible  $\lambda$ -type transition has been observed at 233.96 K.  $C_p^0(298.15\text{ K}) = (69.96 \pm 0.10)\text{ J mol}^{-1}\text{ K}^{-1}$ , and  $S^0(298.15\text{ K}) = (104.22 \pm 0.08)\text{ J mol}^{-1}\text{ K}^{-1}$ . High-temperature enthalpy increments of solid as well as liquid CsOH have been measured from 440 to 683 K by drop calorimetry. In combination with DSC-measurements the orthorhombic/cubic transition and the melting point were located at  $(498.2 \pm 0.5)\text{ K}$  and  $(615.5 \pm 0.5)\text{ K}$ , respectively.

**Keywords:** Cesium hydroxide, CsOH, adiabatic calorimetry, drop calorimetry, phase transitions, thermodynamic properties, thermophysical properties.

### 1. INTRODUCTION

Although solid cesium hydroxide is included in the thermochemical compilations by the JANAF team [1] and Glushko *et al.* [2], the experimental basis for these assessments is rather poor. The enthalpy of formation has been derived from measurements made more than 80 years ago; heat-capacity measurements have not been reported. The tabulations are thus mainly based on estimated quantities. Because CsOH is of interest as a potential reaction product of the core-coolant interaction in LWR-reactor accidents, we made a systematic investigation of its thermochemical properties. In recent papers the vapour pressure, measured by transpiration technique [3], and a redetermination of the enthalpy of formation by solution calorimetry [4], were reported. The present paper completes our investigations of condensed CsOH: low-temperature heat capacities have been measured by adiabatic calorimetry and enthalpy increments for the solid as well as the liquid have been measured by drop calorimetry. Additional information on the high-temperature phase transitions has been obtained by DSC. From these data, smoothed thermodynamic functions have been calculated up to 1000 K.

### 2. EXPERIMENTAL

The preparation of CsOH from cesium metal has been described before [4]. For the present study three different samples have been used whose chemical compositions are given in Table 1. Cesium was determined gravimetrically with kalignost;  $\text{CO}_3^{2-}$  was analysed by titration with  $\text{HCl}(aq)$ .

For the low-temperature heat capacity measurements 21.4469 g of the CsOH-1 sample was loaded into the gold-plated copper calorimeter (laboratory designation W-99) provided with a screw-type closure with a stainless-steel knife edge and an annealed gold gasket. The loaded calorimeter was evacuated and 2.7 kPa of helium gas was added at 300 K to facilitate thermal contact between sample and calorimeter.

Heat-capacity measurements were made in the range 5–345 K in the Mark XIII adiabatic cryostat [5]. The calorimeter was surrounded by a shield system provided with automatic temperature control. A Leeds and Northrup capsule-type platinum-resistance thermometer (laboratory designation A-5) was used for temperature determinations. The thermometer was calibrated at the NBS against IPTS-1948 (as textually revised in 1960) [6] for temperatures above 90.2 K, against the NBS provisional scale from 10 to 90 K, and by the calibration technique of McCrackin and Chang [7] below 10 K. These calibrations are judged to reproduce thermodynamic temperatures to within 0.03 K from 10 to 90 K and to within 0.04 K above 90 K. Determinations of mass, current, voltage and time are referred to standardizations and calibrations performed at the NBS. The accuracy of a single heat-capacity measurement is considered to be about 0.5% from 10 to 15 K increasing to about 0.1% between 30 and 350 K.

The enthalpy increments above 298.15 K were measured in an isothermal diphenyl ether calorimeter which has been described previously [8]. Briefly, the sample is enclosed in a spherical silver ampoule (15 ppm total metal impurity) with a 0.25 mm wall

Table 1. Analytical results for CsOH; mass fraction  $w$ 

Sample code	$10^2 w(\text{Cs})$		$10^2 w(\text{Cs}_2\text{CO}_3)$
	Found	Calc.†	
1	$88.41 \pm 0.06$	88.66	0.27
2	$88.63 \pm 0.05$	88.66	< 0.02
3	$88.68 \pm 0.03$	88.66	< 0.02

†The molar mass of CsOH was taken as  $141.9127 \text{ g mol}^{-1}$ .

thickness, a 20 mm diameter and a volume of  $3.8 \text{ cm}^3$ . The ampoule is heated in a furnace whose temperature is measured with calibrated Pt to (Pt + 10 mass % Rh) thermocouples to  $\pm 0.1 \text{ K}$ . After thermal equilibration, the ampoule is dropped into the calorimeter. The energy of the ampoule plus the sample now melts solid diphenyl-ether in equilibrium with its liquid in a closed system. The resulting volume increase of the ether is determined by weighing the displaced mercury. The ratio of heat input to mass of mercury making up the volume change is a constant for the apparatus ( $79.8973 \text{ J g}^{-1}$ ) and is obtained by calibration with the NBS standard reference material (No. 720) synthetic sapphire,  $\text{Al}_2\text{O}_3$ . The enthalpy contributions of silver have

been determined separately and are reported elsewhere [9].

The drop calorimetric measurements were made in two series. For the first series  $7.81521 \text{ g}$  CsOH-2 was enclosed in an ampoule of  $4.01356 \text{ g}$ . For the second series the weights were  $4.90927 \text{ g}$  of CsOH-3 and  $3.86517 \text{ g}$ , respectively. All masses were corrected for weighing in argon to masses in vacuum. A correction was made to account for the difference in enthalpy between the final calorimeter temperature ( $300.06 \text{ K}$ ) and the standard reference temperature,  $298.15 \text{ K}$ , using  $C_p^0(298.15 \text{ K})$ .

The transition temperatures for CsOH were recorded directly in a Mettler DSC apparatus (type TA-13) by heating CsOH in a sealed silver crucible at a heating rate of  $5 \text{ K min}^{-1}$ , using the melting points of Sn and Zn as reference. The temperatures were recorded as onset values; the indicated uncertainty is the standard deviation of a number of DSC runs.

### 3. RESULTS

The results of the low-temperature heat capacity measurements are given in Table 2; the indi-

Table 2. Experimental low-temperature heat capacities of CsOH in  $\text{J mol}^{-1} \text{ K}^{-1}$ 

$T(\text{K})$	$C_p^0$	$T(\text{K})$	$C_p^0$	$T(\text{K})$	$C_p^0$
Series I		76.49	36.23	279.36	70.02
5.63	0.172	80.95	37.42	286.62	69.95
6.20	0.250	85.42	38.51	293.88	69.91
6.86	0.380	90.17	39.55	301.14	69.95
7.55	0.563	95.20	40.50	308.37	70.05
8.28	0.805	100.23	41.37	315.60	70.30
9.13	1.137	105.27	42.22	322.82	70.58
10.12	1.586	110.33	43.05	330.06	70.84
11.11	2.115	115.40	43.86	337.29	71.07
12.13	2.724	120.49	44.65	344.04	71.32
13.30	3.519	125.83	45.43	Series II	
14.60	4.469	131.42	46.24	219.22	65.03
15.93	5.489	137.03	47.02	221.25	66.52
17.30	6.563	142.64	47.77	223.24	68.17
18.70	7.660	144.81	48.04	225.28	70.62
20.12	8.776	148.29	48.52	227.36	73.80
21.57	9.892	150.68	48.82	228.88	76.70
23.04	11.00	156.81	49.67	229.87	78.48
24.79	12.28	162.95	50.53	230.84	82.87
26.80	13.71	169.09	51.42	231.79	85.90
28.83	15.09	175.23	52.37	232.70	90.91
31.05	16.57	181.63	53.44	233.58	96.78
33.47	18.11	188.28	54.63	234.45	92.80
35.90	19.58	194.93	55.97	235.38	80.27
38.53	21.10	201.56	57.61	236.36	76.25
41.36	22.63	208.18	59.66	237.37	74.43
44.21	24.11	214.77	62.39	238.39	73.16
46.71	25.36	221.54	66.73	239.41	72.80
49.63	26.75	228.39	76.40	240.92	72.41
53.01	28.25	235.16	84.35	242.92	71.96
56.39	29.66	242.57	72.06	244.92	71.46
60.03	31.07	250.22	71.01	246.93	71.06
63.93	32.46	257.53	70.56	248.94	71.02
67.85	33.74	264.81	70.27	Series III	
72.04	34.99	272.09	70.10	221.41	66.65
				249.10	71.09

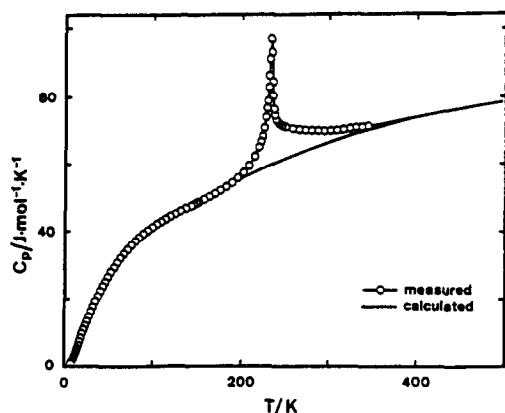


Fig. 1. The low-temperature heat capacity of CsOH.

vidual measurements are plotted in Fig. 1 as a function of temperature. The data were fitted to a power series in orthogonal polynomials as described by Justice [10], from which the smoothed thermodynamic functions in Table 3 were calculated:  $C_p^0(298.15 \text{ K}) = (69.96 \pm 0.10) \text{ J mol}^{-1} \text{ K}^{-1}$ , and  $S^0(298.15 \text{ K}) = (104.22 \pm 0.08) \text{ J mol}^{-1} \text{ K}^{-1}$ .

A reversible  $\lambda$ -type transition with a peak maximum of 233.96 K was observed in the heat capacity of CsOH. The extension of the excess contribution is very broad, ranging from 190 to about 400 K. The enthalpy and entropy of transition were calculated from the excess heat capacity which was obtained by subtracting the lattice heat capacity from the experimental results.

The contribution of the lattice was determined from the single parameter phonon distribution lattice fitting theory of Komada and Westrum [11] yielding  $\theta_{\text{KW}} = 143.5$ . This fitting procedure allows for acoustic as well as optical modes and can therefore be used at high temperatures. We thus obtain  $\Delta_{\text{tr}} H^0 = 958 \text{ mol}^{-1} (= 115.2 \text{ R})$  and  $\Delta_{\text{tr}} S^0 = 4.095 \text{ J mol}^{-1} \text{ K}^{-1} (= 0.492 \text{ R})$ .

The results of the 27 drop calorimetric measurements are given in Table 4, and are plotted in Fig. 2. Two discontinuities have been observed: the solid state orthorhombic/cubic transformation and the melting point (see Discussion). The data have been fitted to three polynomial equations. For the orthorhombic phase we obtained:

$$\begin{aligned} \{H^0(T) - H^0(298.15 \text{ K})\} / \text{J mol}^{-1} &= 57.8256(T/\text{K}) \\ &+ 20.3495 \cdot 10^{-3}(T/\text{K})^2 - 19049.6 \end{aligned}$$

applying  $C_p^0(T) = 69.96 \text{ J mol}^{-1} \text{ K}^{-1}$  and  $\{H^0(T) - H^0(298.15 \text{ K})\} = 0$  at  $T = 298.15 \text{ K}$  as boundary conditions. This function joins smoothly the low-temperature data discussed above. For the cubic phase we obtained:

$$\begin{aligned} \{H^0(T) - H^0(298.15 \text{ K})\} / \text{J mol}^{-1} \\ = 72.676(T/\text{K}) - 15997.7 \end{aligned}$$

Table 3. Experimental enthalpy increments of CsOH

$T(\text{K})$	$\{H^0(T) - H^0(298.15 \text{ K})\}(\text{J mol}^{-1})$		$\delta(\%)$
	Exp.	Calc.	
439.5	10305	10295	0.09
449.3	11033	11039	-0.06
458.9	11774	11772	0.02
468.4	12474	12501	-0.21
478.5	13268	13279	-0.18
488.3	14074	14039	0.25
498.2	14810	—	—
508.0	20999	20922	0.37
517.8	21605	21634	-0.13
527.8	22394	22361	0.15
537.8	23019	23087	-0.30
547.5	23789	23792	-0.01
558.4	24628	24585	0.17
567.9	25149	25275	-0.50
573.2	25620	25660	-0.16
582.4	26350	26329	0.08
588.3	26756	26758	-0.01
597.7	27533	27441	0.33
622.8	36995	37188	-0.39
626.3	37569	37436	0.35
633.1	38060	38014	0.12
643.5	38994	38898	0.25
653.4	39643	39740	-0.24
663.4	40478	40590	-0.28
673.5	41492	41449	0.10
678.7	41829	41891	-0.15
683.4	42389	42291	0.23

Table 4. Thermophysical functions of CsOH from 5 to 340 K

$T$ (K)	$C_p^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$S^0$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$-\{G^0(T) - H^0(0 \text{ K})\}/T$ (J mol <sup>-1</sup> K <sup>-1</sup> )	$H^0(T) - H^0(0 \text{ K})$ (J mol <sup>-1</sup> )
5	(0.125)	(0.058)	(0.025)	(0.158)
10	1.513	0.449	0.108	3.376
15	4.773	1.638	0.399	18.53
20	8.680	3.542	0.931	52.14
25	12.43	5.887	1.688	105.1
30	15.88	8.464	2.592	176.0
40	21.90	13.89	4.739	365.9
50	26.92	19.32	7.109	610.6
60	31.04	24.61	9.595	901.2
70	34.40	29.66	12.10	1228.9
80	37.19	34.44	17.05	1587.3
100	41.36	43.22	19.46	2375.5
120	44.56	51.04	24.09	3235.3
140	47.42	58.14	28.45	4155.5
160	50.10	64.64	32.57	5130.9
180	53.15	70.71	36.48	6161.9
200	57.19	76.50	40.19	7262.7
220	65.55	82.28	46.78	8475.8
240	72.38	88.87	47.17	10007.3
260	70.51	94.63	50.67	11430.0
280	69.97	99.83	54.00	12833.5
300	69.97	104.65	57.22	14231.9
320	70.43	109.19	60.32	15634.6
340	71.17	113.48	63.32	17051.4
273.15	70.05	98.09	52.87	12353.7
298.15	69.96	104.22	56.92	14103.1

and for the liquid phase:

$$\{H^0(T) - H^0(298.15 \text{ K})\}/\text{J mol}^{-1} \\ = 85.027(T/\text{K}) - 15816.7.$$

The orthorhombic/cubic phase transition and the melting point are obtained in DSC runs as

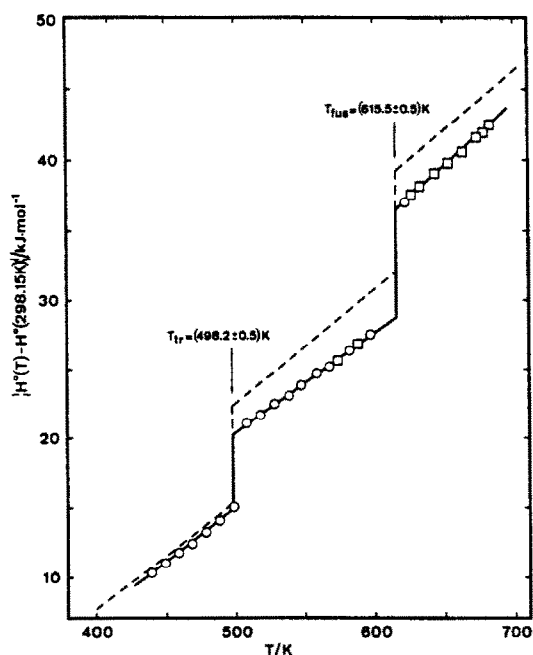


Fig. 2. The high-temperature enthalpy increments of CsOH.

sharp and reproducible peaks, and are located at  $(498.2 \pm 0.5) \text{ K}$  and  $(615.5 \pm 0.5) \text{ K}$ , respectively. The enthalpy changes associated with these transitions have been calculated from the three equations above as  $\Delta_{\text{tr}} H^0(498.2 \text{ K}) = 5400 \text{ J mol}^{-1}$  and  $\Delta_{\text{fus}} H^0(615.5 \text{ K}) = 7783 \text{ J mol}^{-1}$ .

The smoothed thermochemical functions above room temperature are listed in Table 5. The enthalpy of formation of  $\text{CsOH}(s)$  was taken from Ref. 4, and the reference states of the elements from Glushko *et al.* [2].

#### 4. DISCUSSION

The polymorphism of CsOH has been studied by Jacobs *et al.* [12–15] who used DSC, infrared/Raman spectroscopic, X-ray, and neutron diffraction techniques by Bastow *et al.* [16], who employed DTA, dielectric constant, and neutron diffraction measurements and by Haas and Schindewolf [17] using electrical conductivity measurements. These studies established three polymorphs of CsOH: an orthorhombic low-temperature modification (LTM), an orthorhombic room-temperature modification (RTM), and a cubic high-temperature modification (HTM). Amm *et al.* [18] also observed these modifications in CsOD.

In their earlier work Jacobs *et al.* [12] reported the low-temperature phase transformation at about 232 K by DSC, in good agreement with the present results. Their initial spectroscopic study [14] indicated different structural features: weak hydrogen bonds being present in the LTM and absent in the RTM.

Table 5. The thermal properties in CsOH transformations

$T(K)$	Nature	$\Delta_{tr}H^0(J mol^{-1})$	$\Delta_{tr}S^0(J mol^{-1} K^{-1})$
233.96	Ferroelectric	958	4.095
498.2	Orthorhombic/cubic	5400	10.84
615.5	Fusion	7783	12.65

The more recent DSC-results by Jacobs *et al.* [13] do not show the transformation, which is supported by a study of the temperature shift of the OD stretching frequency in isotopically diluted CsOH [15]. However, the authors do not comment on this discrepancy.

The low-temperature transition was located by Bastow *et al.* at 232 K, who found the LTM to be anti-ferroelectrically ordered. They concluded that the phase transformation in CsOH probably involves coherent tunneling of  $H_s$  to reverse the polarities of chains of oxygen atoms linked by weak hydrogen bonds. Amm *et al.* [18] concluded from a NMR study of CsOD that reorientational motion of the OD ion occurs in the RTM but not in the LTM.

From the similarity with the low-temperature transformations in KOH and KOD [19], and especially NaOD [20], which was explored by low-temperature X-ray diffraction, Bastow *et al.* suggested the transition in CsOH to be first order. However, a comparison of recent low-temperature heat capacity data for KOH and KOD by White *et al.* [21] and NaOD by White and Moore [22] with the present data for CsOH, shows a distinct difference. The transitions in KOH, KOD and NaOD are sharp, the widths being 10, 21 and 18 K, respectively. White calculated the excess heat capacity assuming a discontinuity of the lattice heat capacity (first order), and obtained  $\Delta_{tr}S = 0.121 R$ ,  $0.126 R$  and  $0.103 R$ , respectively. In contrast, the width of the transition in CsOH is very broad, about 210 K, indicating a non-isothermal effect, and since the high-temperature data fit the same  $\theta_{KW}$  as the low-temperature data, our approach of continuity of the lattice heat capacity

through the transition (second order) therefore seems correct. The entropy of transition in CsOH calculated in this way,  $\Delta_{tr}S = 0.492 R$ , is significantly higher than in KOH, KOD and NaOD. In case the phase transformation is assumed to be solely the results of independent ordering of the dipoles, the theoretical value of  $\Delta_{tr}S$  would be  $R \ln 2$  ( $= 0.693R$ ).

The values for the temperatures of the orthorhombic-to-cubic and the cubic-to-liquid transitions presented here,  $(498.2 \pm 0.5) K$  and  $(615.5 \pm 0.5) K$ , respectively, are in fair agreement with previous data. Cohen-Adad and Ruby [23] reported 488 and 619 K, Reshetnikov and Baranskaya [24] 493 and 588 K, and Jacobs *et al.* [12, 13] 497.5 and 612 K, respectively. In addition, Jacobs and Harbrecht [12] as well as Reshetnikov and Baranskaya [24] reported a thermal effect around 410 K, which was not observed in the present study. This effect is probably due to the loss of some residual water [25]. The values for the enthalpies associated with these transitions are, however, in poor agreement. Reshetnikov and Baranskaya [24] obtained 6070 and 4560  $J mol^{-1}$  and Jacobs *et al.* [12, 13] 7120 and 7400  $J mol^{-1}$ , respectively, compared with 5400 and 7783  $J mol^{-1}$ , as obtained in this study.

The present thermodynamic data for CsOH deviate considerably from the DSC results of Jacobs *et al.* Apart from the absence of the low-temperature transition in the data of Jacobs *et al.*, the present data suggest a constant  $C_p$  for the RTM and HTM, whereas the data of Jacobs *et al.* show a strong temperature dependence. This may be attributed to the presence of carbonate or water impurities and the use of the inherently less accurate DSC technique.

Table 6. Thermodynamic functions of CsOH(*s, l*)

$T$ (K)	$C_p^0$ ( $J mol^{-1} K^{-1}$ )	$S^0$ ( $J mol^{-1} K^{-1}$ )	$-\{G^0 - H^0(298)\}/T$ ( $J mol^{-1} K^{-1}$ )	$\{H^0 - H^0(298.15 K)\}$ ( $J mol^{-1}$ )	$\Delta_f H^0(T)$ ( $J mol^{-1}$ )	$\Delta_f G^0(T)$ ( $J mol^{-1}$ )
298.15	69.960	104.220	104.220	0	-416440	-372072
300	70.035	104.653	104.221	130	-416424	-371797
400	74.104	125.358	107.017	7337	-417492	-356380
498.2	78.102	142.050	112.323	14810	-416048	-341543
498.2	72.676	152.889	112.323	20209	-410648	-341543
500	72.676	153.511	112.470	20340	-410629	-341282
600	72.676	166.401	120.338	27608	-409452	-327523
615.5	72.676	168.255	121.570	28734	-409264	-325468
615.5	85.027	180.900	121.570	36517	-401481	-325468
700	85.027	191.838	129.407	43702	-399419	-315101
800	85.027	203.192	137.936	52205	-396981	-303221
900	85.027	213.207	145.754	60708	-394586	-291646
1000	85.027	222.165	152.955	69210	-460011	-276745

## REFERENCES

1. Chase M. W. *et al.*, JANAF Thermochemical Tables, 3rd Edition, *J. phys. Chem. Ref. Data* **14**, Suppl. 1 (1978-82).
2. Glushko V. P. *et al.*, *Termodinamicheskie Svoistva Individual'nykh Veshchestv*, Tom IV. Nauk, Moskva (1978-1982).
3. Konings R. J. M. and Cordfunke E. H. P., *J. Chem. Thermodynam.* **20**, 103 (1988).
4. Konings R. J. M., Cordfunke E. H. P. and Ouweltjes W., *J. Chem. Thermodynam.* **20**, 777 (1988).
5. Westrum E. F., Jr, Furukawa G. T. and McCullough J. P., in *Experimental Thermodynamics* Vol. I. (Edited by D. W. Scott and J. P. McCullough). Butterworths (1968).
6. Stimson H. F., *J. Res. natn. Bur. Stand.* **65A**, 139 (1961).
7. McCrackin F. L. and Change S. S., *Rev. scient. Instrum.* **46**, 550 (1975).
8. Cordfunke E. H. P., Muis R. P., and Prins G., *J. Chem. Thermodynam.* **11**, 819 (1979).
9. Cordfunke E. H. P. and Konings R. J. M., *Thermochim. Acta* **157**, 315 (1989).
10. Justice B. H., Thermal data fitting with orthogonal functions and combined table generation. The FITAB program project report COO-1149-143. February 1969. Department of Chemistry, The University of Michigan, Ann Arbor.
11. Komada N. and Westrum E. F., Jr, *J. Chem. Thermodynam.* (submitted).
12. Jacobs H. and Harbrecht B., *Z. Naturf.* **36B**, 270 (1981).
13. Jacobs H., Mach B., Harbrecht B., Lutz H. D. and Henning J. A., *Z. anorg. allg. Chem.* **544**, 55 (1987).
14. Lutz H. D., Henning J., Jacobs H. and Mach B., *J. molec. Struct.* **145**, 277 (1986).
15. Henning J., Lutz H. D., Jacobs H. and Mach B., *J. molec. Struct.* **196**, 113 (1989).
16. Bastow T. J., Elcombe M. M. and Howard C. J., *Solid St. Commun.* **62**, 149 (1987).
17. Haas K. H. and Schindewolf U., *Ber. Bunsenges. Phys. Chem.* **87**, 346 (1983).
18. Amm D. T., Segel S. L. and Jeffrey K. R., *Can. J. Phys.* **64**, 22 (1986).
19. Bastow T. J., Elcombe M. M. and Howard C. J., *Solid St. Commun.* **57**, 339 (1986).
20. Bastow T. J., Elcombe M. M. and Howard C. J., *Solid St. Commun.* **59**, 257 (1986).
21. White M. A., Perrot A., Britte D. and Oort M. J. M. van, *J. chem. Phys.* **89**, 4346 (1988).
22. White M. A. and Moore S. A., *J. chem. Phys.* **85**, 4629 (1986).
23. Cohen-Adad M. M. and Ruby C., *Compt. rend (Paris)* **258**, 6163 (1964).
24. Reshetnikov N. A. and Baranskaya E. V., *Izv. Vyssh. Ucheb. Zaved. Khim. Khim. Teknol.* **10**, 196 (1967).
25. Johansson L. G. and Kazikowski S., Report LACE-TR-072.