for a generalized composition $(A_{3-x}B_x)(B_{1-x-y}A_{x+y})$ where x is a measure of the order parameter and y represents the deviation from stoichiometry. The two expressions are identical when $r_a = 1 - x/3$, $r_b = 1 - (x + y)$, and $y = 1 - 4\beta$. The order parameters are functionally related by $S_b = [3\beta/(1 - \beta)] S_a$. Analysis of the X-ray reflections yields one order parameter only, e.g. as a site-occupation factor, and it is therefore not possible to determine both the degree of order and the stoichiometry from the X-ray data alone, unless the scale factor and the Debye–Waller factors can be determined independently.

We refined a site-occupation factor for the A atoms assuming $y = 0.25$, 0.20 and zero. Other parameters refined were anisotropic temperature vibration parameters for the A atoms, scale factor, an overall temperature factor parameter and an extinction parameter. The site-occupation parameter is highly correlated with the scale factor. It refines to 1.003 for $y = 0.25$ and to 0.993 for $y = 0.20$. The vibration parameters are also practically the same for the two y values. The extinction is moderate, as minimum transmission is 75%. R for both y values is 3.4% for 122 independent reflections and six parameters. Table 1 shows the parameters obtained for the stoichiometry $Nb_3Ge_{0.8}Nb_{0.2}$.

The temperature vibration parameters are physically meaningful considering the high melting point (2273 K) of the compound. The smallest vibration amplitude of the Nb atoms is in the direction of the shortest Nb–Nb

Table 1. *Atomic coordinates, thermal parameters* (Å^2) *and site-occupation factor of* $Nb_3Ge_{0.8}Nb_{0.2}$

	x	y	z	$U_{11} \times 10^4$	$U_{33} \times 10^4$	Occupation factor
Nb	0	$\frac{1}{2}$	$\frac{1}{4}$	63 (5)	40 (4)	0.993 (6)
Ge	0	0	0	57 (2)		0.80
Nb	0	0	0	57		0.20

bond as would be expected. The order parameter for the Nb atoms on the A sites is 1 within experimental uncertainty. The order parameter S_B is thus 0.75. S_B does not, however, really measure the kind of ordering of the B sites which would decrease the cubic symmetry to tetragonal in the case of a complete ordering of the atoms on the B sites. As mentioned above no indication of partial ordering on the B sites has been observed. This observation agrees with our results for the ternary compound V_6GaSb (Rasmussen & Hazell, 1978) which has the A15 structure with V atoms completely occupying the A sites and with random distribution of Ga and Sb on the B sites.

Refinements of data from other single-phase samples prepared from floating zone melting of Nb and Ge are essentially in agreement with the results reported here. These data were taken over a more limited range of $\sin\theta/\lambda$ and not corrected for systematic errors to the same extent as the data taken with Ag $K\alpha$ radiation.

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Neutron Diffraction Study of Sodium Bromide Dihydrate*

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Abstract. $NaBr.2H_2O$, monoclinic, $P2_1/c$, $a = 6.575$ (2), $b = 10.456$ (5), $c = 6.776$ (2) Å, $\beta = 113.38$ (2)°, $Z = 4$. The structure has been determined from single-crystal neutron diffraction data at 295 K. Each water molecule is tetrahedrally coordinated by two Na^+ ions and two Br^- ions. The $O–H\cdots Br^-$ bonds involving $H_2O(1)$ are similar in

length, 2·398 (3) and 2·414 (3) Å; those involving $H_2O(2)$ differ markedly, 2·435 (3) and 2·827 (4) Å.

Introduction. The crystal structure of sodium bromide dihydrate, $NaBr.2H_2O$, was determined by Culot, Piret & Van Meerssche (1962) and Haaf & Carpenter (1964) from X-ray diffraction data. The structure contains two crystallographically non-related water molecules bonded to the Br^- ions by rather long hydrogen bonds. The structure thus offers an opportunity to study the geometry of a weakly bonded water molecule in a simple ionic solid. However, the positions of the H atoms were not determined in the X-ray diffraction studies. Some information as to their positions was obtained by Van Meerssche, Dereppe & Lobo (1962) from proton magnetic resonance data and by Ladd (1968) from lattice-energy calculations. Additional information was obtained by Håland & Pedersen (1973) on the deuterated salt using deuteron magnetic resonance (DMR).

The crystal used for the data collection was grown from an aqueous solution of sodium bromide and ground to a sphere of radius 2·3 mm. The intensity data were collected at the Swedish Atomic Energy R2 reactor at Studsvik using a Hilger & Watts four-circle diffractometer controlled by a PDP-8 computer. The neutron flux at the specimen was $1·26 \times 10^4$ neutron $mm^{-2} s^{-1}$ at a wavelength of 1·210 Å. A region of reciprocal space out to $\sin \theta/\lambda = 0·693$ Å^{-1} was examined using the ω–2θ step-scan technique. Three standard reflexions were measured at regular intervals. No significant changes were observed. 1263 independent reflexions were measured. The intensities were corrected for Lorentz and absorption effects (spherical crystal). The linear absorption coefficient μ was determined experimentally to be 0·156 mm^{-1}, which corresponds to a value of $39·6 \times 10^{-28}$ m^2 for the incoherent scattering cross section for H.

The atomic positions of the non-hydrogen atoms given by Haaf & Carpenter (1964) were used initially, and a least-squares refinement of the scale factor, followed by a three-dimensional difference Fourier synthesis provided approximate positions of the H atoms. The structure was then refined, the function $\sum w(|F_o| -$

$|F_c|)^2$ being minimized with the full-matrix least-squares program *UPALS*. The reflexions were assigned weights $w = 1/\sigma^2(F)$ where $\sigma^2(F) = \sigma_{count}^2(F^2)/4F^2 + (0·02F)^2$. The first term is based on counting statistics.

The refinements, based on the 906 reflexions with intensities greater than $3\sigma_{count}$, comprised 24 positional and 48 anisotropic thermal parameters, one overall scale factor and one isotropic extinction parameter. The final agreement factors were $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0·045$ and $R_w = [|\sum w(|F_o| - |F_c|)^2|/\sum wF_o^2]^{1/2} = 0·043$. The standard deviation of an observation of unit weight was 1·23. The final atomic coordinates are given in Table 1.* The F_o values were corrected for isotropic extinction (Coppens & Hamilton, 1970). The refined value of the isotropic extinction parameter g was $2·62 (12) \times 10^4$.

An anisotropic extinction correction was also attempted but resulted in no further improvement. The coherent scattering amplitudes used were $b_{Na} = 0·360$, $b_{Br} = 0·680$, $b_O = 0·580$ and $b_H = -0·374 \times 10^{-14}$ m (Bacon, 1972). Since the thermal-vibration parameters of one of the H atoms were rather large (*cf.* Table 1), a refinement was made including third-cumulant vibration parameters for all H atoms; however, this resulted in no significant improvement and none of the additional parameters were significantly different from zero.

The computer programs used have been described by Lundgren (1975).

Discussion. The atomic position of Br (Table 1) has been determined to the same precision as in the X-ray diffraction studies. The standard deviations in the O positions are almost a factor of ten better in this study compared to those of the earlier studies. A stereoscopic view of the structure is given in Fig. 1. Some interatomic distances and angles are given in Tables 2 and 3 and Figs. 2 and 3. A detailed discussion of the general aspects of the structure is given in the X-ray

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34387 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Atomic coordinates* $(\times 10^4)$ *and r.m.s. components* R_i $(\times 10^3$ Å) *along the principal axes associated with the anisotropic thermal parameters*

	x	y	z	R_1	R_2	R_3
Na	157 (3)	1686 (2)	4566 (3)	181 (2)	196 (2)	214 (2)
Br	2964 (2)	1191 (1)	2121 (2)	173 (1)	191 (1)	223 (1)
O(1)	7903 (2)	3131 (1)	1772 (2)	188 (2)	209 (2)	223 (1)
H(11)	7737 (6)	3980 (3)	2211 (5)	212 (3)	252 (3)	289 (4)
H(21)	6442 (6)	2908 (4)	884 (7)	217 (4)	285 (4)	364 (4)
O(2)	2156 (2)	4899 (1)	2192 (2)	186 (2)	191 (2)	218 (2)
H(12)	3616 (4)	5137 (3)	2338 (5)	208 (3)	245 (3)	281 (3)
H(22)	2329 (5)	4637 (3)	3599 (4)	209 (3)	247 (3)	276 (3)

Table 2. *Interatomic angles* (°) *in* NaBr.2H$_2$O

H(11)—O(1)—H(21)	102·5 (4)	H(12)—O(2)—H(22)	104·7 (3)
O(1)—Na—O(1)′	95·52 (9)	O(1)—Na—Br′	92·06 (8)
O(1)—Na—O(2)′	91·54 (9)	O(1)′—Na—Br′	88·45 (7)
O(1)′—Na—O(2)	83·68 (7)	O(2)—Na—Br	90·82 (8)
O(1)′—Na—O(2)′	86·98 (8)	O(2)—Na—Br′	93·05 (8)
O(2)—Na—O(2)′	83·30 (8)	O(2)′—Na—Br	89·94 (7)
O(1)—Na—Br	89·74 (7)	Br—Na—Br′	94·32 (7)

Table 3. *Distances* (Å) *and angles* (°) *associated with the hydrogen bonds in* NaBr.2H$_2$O

X—H$\cdots Y$	X—H	H$\cdots Y$	$X \cdots Y$	$\angle X$—H$\cdots Y$
O(1)—H(11)$\cdots$Br	0·957 (3)	2·435 (3)	3·387 (2)	173·2 (3)
O(1)—H(21)$\cdots$Br	0·938 (4)	2·827 (4)	3·586 (2)	138·7 (3)
O(2)—H(12)$\cdots$Br	0·958 (3)	2·398 (3)	3·339 (2)	167·3 (3)
O(2)—H(22)$\cdots$Br	0·955 (3)	2·414 (3)	3·366 (2)	174·7 (3)
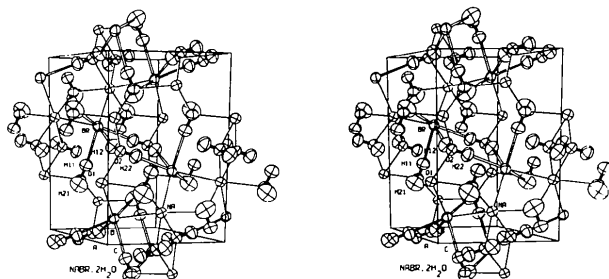
Fig. 1. A stereoscopic view of the structure of NaBr.2H$_2$O. The thermal ellipsoids are drawn to include 50% probability.
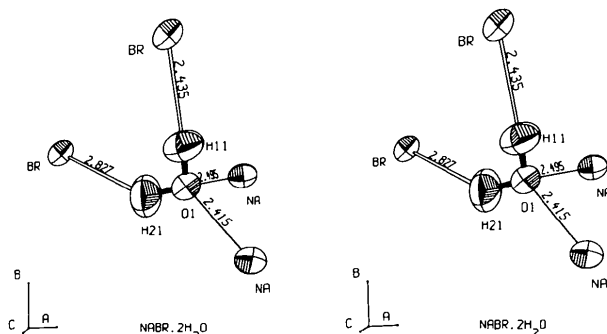
Fig. 2. A stereoscopic view of the coordination about H$_2$O(1).

diffraction study of the isotypic NaCl.2H$_2$O structure, where the two salts are also compared (Klewe & Pedersen, 1974). In the remaining part of the paper we focus our attention on the positions of the H atoms, and on the bonding and geometry of the water molecules.

In Table 4, the positions of the deuterons deduced from DMR are compared with the positions of the H atoms found in this study. Since the DMR method locates the D atoms relative to the O atoms, the D positions in Table 4 have been changed to refer to the O
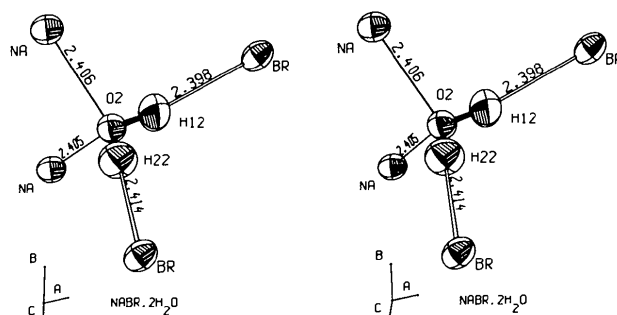
Fig. 3. A stereoscopic view of the coordination about H$_2$O(2).

Table 4. *A comparison between the positions of the* D *atoms found in the NMR study* (*Håland & Pedersen,* 1973) *and the positions of the* H *atoms found in this study*

Δ is the difference between the neutron diffraction coordinate and the NMR coordinate. σ is the estimated standard deviation in the neutron diffraction coordinate.

	Label in NMR study	$\Delta x/\sigma$	$\Delta y/\sigma$	$\Delta z/\sigma$
H(11)	H$_{21}$	−3	−4	−3
H(21)	H$_{22}$	4	9	11
H(12)	H$_{12}$	9	2	5
H(22)	H$_{11}$	18	3	−7

positions found in this study. The H positions found by the two methods are clearly not exactly equal. This is not unexpected since the location of the D atoms relative to the water O positions was based on two assumptions. (1) The z principal axis of the electric-field gradient at the deuteron site in the static molecule is parallel to the OD bond. (2) The length of the OD bond is 0·974 Å. Furthermore, the DMR study was performed on the deuterated salt and the neutron diffraction study on the ordinary salt.

The angles between the z principal axis of the electric-field gradient at the deuterons and the O—H directions range from 1·4 to 2·6°. These angles are small but may still account for a substantial part of the discrepancy found between the D and H positions obtained by the two methods. Also, the OD bond length chosen (0·974 Å) is longer than the distances calculated from the atomic positions found here.

The coordination of the water molecules is shown in Figs. 2 and 3. Both water molecules are tetrahedrally coordinated by two Na$^+$ and two Br$^-$ ions. The coordination about H$_2$O(2) is somewhat more regular than that about H$_2$O(1). The Na—O—Na angles are both smaller than the tetrahedral angle. Three of the Na—O distances are nearly equal, about 2·41 Å, but the fourth [Na—O(1)] is significantly longer, 2·495 Å.

Three of the hydrogen bonds have an H$\cdots$Br distance of about 2·40 Å, whereas the fourth is

markedly longer, 2·827 (4) Å. The three shorter bonds do not deviate by more than about 10° from linearity, whereas the fourth [O(1)—H(21)···Br] deviates by 41·3°. It may thus be concluded that three of the H atoms are engaged in bonds of approximately equal strength and the fourth, H(21), is engaged in a much weaker bond. This agrees with the conclusion drawn by Schiffer & Hornig (1969) from the vibrational spectrum. This remarkable difference in hydrogen-bond strength is also reflected in the thermal-vibration parameters of the H atoms (cf. Table 1): the root-mean-square amplitudes of vibration of H(21) are considerably larger than those of the other three H atoms, which have very similar vibration ellipsoids. The mean dimensions of an isolated water molecule in the ground vibrational state are: $r(O-H) = 0.974$ Å, $r(H-H) = 1.537$ Å and $\angle HOH = 104.54°$ (Kuchitsu & Bartell, 1962; Shibata & Bartell, 1965). From the data in Table 3, it can be seen that the O—H distances are somewhat shorter here. This tendency is opposite to the generally expected lengthening of the O—H bond on hydrogen-bond formation. We also see that the HOH angle in $H_2O(1)$ is smaller, $102.5°$, and in $H_2O(2)$ nearly equal to the value in the isolated molecule. However, the dimensions here have been calculated directly from the final mean atomic positions. These positions differ from the true mean positions because of the inadequate treatment of the vibrations in the analysis of the diffraction data. In particular, the presence of large-amplitude librations is suggested by the appearance of the thermal ellipsoids. Such librations would lead to a shift in the apparent H positions towards the O atom when the structure is refined using standard anisotropic thermal parameters. This is consistent with the observations that (1) the O(1)—H(21) bond, 0·938 Å, is significantly shorter than the three other O—H bonds, 0·955–

0·958 Å, and (2) the amplitudes of vibration of H(21) are significantly larger than those of the remaining three H atoms. A discussion of the internal geometry of the water molecule will therefore have to be postponed until a more realistic description of the vibrational motions has been obtained.

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Ammonium Thiosulphate

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Abstract. $(NH_4)_2S_2O_3$, monoclinic, $C2$, $a = 10.230$ (4), $b = 6.500$ (2), $c = 8.820$ (3) Å, $\beta = 94.66$ (2)°, $V = 585$ Å³, $Z = 4$, $D_c = 1.684$ Mg m⁻³, Nb-filtered Mo $K\alpha$ radiation, $\mu = 0.80$ mm⁻¹; 936 independent diffractometer data up to $\sin\theta/\lambda = 0.71$ Å⁻¹ at room temperature; final $R(F) = 0.032$. The structure consists of NH_4 and S_2O_3 tetrahedra interconnected by hydrogen bonds. All but two H atoms were located by difference methods. One of the NH_4 groups is possibly disordered at room temperature.

Introduction. Crystals of $(NH_4)_2S_2O_3$ were grown from aqueous solution. A crystal 0·5 × 0·6 × 0·65 mm was selected. Precession photographs confirmed the lattice