Zeitschrift: Helvetica Physica Acta

Band: 41 (1968)

Heft: 6-7

Artikel: X-ray investigation of modifications III and IV of NH4Br and ND4Br at temperatures between -56° and -192°C

Autor: Hovi, V. / Paavola, Kirsti / Urvas, O.

DOI: https://doi.org/10.5169/seals-113950

Man gewinnt auch den Eindruck, dass dies für ihn kein Ziel war. Er beschreibt selbst seine Methode etwa so: Man mache eine Hypothese und suche durch logische Schlüsse ihre Konsequenzen abzuleiten. Dabei kommt es nicht so sehr darauf an, ob die Hypothese richtig oder falsch ist, sondern das wichtigste ist, dass sie bequem (*commoda*) ist.

Newton konnte sein Gravitationsgesetz quantitativ erproben. Etwas ähnliches war für Bošković nicht möglich. Newton konnte auch die nötigen mathematischen Methoden erfinden. Das wäre für Bošković bei seinem Problem nicht möglich gewesen. Dazu bedurfte es noch der Entdeckung der Ionenkräfte und der Austauschkräfte der Quantentheorie und noch vieles mehr. Und es musste ein langer und mühsamer Weg durchschritten werden, um die nötigen experimentellen Daten und Unterlagen herbeizuschaffen. Seine Theorie war ein Versuch, ein Vorhaben durchzuführen, das mit den damals zugänglichen Hilfsmitteln nicht durchgeführt werden konnte. Bošković war fast 200 Jahre mit seinen Ideen voraus, wir aber können eben in diesen Ideen die moderne Festkörpertheorie *in statu nascendi* erblicken.

X-Ray Investigation of Modifications III and IV of NH_4Br and ND_4Br at Temperatures between −56° and −192 °C

by **V. Hovi, Kirsti Paavola,** and **O. Urvas**
Wihuri Physical Laboratory, University of Turku, Finland

(29. IV. 68)

Abstract. The lattice parameters of modifications III and IV of NH_4Br and ND_4Br were determined between − 56° and − 192 °C at 27 and 28 temperatures, respectively. The low-temperature Debye-Scherrer method used is previously described by Hovi et al. [1]. The transition of NH_4Br below − 165 °C, observed by Stephenson et al. [2] by specific heat measurements, was found to be a structural one between CsCl and tetragonal structures. It was accompanied by a discontinuous 2.24% volume expansion with increasing temperature at − 171 °C. In the case of ND_4Br, the corresponding volume change turned out to be 2.23% at − 109 °C. At the transition III → II of ND_4Br at − 58 °C the decrease of the molar volume with increasing temperature was 0.41%.

Introduction

Below room temperature, the following modifications of NH_4Br and ND_4Br have been observed [2–8 and present paper[1])]:

Mod. II (CsCl structure)	$\xleftarrow[ND_4Br \text{ about } -58\,^\circ C]{NH_4Br \text{ about } -38\,^\circ C}\rightarrow$	Mod. III (Tetragonal, nearly CsCl structure)
Mod. III (Tetragonal, nearly CsCl structure)	$\xleftarrow[ND_4Br \text{ about } -109\,^\circ C]{NH_4Br \text{ about } -171\,^\circ C}\rightarrow$	Mod. IV (CsCl structure)

[1]) Refers to the transition III → IV of NH_4Br.

In the present investigation attention was paid to all these transitions, except the II → III transition of NH_4Br. The only systematic X-ray investigation of NH_4Br and ND_4Br is apparently the measurement of the lattice parameters of NH_4Br at temperatures between 22 and − 125 °C by Hovi et al. [1]. Below − 125 °C, only the single observations by Ketelaar [4] at − 140 °C and by Weigle and Saini [6] at − 145 °C have been carried out for this salt. For ND_4Br, we have found only the observations by Ketelaar [4] at − 30 °C, − 73 °C, and − 140 °C.

The object of the present work was to investigate, by means of X-ray diffraction, the lattice expansion and the structural changes of NH_4Br and ND_4Br at temperatures between − 56° and − 192 °C. The lattice parameters, the molar volumes and their changes at the transitions, and the ratios of the two equal lattice parameters to the third one of the tetragonal modification III were determined as functions of temperature.

Measurements and Results

For the measurements of the lattice parameters the low-temperature Debye-Scherrer method described by Hovi et al. [1] was used. Diffraction lines of both NH_4Br and ND_4Br were recorded on the same film. The temperature of the specimen was observed by means of two copper-constantan thermocouples, one of which was

	NH_4Br			ND_4Br		
t (°C)	$a_{1,2}$ (Å)	a_3 (Å)	$a_{1,2}/a_3$	$a_{1,2}$ (Å)	a_3 (Å)	$a_{1,2}/a_3$
− 56	4.050	4.063	0.9966	4.048		
− 58	4.050	4.064	0.9967	4.048		
− 61	4.049	4.065	0.9963	4.048	4.063	0.9964
− 63	4.050	4.064	0.9964	4.048	4.060	0.9971
− 66				4.048	4.063	0.9965
− 71	4.049	4.064	0.9961	4.047	4.061	0.9967
− 78	4.048	4.064	0.9960	4.047	4.061	0.9966
− 85	4.046	4.064	0.9957	4.046	4.062	0.9961
− 86	4.047	4.063	0.9960	4.046	4.061	0.9964
− 92	4.045	4.061	0.9961	4.044	4.058	0.9966
− 98	4.044	4.060	0.9961	4.043	4.059	0.9960
− 105	4.044	4.061	0.9958	4.043	4.060	0.9959
− 109	4.045	4.061	0.9959	4.044	4.059	0.9962
− 110	4.044	4.061	0.9957	4.019		
− 112	4.042	4.059	0.9956	4.017		
− 116	4.043	4.060	0.9959	4.018		
− 121	4.041	4.056	0.9961	4.016		
− 124	4.040	4.057	0.9955	4.015		
− 135	4.039	4.055	0.9960	4.014		
− 138	4.038	4.054	0.9961	4.014		
− 152	4.037	4.054	0.9957	4.012		
− 156	4.036	4.052	0.9962	4.011		
− 169	4.035	4.052	0.9960	4.010		
− 171	4.009			4.010		
− 176	4.010			4.009		
− 192	4.009			4.009		
− 192	4.008			4.008		
− 192	4.008			4.009		

located above and the other below the specimen in the cooling nitrogen flow. The errors in the temperatures given in the Table are estimated to be within $\pm$ 1 °C.

The NH_4Br used was of the quality 'pro analysi' by the May & Baker Ltd, England. ND_4Br was prepared in this laboratory from NH_4Br by eight consecutive recrystallizations from D_2O solution. The deuterium content of the D_2O by the Norsk Hydro was guaranteed to be 99.7%. According to the density measurements of an identically prepared ND_4NO_3 sample [9, 10], the deuterium content of the ND_4Br sample should be at least 90%.

The Table shows the values obtained for the lattice parameters and the axial ratios of NH_4Br and ND_4Br. A polynomial regression analysis [6] of these data yielded the following first and second order polynomials for the lattice parameters ($a_1 = a_2 = a_{1,2}$, a_3), molar volumes (V), and axial ratios ($a_{1,2}/a_3$) of NH_4Br and ND_4Br as functions of temperature:

NH_4Br Modification III (temperatures between − 56° and − 171 °C)

$$a_{1,2} = 4.059 + 0.1425 \times 10^{-3}\, t,$$
$$a_3 = 4.066 - 0.1934 \times 10^{-4}\, t - 0.6631 \times 10^{-6}\, t^2,$$
$$V = 40.322 + 0.2546 \times 10^{-2}\, t - 0.6856 \times 10^{-5}\, t^2,$$
$$a_{1,2}/a_3 = 0.9982 + 0.3875 \times 10^{-4}\, t + 0.1584 \times 10^{-6}\, t^2.$$

Modification IV (temperatures below − 171 °C)
See the Table.

ND_4Br Modification II (temperatures between 132° and − 58 °C)
See the Table.

Modification III (temperatures between − 58° and − 109 °C)

$$a_{1,2} = 4.055 + 0.1147 \times 10^{-3}\, t,$$
$$a_3 = 4.068 + 0.1268 \times 10^{-3}\, t + 0.4039 \times 10^{-6}\, t^2,$$
$$V = 40.313 + 0.4119 \times 10^{-2}\, t + 0.7615 \times 10^{-5}\, t^2,$$
$$a_{1,2}/a_3 = 0.9972 + 0.5253 \times 10^{-5}\, t - 0.5027 \times 10^{-7}\, t^2.$$

Modification IV (temperatures below − 109 °C)

$$a = 4.054 + 0.4365 \times 10^{-3}\, t + 0.1042 \times 10^{-5}\, t^2,$$
$$V = 40.107 + 0.1272 \times 10^{-1}\, t + 0.3041 \times 10^{-4}\, t^2.$$

The temperature dependences of the molar volumes of NH_4Br and ND_4Br between − 56° and − 193 °C are illustrated by Figures 1a and 1b.

On the basis of the results obtained the following remarks can be made:

The transition of NH_4Br below − 165 °C, observed by STEPHENSON et al. [2] by specific heat measurements, appears to be a structural one between CsCl (Mod. IV) and tetragonal (Mod. III) structures. It is accompanied by a discontinuous 2.24% volume expansion with increasing temperature at − 171 °C. At the corresponding transition of ND_4Br at − 109 °C the volume change is 2.23%. According HOVI et al. [1] the molar volume of NH_4Br decreases by 0.40% with increasing temperature at the transition III → II at − 38 °C. We found that at the corresponding transition of ND_4Br at − 58 °C the decrease of the molar volume with increasing temperature is 0.41%. It is interesting to note that, although the transition temperatures undergo large alterations upon replacement of H by D in NH_4Br [12], the relative molar volume changes at the transitions II → III and III → IV remain practically unaltered.

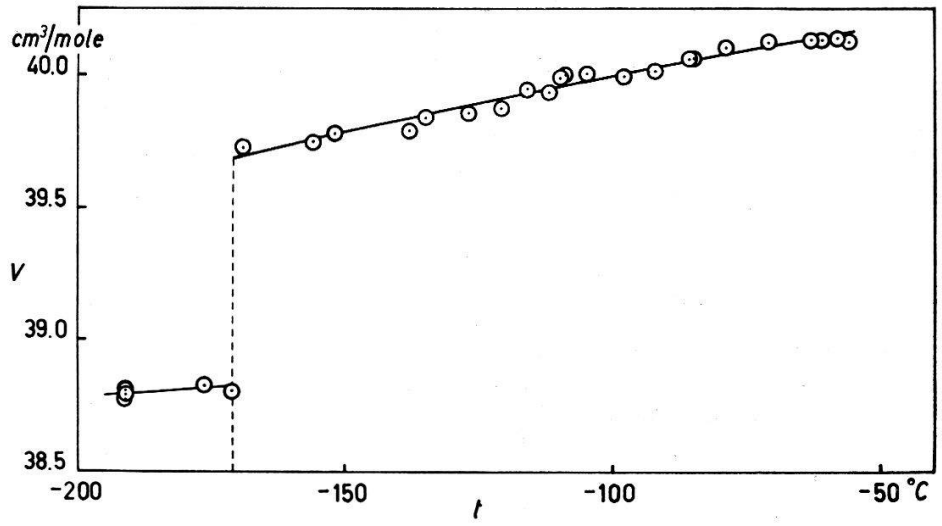

Figure 1a

The temperature dependence of the molar volume of NH_4Br between − 56° and − 192 °C.

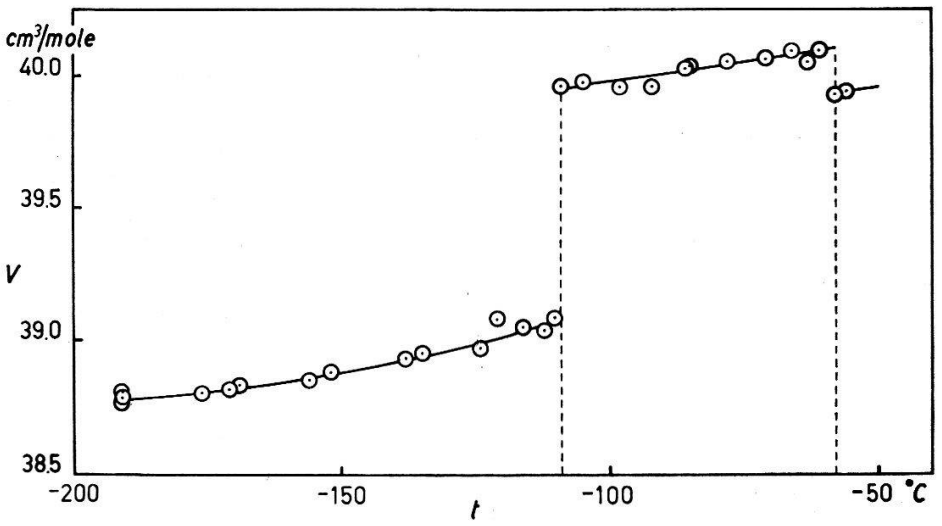

Figure 1b

The temperature dependence of the molar volume of ND_4Br between − 56° and − 192 °C.

It was found that the transition velocity of ND_4Br at the transition III → IV is much higher than that of NH_4Br at the corresponding transition. The transition III → IV of ND_4Br seems to take place practically as soon as the transition temperature has been reached. In the case of NH_4Br, the specimen had to be kept at − 190 °C for about two hours before the transition was completed. The higher transition temperature of ND_4Br is probably one reason for this behaviour. Another one may be the fact that the axial ratio of the tetragonal phase of ND_4Br is slightly closer to unity than that of NH_4Br, as can be seen from the Table .

A more detailed account of this work will be published in Ann. Acad. Sci. Fenn. A VI.

Acknowledgments

The writers wish to express their gratitude to the National Research Council for Sciences (Valtion Luonnontieteellinen Toimikunta), Finland, for financial support in 1967 and 1968.

One of us (V. H.) is indebted to the Wihuri Foundation, Finland, for a scholarship in 1967, while another (O. U.) wishes to thank Leo and Regina Wainstein Foundation, Finland, for a scholarship in 1967.

The computing time obtained for this investigation from the Computing Centre of the University of Turku, Finland, is gratefully acknowledged.

References

[1] V. Hovi, K. Heiskanen, M. Varteva, Ann. Acad. Sci. Fenn. [A] *VI*, No. 144 (1964); Proc. 9th Internat. Conf. Low Temp. Physics, Part B, 1179 (1965), Columbus, Ohio, USA.
[2] C. C. Stephenson, H. E. Adams, J. chem. Phys. *20*, 1658 (1952).
[3] J. L. Grenshaw, I. Ritter, Z. phys. Chem. *B16*, 143 (1932).
[4] J. A. A. Ketelaar, Nature *134*, 250 (1934).
[5] A. Smits, D. Tollenaar, F. A. Kröger, Z. phys. Chem. *B41*, 215 (1938).
[6] J. Weigle, H. Saini, Helv. phys. Acta *9*, 515 (1936).
[7] A. Smits, J. A. A. Ketelaar, G. J. Muller, Z. phys. Chem. *A175*, 359 (1936).
[8] A. Smits, D. Tollenaar, Z. phys. Chem. *B52*, 222 (1942).
[9] S. Jaakkola, J. Pöyhönen, P. Nissilä, to be published in Ann. Acad. Sci. Fenn. [A] *VI* (1968).
[10] J. Pöyhönen, P. Nissilä, S. Jaakkola, Ann. Acad. Sci. Fenn. [A] *VI*, No. 273 (1968).
[11] B. Ostle, *Statistics in Research* (The Iowa State College Press, 1964), Chapter 6.
[12] V. S. Kogan, Usp. Fiz. Nauk *78*, 579 (1962).

Direct Electron-Hole Recombination in Cadmium Sulfide

by **L. Huldt**

Department of Physics III, Royal Institute of Technology, Stockholm, Sweden

(1. V. 68)

Abstract. By strong photoexcitation of single crystals of CdS, free carriers were generated, whose number appeared to be proportional to the cubic root of exciting light intensity. It is suggested that this behaviour is due to direct radiative recombination between free holes and electrons. The recombination coefficient, as obtained from a modified van Roosbroeck-Shockley calculation and experimental data, gives reasonable order of magnitude of hole lifetime and diffusion length, and further gives an order of magnitude of the hole diffusion coefficient that is consistent with previous determinations.

In the compound semiconductors of IIB-VIA type, like cadmium sulfide, the electrical conductivity is known always to be n-type [1–3]. It is believed that holes, injected or photoelectrically created, are trapped in deeplying centers after a short time. Only indirectly, from investigations including magnetic phenomena, one can estimate the magnitude of the mobility and lifetime of holes in CdS to about (1/10) $\mu_n \simeq 20$ cm^2/volt sec and 10^{-8} to 10^{-6} sec, respectively [3–6].