

**Zeitschrift:** Helvetica Physica Acta

**Band:** 41 (1968)

**Heft:** 6-7

**Artikel:** X-ray investigation of modifications III and IV of NH<sub>4</sub>Br and ND<sub>4</sub>Br at temperatures between -56° and -192°C

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

**DOI:** <https://doi.org/10.5169/seals-113950>

### **Nutzungsbedingungen**

Die ETH-Bibliothek ist die Anbieterin der digitalisierten Zeitschriften. Sie besitzt keine Urheberrechte an den Zeitschriften und ist nicht verantwortlich für deren Inhalte. Die Rechte liegen in der Regel bei den Herausgebern beziehungsweise den externen Rechteinhabern. [Siehe Rechtliche Hinweise.](#)

### **Conditions d'utilisation**

L'ETH Library est le fournisseur des revues numérisées. Elle ne détient aucun droit d'auteur sur les revues et n'est pas responsable de leur contenu. En règle générale, les droits sont détenus par les éditeurs ou les détenteurs de droits externes. [Voir Informations légales.](#)

### **Terms of use**

The ETH Library is the provider of the digitised journals. It does not own any copyrights to the journals and is not responsible for their content. The rights usually lie with the publishers or the external rights holders. [See Legal notice.](#)

**Download PDF:** 01.04.2025

**ETH-Bibliothek Zürich, E-Periodica, <https://www.e-periodica.ch>**

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 $\text{NH}_4\text{Br}$ and $\text{ND}_4\text{Br}$ at Temperatures between $-56^\circ$ and $-192^\circ\text{C}$

by V. Hovi, Kirsti Paavola, and O. Urvas

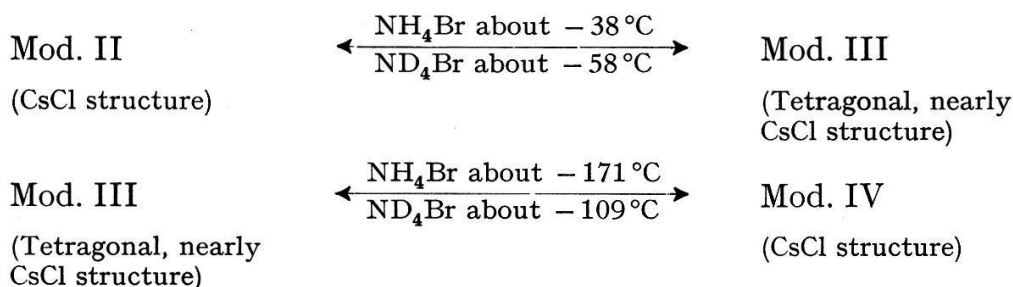
Wihuri Physical Laboratory, University of Turku, Finland

(29. IV. 68)

*Abstract.* The lattice parameters of modifications III and IV of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  were determined between  $-56^\circ$  and  $-192^\circ\text{C}$  at 27 and 28 temperatures, respectively. The low-temperature Debye-Scherrer method used is previously described by Hovi et al. [1]. The transition of  $\text{NH}_4\text{Br}$  below  $-165^\circ\text{C}$ , 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  $-171^\circ\text{C}$ . In the case of  $\text{ND}_4\text{Br}$ , the corresponding volume change turned out to be 2.23% at  $-109^\circ\text{C}$ . At the transition III  $\rightarrow$  II of  $\text{ND}_4\text{Br}$  at  $-58^\circ\text{C}$  the decrease of the molar volume with increasing temperature was 0.41%.

### Introduction

Below room temperature, the following modifications of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  have been observed [2–8 and present paper<sup>1)</sup>]:



<sup>1)</sup> Refers to the transition III  $\rightarrow$  IV of  $\text{NH}_4\text{Br}$ .

In the present investigation attention was paid to all these transitions, except the II  $\rightarrow$  III transition of  $\text{NH}_4\text{Br}$ . The only systematic X-ray investigation of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  is apparently the measurement of the lattice parameters of  $\text{NH}_4\text{Br}$  at temperatures between 22 and  $-125^\circ\text{C}$  by HOVI et al. [1]. Below  $-125^\circ\text{C}$ , only the single observations by KETELAAR [4] at  $-140^\circ\text{C}$  and by WEIGLE and SAINI [6] at  $-145^\circ\text{C}$  have been carried out for this salt. For  $\text{ND}_4\text{Br}$ , we have found only the observations by KETELAAR [4] at  $-30^\circ\text{C}$ ,  $-73^\circ\text{C}$ , and  $-140^\circ\text{C}$ .

The object of the present work was to investigate, by means of X-ray diffraction, the lattice expansion and the structural changes of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  at temperatures between  $-56^\circ$  and  $-192^\circ\text{C}$ . 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  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  were recorded on the same film. The temperature of the specimen was observed by means of two copper-constantan thermocouples, one of which was

$t$ ( $^\circ\text{C}$ )	$\text{NH}_4\text{Br}$			$\text{ND}_4\text{Br}$		
	$a_{1,2}$ ( $\text{\AA}$ )	$a_3$ ( $\text{\AA}$ )	$a_{1,2}/a_3$	$a_{1,2}$ ( $\text{\AA}$ )	$a_3$ ( $\text{\AA}$ )	$a_{1,2}/a_3$
- 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  $\pm 1^\circ\text{C}$ .

The  $\text{NH}_4\text{Br}$  used was of the quality 'pro analysi' by the May & Baker Ltd, England.  $\text{ND}_4\text{Br}$  was prepared in this laboratory from  $\text{NH}_4\text{Br}$  by eight consecutive recrystallizations from  $\text{D}_2\text{O}$  solution. The deuterium content of the  $\text{D}_2\text{O}$  by the Norsk Hydro was guaranteed to be 99.7%. According to the density measurements of an identically prepared  $\text{ND}_4\text{NO}_3$  sample [9, 10], the deuterium content of the  $\text{ND}_4\text{Br}$  sample should be at least 90%.

The Table shows the values obtained for the lattice parameters and the axial ratios of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$ . 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  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  as functions of temperature:

*NH<sub>4</sub>Br* Modification III (temperatures between  $-56^\circ$  and  $-171^\circ\text{C}$ )

$$a_{1,2} = 4.059 + 0.1425 \times 10^{-3} t,$$

$$a_3 = 4.066 - 0.1934 \times 10^{-4} t - 0.6631 \times 10^{-6} t^2,$$

$$V = 40.322 + 0.2546 \times 10^{-2} t - 0.6856 \times 10^{-5} t^2,$$

$$a_{1,2}/a_3 = 0.9982 + 0.3875 \times 10^{-4} t + 0.1584 \times 10^{-6} t^2.$$

Modification IV (temperatures below  $-171^\circ\text{C}$ )

See the Table.

*ND<sub>4</sub>Br* Modification II (temperatures between  $132^\circ$  and  $-58^\circ\text{C}$ )

See the Table.

Modification III (temperatures between  $-58^\circ$  and  $-109^\circ\text{C}$ )

$$a_{1,2} = 4.055 + 0.1147 \times 10^{-3} t,$$

$$a_3 = 4.068 + 0.1268 \times 10^{-3} t + 0.4039 \times 10^{-6} t^2,$$

$$V = 40.313 + 0.4119 \times 10^{-2} t + 0.7615 \times 10^{-5} t^2,$$

$$a_{1,2}/a_3 = 0.9972 + 0.5253 \times 10^{-5} t - 0.5027 \times 10^{-7} t^2.$$

Modification IV (temperatures below  $-109^\circ\text{C}$ )

$$a = 4.054 + 0.4365 \times 10^{-3} t + 0.1042 \times 10^{-5} t^2,$$

$$V = 40.107 + 0.1272 \times 10^{-1} t + 0.3041 \times 10^{-4} t^2.$$

The temperature dependences of the molar volumes of  $\text{NH}_4\text{Br}$  and  $\text{ND}_4\text{Br}$  between  $-56^\circ$  and  $-193^\circ\text{C}$  are illustrated by Figures 1a and 1b.

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

The transition of  $\text{NH}_4\text{Br}$  below  $-165^\circ\text{C}$ , 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  $-171^\circ\text{C}$ . At the corresponding transition of  $\text{ND}_4\text{Br}$  at  $-109^\circ\text{C}$  the volume change is 2.23%. According HOVI et al. [1] the molar volume of  $\text{NH}_4\text{Br}$  decreases by 0.40% with increasing temperature at the transition III  $\rightarrow$  II at  $-38^\circ\text{C}$ . We found that at the corresponding transition of  $\text{ND}_4\text{Br}$  at  $-58^\circ\text{C}$  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  $\text{NH}_4\text{Br}$  [12], the relative molar volume changes at the transitions II  $\rightarrow$  III and III  $\rightarrow$  IV remain practically unaltered.

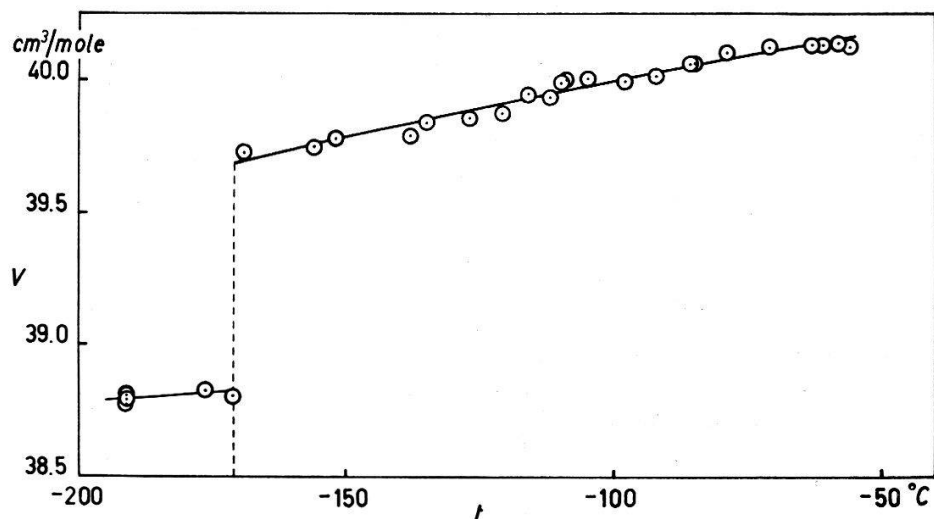


Figure 1a

The temperature dependence of the molar volume of  $\text{NH}_4\text{Br}$  between  $-56^\circ$  and  $-192^\circ\text{C}$ .

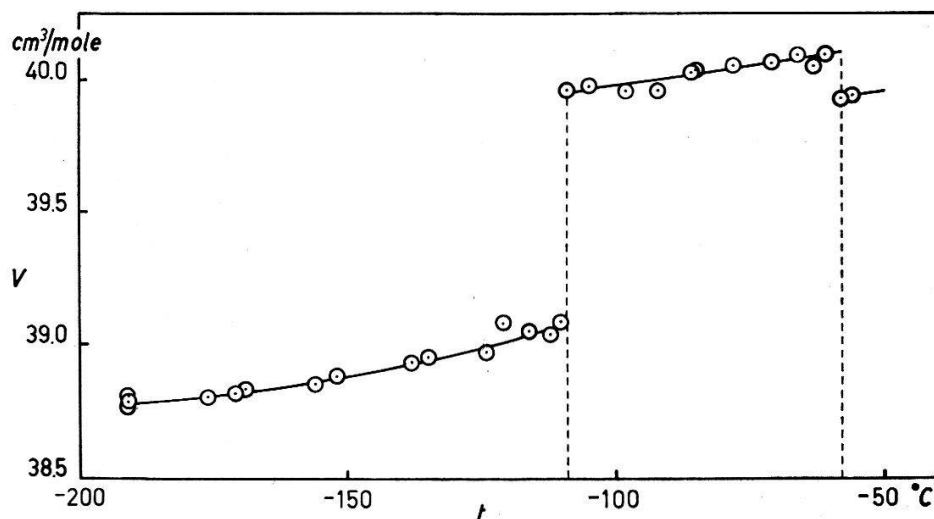


Figure 1b

The temperature dependence of the molar volume of  $\text{ND}_4\text{Br}$  between  $-56^\circ$  and  $-192^\circ\text{C}$ .

It was found that the transition velocity of  $\text{ND}_4\text{Br}$  at the transition  $\text{III} \rightarrow \text{IV}$  is much higher than that of  $\text{NH}_4\text{Br}$  at the corresponding transition. The transition  $\text{III} \rightarrow \text{IV}$  of  $\text{ND}_4\text{Br}$  seems to take place practically as soon as the transition temperature has been reached. In the case of  $\text{NH}_4\text{Br}$ , the specimen had to be kept at  $-190^\circ\text{C}$  for about two hours before the transition was completed. The higher transition temperature of  $\text{ND}_4\text{Br}$  is probably one reason for this behaviour. Another one may be the fact that the axial ratio of the tetragonal phase of  $\text{ND}_4\text{Br}$  is slightly closer to unity than that of  $\text{NH}_4\text{Br}$ , 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. B* *16*, 143 (1932).
- [4] J. A. A. KETELAAR, *Nature* *134*, 250 (1934).
- [5] A. SMITS, D. TOLLENAAR, F. A. KRÖGER, *Z. phys. Chem. B* *41*, 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. A* *175*, 359 (1936).
- [8] A. SMITS, D. TOLLENAAR, *Z. phys. Chem. B* *52*, 222 (1942).
- [9] S. JAAKKOLA, J. PÖYHÖNEN, P. NISSLÄ, to be published in *Ann. Acad. Sci. Fenn. [A] VI* (1968).
- [10] J. PÖYHÖNEN, P. NISSLÄ, 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. Huld

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  $(1/10) \mu_n \simeq 20 \text{ cm}^2/\text{volt sec}$  and  $10^{-8}$  to  $10^{-6}$  sec, respectively [3-6].