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Preparation, Crystal Structure, and Ionic Conductivity of Digallium Tribromide, Ga_2Br_3*

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Ga_2Br_3 was prepared by reduction of $GaBr_3$ with Ga in sealed glass ampoules. Thermal behavior, Raman and mass spectra, ionic conductivity, as well as the crystal structure were investigated. Ga_2Br_3 is the most metal-rich gallium bromide. According to X-ray results Ga_2Br_3 is identical with the formerly described "GaBr." The crystal structure has been solved on the basis of diffractometer data: orthorhombic space group *Pnma* ($a = 1253.7(7)$ pm, $b = 1547.4(8)$ pm, $c = 1253.4(5)$ pm, $Z = 16$). The structure contains pairwise associated ecliptic anions $[Ga_2Br_6]^{2-}$ with metal–metal single bonds. The coordination polyhedra around the three Ga^+ atoms are cubes and tricapped trigonal prisms of bromine atoms. A remarkable feature of the crystal structure is the vacancy in the Ga^+ partial structure, corresponding to the formulation $Ga_4\square[Ga_4Br_{12}]$. They lead to Ga^+ ion conductivity with an activation enthalpy of 0.8 eV. The conductivity at 400 K is $1.5 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$. The material decomposes at 427 K.

Introduction

Gallium and halogens form several binary compounds, in which trivalent metal atoms as well as mixed mono-, di-, and trivalent metal atoms exist. Recently we described the metal-rich part of the system Ga/I (*1*), especially the compounds GaI_2 as well as Ga_2I_3. One could expect that in the bromide and chloride system compounds with the same stoichiometries also exist. Preliminary investigations of the reduction of $GaBr_3$ with Ga by Corbett and Hershaft (*2*) indicated the existence of a gallium mono- and sesquibromide. These results were later supported by Raman spectroscopic investigations of reduced gallium halides (*3, 4, 11*), which proved the existence of a $[Ga_2Br_6]^{2-}$ anion with a direct gallium–gallium bond. Thermoanalytical investigations by Mascherpa-Corral and Potier (*19*) of the system $GaBr_3$–Ga indicated the existence of the compound "GaBr" between Ga and $GaBr_2$. Here we report the preparation, crystal structure, spectroscopic investigation, and ionic conductivity of digallium tribromide.

2. Experimental Details

2.1. Preparation

We have prepared Ga_2Br_3 according to the following methods:

(a) The reduction of gallium tribromide with a small excess of gallium as used by Corbett and Hershaft (*1*).

(b) The reaction of gallium with mercury dibromide according to

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* In memoriam Wilhelm Klemm.

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$$4\,Ga + 3HgBr_2 \rightarrow 3Hg\downarrow + 2Ga_2Br_3.$$

This method has been described by Carlson, Griswold, and Kleinberg (5).

(c) The direct reaction of the elements in stoichiometric amounts also leads to a suitable product.

Method (b) has the disadvantage of forming mercury as an impurity, which might cause errors in conductivity measurements. Method (a) obviously provides the most well-defined compound with the smallest amount of impurities.

Ga_2Br_3. Eight grams of $GaBr_3$ (25.9 mmole) (freshly sublimed) and 1.8 g Ga (25.9 mmole) are filled into a Solidex glass ampoule (20 mm ϕ and 120 mm in length) under inert conditions (Ar) and sealed under 1 bar Ar pressure. The entire mixture is heated to 523 K in a tube furnace with the tube inclined at about 30° and kept at that temperature for 100 hr. After cooling to room temperature, a colorless phase and traces of excess gallium could be recognized. Quadratic platelets were formed on the surface of the cooled melt. Annealing of the pale yellow melt at 427 K yielded rectangular colorless platelets within some days.

2.2. *Analyses*

The chemical analyses were performed on selected single crystals of Ga_2Br_3. The crystals were weighted into thin-walled Lindemann capillaries, which were broken in a Teflon container under concentrated HNO_3. The determination of Ga was done by ICP (inductive coupled plasma) and of Br by potentiometric titration on different independent samples. The sample weights were approximately 10–15 mg. Typical results are (calculated values) Ga: 36.1 ± 2.0% (36.78) and Br: 63.6 ± 2.3% (63.22).

2.3. *X-Ray Powder Investigations*

The investigations of polycrystalline samples were performed with the modified Guinier technique (*6*) with Cu$K\alpha_1$ radiation in capillaries of 0.1-mm diameter. The diagrams calculated with the parameters from Table I and II are in excellent agreement with the observed powder patterns. Figure 1 shows a comparison of the data for "GaBr" from (*2*) and the calculated pattern based on single crystal data. Taking into account the lack of resolution of Debye patterns, the formerly described "GaBr" is identical with Ga_2Br_3.

2.4. *X-Ray Single Crystal Investigations*

Single crystals were isolated from the annealed products in a glove box (MB Braun, Munich, $O_2 \leq 0.5$ ppm; $H_2O \leq 0.5$ ppm) with an integrated microscope. Suitable colorless platelets with a size of 0.2 × 0.2 × 0.05 mm were fixed with silicon grease in capillaries of 0.3-mm diameter. The capillaries were then sealed using an electrically heated platinum wire. The crystals were tested for symmetry and the lattice constants approximated by means of precession photographs. The observed systematic absences lead to the possible space groups *Pnma* (No. 62) and *Pca*2_1 (No. 29). The

TABLE I

Ga_2Br_3: Crystallographic Details

Formula; molecular weight	Ga_2Br_3; 379.152 a.m.u.
Lattice constants (295 K)	refined 2θ values of 12 *hkl* in the region $20° \leq 2\theta \leq 26°$
a (pm)	1253.7(7)
b (pm)	1547.4(8)
c (pm)	1253.4(5)
Crystal size (mm)	Colorless platelet; 0.2 × 0.2 × 0.05
Space group; *Z*	*Pnma* (No. 62); 16
Molar volume ($cm^3 \cdot mole^{-1}$)	183.04
ρ(calc) ($g \cdot cm^{-3}$)	2.071
Measuring conditions	Syntex R3 four-circle diffractometer; Mo$K\alpha$; graphite monochromator, scintillation counter, 295 K
2θ-range; scan width	$3.5° \leq 2\theta \leq 55.0°$; 1.0°
Measuring speed	1.0°–29.3°/sec, variable
$N(hkl)$; N' (hkl) with $I \geq 3\sigma(I)$	1724; 1429
Absorption correction	Empirically, 9 *hkl*, Ψ scan
Structure solution (*7*) and refinement	Solv. 1.2; all atoms from E-maps; cascade least squares; extinction correction; $w = 1/(\sigma^2 + 0.005F^2)$
Reliability factors R; $R(w)$; Goof	0.062; 0.065; 0.965

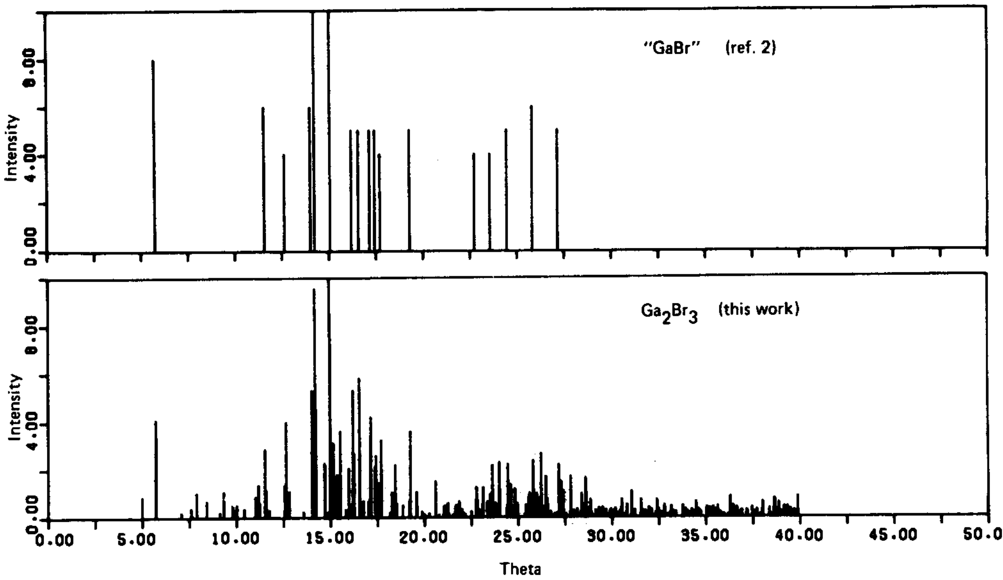

FIG. 1. Calculated powder diagram (10) ($CuK\alpha_1$ = 154.056 ppm) for Guinier geometry and the powder pattern reported for "GaBr" (2).

former proved to be the correct space group. An earlier crystal structure determination with a large single crystal of dimensions 0.5 × 0.5 × 0.1 mm already led to the correct structure, but gave problems due to violations of the extinction rules. No such violations were observed with the small crystal. Further details are summarized in Table I. In the course of the structural refinement, two of the three Ga^+ atoms (Ga(5), Ga(6)) exhibited high isotropic temperature factors. Refinement of the site occupancy factors as well as temperature factors yielded site occupancies of 0.75 and temperature factors with approximately the same size as for Ga(4). The reliability factors decreased by 2%. A final ΔF map yielded only peaks lower than 2 $e/Å^3$.[1]

Volume calculations on the basis of Biltz increments (12) also proved the presence of vacancies in Ga_2Br_3. Using the values (cm^3/mole) 11 (Ga^+), 2 (Ga^{3+}), 25 (Br^-), the calculated volume is 176 cm^3/mole Ga_4Br_6, which is ~7 cm^3/mole less than the observed value of 183 cm^3/mole. According to this calculation, a vacancy (one per unit $Ga_4[Ga_4Br_{12}]$) has a volume of 14 cm^3 which is near the value for one Ga^+ atom.

2.5. *Electrochemical Measurements*

Ga_2Br_3 powder was pressed to pellets of 5–8 mm in diameter and 1–3 mm in height inside an Ar-filled glovebox. These samples were springloaded between two platinum sheet electrodes for ac conductivity measurements and between a reversible gallium electrode and inert platinum electrode for polarization measurements. Purified Ar gas of 1 bar pressure was slowly passed over the cells.

The impedance was measured by the two-phase lock-in amplifier technique (13) and independently with a Hewlett–Packard LF impedance analyzer (Type 4192A) over the frequency range from 5 Hz to 300 kHz. Semicircles followed by straight lines were

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[1] Additional material to this paper can be ordered refering to CSD 51442, with the name(s) of the author(s) and the title of the paper at the Fachinformationszentrum Energie Physik Mathemathik, D-7514 Eggenstein-Leopoldshafen 2, Federal Republic of Germany.

TABLE II

Ga_2Br_3; ATOMIC COORDINATES, ISOTROPIC, AND ANISOTROPIC THERMAL PARAMETERS ($pm^2 \times 10^{-1}$) (STANDARD DEVIATIONS)[a]

Atom	Site	x	y	z	U_{eq}	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ga(1)	4*c*	0.1579(2)	$\frac{1}{4}$	0.3154(2)	29(1)	27(1)	36(2)	25(1)	0	2(1)	0
Ga(2)	4*c*	0.0266(2)	$\frac{1}{4}$	0.4577(2)	28(1)	30(1)	30(2)	26(1)	0	0(1)	0
Ga(3)	8*d*	0.3197(2)	0.3288(2)	0.6130(1)	27(1)	30(1)	23(1)	28(1)	−2(1)	−1(1)	1(1)
Ga(4)	4*c*	0.6897(4)	$\frac{1}{4}$	0.5158(4)	76(2)	77(3)	78(4)	72(3)	0	6(2)	0
Ga(5)[b]	8*d*	−0.0005(4)	0.4440(4)	0.6630(4)	98(2)	115(4)	71(4)	108(4)	20(3)	48(3)	−5(3)
Ga(6)[b]	8*d*	0.3764(4)	0.4375(4)	0.3106(4)	109(3)	120(4)	81(4)	125(4)	−28(4)	35(3)	5(4)
Br(1)	4*c*	0.3486(2)	$\frac{1}{4}$	0.3385(2)	34(1)	25(1)	42(2)	35(1)	0	0(1)	0
Br(11)	8*d*	0.6331(2)	0.3727(2)	0.3001(1)	38(1)	44(1)	36(1)	36(1)	−10(1)	−4(1)	5(1)
Br(2)	4*c*	0.0522(2)	$\frac{1}{4}$	0.6467(2)	32(1)	37(1)	35(2)	23(1)	0	−2(1)	0
Br(22)	8*d*	0.9068(1)	0.3707(1)	0.4404(2)	37(1)	41(1)	34(1)	36(1)	5(1)	2(1)	12(1)
Br(31)	8*d*	0.2151(2)	0.0778(2)	0.5034(1)	36(1)	42(1)	31(1)	36(1)	−6(1)	−3(1)	−10(1)
Br(32)	8*d*	0.4956(1)	0.1146(2)	0.5804(2)	42(1)	32(1)	37(1)	56(1)	2(1)	4(1)	8(1)
Br(33)	8*d*	0.2763(2)	0.1155(2)	0.7878(1)	40(1)	53(1)	40(1)	27(1)	7(1)	4(1)	1(1)

[a] The values for U_{eq} are defined as one-third of the trace of the orthogonalized U_{ij} tensor. The anisotropic temperature exponent takes the form: $-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})$.

[b] The occupancy factors are Ga(5): 0.74(2) and Ga(6): 0.74(2).

observed in the complex impedance plane nearly as expected for ideal Debye equivalent circuits. The diameter of the semicircles was taken as the resistance of the sample. The temperature was varied from room temperature to just below the decomposition point of 427 K. Both heating and cooling runs were performed.

The polarization measurements were restricted to the upper temperature regime since the current was unmeasurably small at lower temperatures.

Using a silver anode and platinum counter electrode in dc polarization measurements, it was possible to titrate silver into Ga_2Br_3 by partial replacement of the gallium atoms.

2.6 *Mass Spectra*

Mass spectra of Ga_2Br_3 were recorded in a quadrupole mass spectrometer (QMG 511, Balzers). At a temperature of 433 K and 100 eV the following peaks were observed: Br^+, $GaBr^+$, $GaBr_2^+$, $GaBr_3^+$, and $Ga_2Br_3^+$. The intensities of the two latter peaks were very low and it is very likely that $Ga_2Br_3^+$is a fragment of $Ga_2Br_4^+$. The appearance potential of $GaBr_3^+$ was found to be 10.5 eV (calc. 10.4 eV), whereas the appearance potential of $Ga_2Br_3^+$ could not be determined due to the low intensity.

2.7 *Thermoanalytical Investigations*

Samples, previously identified by chemical analysis and by Guinier photographs as Ga_2Br_3, were sealed into solidex ampoules. They were investigated by DTA (System 500, Heraeus, heating rate 2 K/min, sample weight ~100 mg, range investigated 273 to 623 K). The first heating yielded only a strong endothermic peak at 409 K (starting at 409 K, maximum at 422 K). The second and third runs show a weak peak at 432 K beside the strong one at 400 K. On cooling, only one strong exothermic peak at 395 K could be observed. The initially colorless samples showed a slightly grey color after the third heating run.

The thermal effects are interpreted as follows:

The strong peak is equivalent to the decomposition of Ga_2Br_3 into Ga_2Br_4 and Ga. The temperature reported by Corbett and Hershaft (*2*) is 431 K. The weak peak in multiple runs is due to the melting of β-Ga_2Br_4, which is reported to occur at 437.5 K (*2*).

Mascherpa-Corral and Potier (*19*) gave similar temperatures. They ascribe the peak at 437 K to the decomposition of "GaBr" into liquid Ga and liquid Ga_2Br_4 and the temperature at 427 K to the formation of an eutecticum between Ga_2Br_4, and "GaBr." From their temperatures reported it seems very likely, that their "GaBr" indeed was Ga_2Br_3. Unfortunately no X-ray data were reported.

The melting peak for elementary Ga should not necessarily be observable, because it is known that contaminated Ga has a strong tendency for supercooling. A more detailed phase diagram of Ga/Br will be reported together with our work on Ga_2Br_4 (*17*).

2.8 Raman Spectroscopic Investigation

The Raman spectrum of $(Npr_4)_2Ga_2Br_6$ in the solid state is well known (*11*). We have performed Raman spectra (10–350 cm^{-1}; 170° back reflection geometry; Ar laser 514.5 nm) on samples sealed into glass cuvettes under Ar. The vibrational representation for an anion $Ga_2Br_6^{2-}$ having D_{3d} symmetry is $3a_{1g} + 3e_g + a_{1u} + 2a_{2u} + 3e_u$, leading to six Raman and five IR active modes. The vibrations of a species with D_{3h} symmetry, as described here, are $3a_1' + 3e' + a_1'' + 2a_2'' + 3e''$, which results in nine Raman active modes and five IR active modes. The following modes have been observed:

									Approx. symmetry
$(Npr_4)_2Ga_2Br_6$ (*11*)	32w	70m	84s	102s	164vvs	228m	236sh	316m	D_{3d}
Ga_2Br_3 (This work)	25m	47w	82vs	106w	163vvs	211s		313m	D_{3h}
β-Ga_2Br_4 (*17*)	27m	40sh 52sh	82vs	106s		210s	268w		T_d

w = weak, m = medium, s = strong, vs = very strong, vvs = very very strong, sh = shoulder.

The comparison between the vibrations of β-Ga_2Br_4 and $Ga_2Br_6^{2-}$ shows that the latter can be clearly distinguished via the 163-cm^{-1} mode and the mode at 313 cm^{-1}. The mode at 163 cm^{-1} is ascribed to ν(Ga–Ga), the latter to the out of phase stretching mode of ν(Ga–Br). From this point of view the differentiation between $Ga_2Br_6^{2-}$ with D_{3d} and D_{3h} symmetry needs further investigation, because only two frequencies are different in the two compounds (47 and 211 cm^{-1}).

3. Results and Discussion

Figure 2 shows a stereographic view of the unit cell, together with a projection of Ga_2Br_3 onto the (a, c) plane. Figure 3 exhibits the main building units as well as the coordination polyhedra of Ga(4), Ga(5), and Ga(6) and Table III gives interatomic distances and angles.

Ga_2Br_3 contains gallium in different oxidation states and can be formulated as $Ga_2[Ga_2Br_6]$. Principal building units are eclipsed $[Ga_2Br_6]^{2-}$ ions (approximate D_{3h} symmetry) with $\bar{d}$(Ga–Ga) = 243.3 pm and $\bar{d}$(Ga–Br) = 240.4 pm. The short Ga–Ga bond is equivalent to a covalent single bond and allows the anion to be formulated with gallium in the oxidation state +2. The observed Ga–Ga bond length agrees with that

TABLE III

Ga_2Br_3; INTERATOMIC DISTANCES [pm] AND ANGLES [°] (STANDARD DEVIATIONS)

Bonds

label	Ga(1)	
1a	Ga(2)	242.7(4)
1b	Br(1)	240.8(4)
1c	Br(11)	240.8(3)*
	Ga(2)	
2a	Ga(1)	242.7(4)
2b	Br(2)	239.1(4)
2c	Br(22)	240.6(2)*
	Ga(3)	
3a	Ga(3)	243.9(6)
3b	Br(31)	238.7(4)
3c	Br(32)	240.8(3)
3d	Br(33)	241.6(3)
	Ga(4)	
4a	Br(32)	331.2(5)*
4b	Br(11)	337.9(5)*
4c	Br(33)	340.2(5)*
4d	Br(22)	343.4(5)*

label	Ga(5)	
5a	Ga(6)	303.4(8)
5b	Br(33)	301.0(6)
5c	Br(2)	308.1(6)
5d	Br(22)	322.8(6)
5e	Br(32)	334.2(6)
5f	Br(22)	335.9(6)
5g	Br(31)	338.0(6)
5h	Br(11)	371.0(6)
5i	Br(33)	391.6(6)
	Ga(6)	
5a	Ga(5)	303.4(8)
6b	Br(1)	294.3(6)
6c	Br(31)	316.0(5)
6d	Br(22)	333.3(6)
6e	Br(33)	336.6(7)
6f	Br(11)	337.3(6)
6g	Br(32)	345.7(6)
6h	Br(11)	349.8(6)
6i	Br(32)	378.4(6)

Br(1)	
Ga(1)	240.8(4)
Ga(6)	294.3(6)*
Ga(3)	366.8(3)*
Br(11)	373.1(4)*
Br(31)	376.5(3)*
Br(22)	403-0(3)*
Br(11)	406.9(4)*
Br(11)	
Ga(1)	240.8(3)
Ga(6)	337.3(6)
Ga(4)	337.9(5)
Ga(6)	349.8(6)
Br(1)	373.1(4)
Br(11)	379.7(6)
Br(22)	385.6(3)
Br(32)	391.8(3)
Ga(2)	397.9(3)
Br(31)	401.4(3)
Br(1)	406.9(4)
Br(33)	407.7(5)

Br(2)	
Ga(2)	239.1(4)
Ga(5)	308.1(6)*
Ga(3)	359.3(4)*
Br(22)	367.4(3)*
Br(31)	380.8(3)*
Br(33)	391.8(4)*
Br(32)	407.3(4)*
Br(22)	
Ga(2)	240.6(2)
Ga(5)	322.8(6)
Ga(6)	333.3(6)
Ga(5)	335.9(6)
Ga(4)	343.4(5)
Br(31)	362.0(4)
Br(2)	367.4(3)
Br(22)	373.5(4)
Br(33)	378.5(3)
Br(11)	385.6(3)
Ga(1)	398.2(3)
Br(31)	402.5(4)
Br(1)	403.0(3)

Br(31)	
Ga(3)	238.7(4)
Ga(6)	316.0(5)
Ga(5)	338.0(6)
Ga(2)	360.7(4)
Br(22)	362.0(4)
Ga(1)	362.9(3)
Br(32)	369.1(3)
Br(33)	369.3(2)
Br(1)	376.5(3)
Br(2)	380.8(3)
Ga(5)	398.4(6)
Br(11)	401.4(3)
Br(22)	402.5(4)
Br(33)	403.2(4)
Br(32)	
Ga(3)	240.8(3)
Ga(4)	331.2(5)
Ga(5)	334.2(6)
Ga(6)	345.7(6)
Br(31)	369.1(3)
Br(33)	378.4(3)

Br(33)	
Ga(3)	241.6(3)
Ga(5)	301.0(6)
Ga(6)	336.6(7)
Ga(4)	340.2(5)
Br(31)	369.3(2)
Br(32)	378.4(3)
Br(22)	378.5(3)
Br(32)	388.8(3)
Ga(5)	391.6(6)
Br(2)	391.8(4)
Ga(3)	399.9(4)
Br(31)	403.2(4)
Br(11)	407.7(5)
Ga(6)	378.4(6)
Br(33)	388.8(3)
Br(11)	391.8(3)
Ga(3)	400.2(4)
Br(2)	407.3(4)
Br(32)	408.1(6)

Angles

Ga(1)	
Br(11)-Br(11)	104.1(1)
Br(11)-Br(1)	101.6(1)*
Br(11)-Ga(2)	110.7(1)*
Br(1) -Ga(2)	125.8(1)
Ga(2)	
Br(22)-Br(22)	101.8(1)
Br(22)-Br(2)	100.0(1)*
Br(22)-Ga(1)	110.9(1)*
Br(2) -Ga(1)	129.6(1)
Ga(3)	
Br(31)-Br(32)	100.7(1)
Br(31)-Br(33)	100.5(1)
Br(31)-Ga(3)	127.3(1)
Br(32)-Br(33)	103.3(1)
Br(32)-Ga(3)	111.3(1)
Br(33)-Ga(3)	110.9(1)

Note. Asterisk indicates a multiplicity of 2.

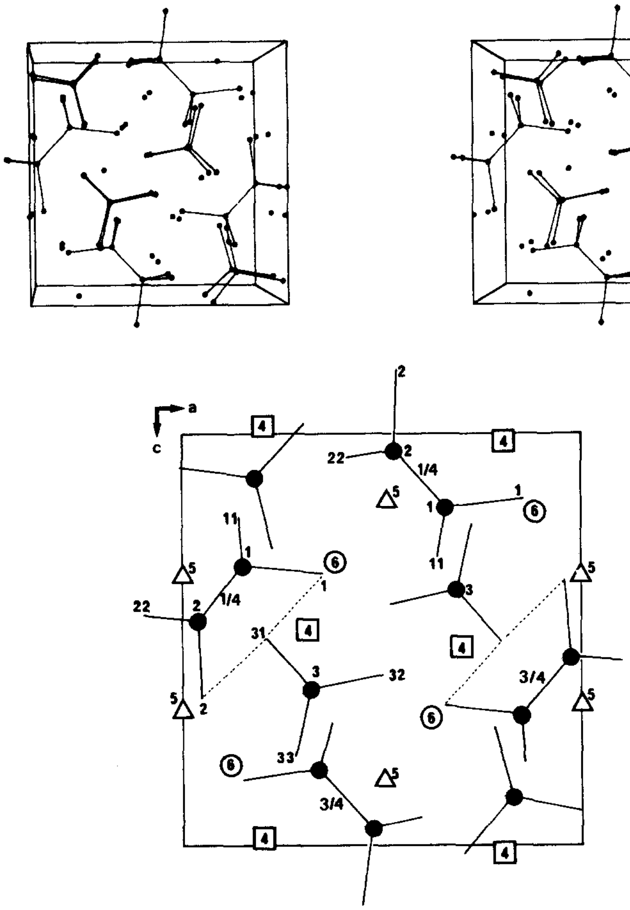

FIG. 2. Top: stereographic view of the Ga_2Br_3 unit cell. Bottom: projection of Ga_2Br_3 on to the (*a*, *c*) plane (black dots = Ga(1), Ga(2), and Ga(3); without circles = bromine atoms; open symbols = Ga(4), Ga(5), and Ga(6).

of $(Npr_4)_2Ga_2Br_6$ (*8*) (*d*(Ga–Ga) = 241.9(5) pm). In this compound the $Ga_2Br_6^{2-}$ anion is in the staggered conformation. The eclipsed conformation together with the specific association of two anions might be responsible for the somewhat longer metal–metal bond as well as for the longer metal–bromine bonds ($\bar{d}$(Ga–Br) = 236.2 pm in (*8*) in Ga_2Br_3. The close approach of two $Ga_2Br_6^{2-}$ anions leads to intermolecular contacts with $\bar{d}$(Br–Br) = 380 pm. This distance agrees to the van der Waals distance of Br (2 × 190 pm) and is of course considerably larger than the distances between bromine atoms bonded to one metal atom (*d*(Br...Br) = 265–272 pm). Yet, the pronounced differentiation of bond angles in the Ga_2Br_6 unit support an interaction between the two anions. The angles to the "bridging" bromine atoms are increased to 127°, whereas the angles to "terminal" bromine atoms are 111°. The angles between the two terminal Ga–Br bonds are reduced to 102°. The same tendency with respect to the terminal Ga–Br bonds has been observed in $(Npr_4)_2Ga_2Br_6$ (*8*).

The observed bond lengths *d*(Ga–Br) correspond to the sum of the ionic radii

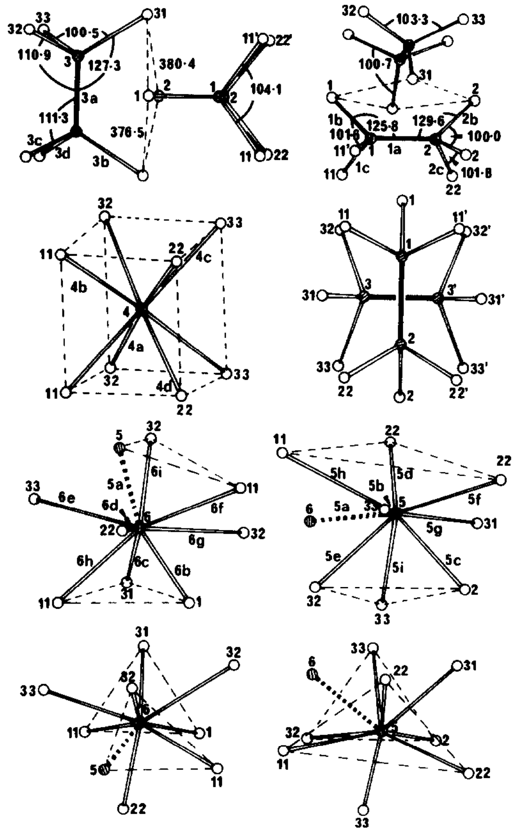

FIG. 3. $[Ga_2Br_6]^{2-}$ anions with the crystallographic labeling, mean bond distances, angles, and coordination polyhedra around Ga^+ cations. Ga–Ga bonds have been indicated by solid lines, Ga–Br bonds by open lines. Some van der Waals contacts are indicated by broken lines. For the bond labels cf. Table III. Br, open circles; Ga, hatched circles.

$r[Ga^{3+}(CN = 4)] = 47$ pm and $r(Br^-) = 195$ pm, as well as to the sum of covalent radii ($r(Ga) = 126$, $r(Br) = 114$ pm (*15*). But as the electronegativities of Ga and Br differ by 1.15 the bonds have approximately 30% ionic character and should be shortened. A correction of the Schomaker–Stevenson type obviously overestimates this effect, as the calculated distance (229.7 pm) becomes much too short.

The Ga^+ ions have two different coordination polyhedra (Fig. 3). Ga(4) is coordinated by eight bromine atoms, forming a distorted CsCl-like arrangement with $\bar{d}$(Ga(4)–Br) = 337.3 pm. The Ga(5) and Ga(6) atoms are coordinated by eight bromine atoms and one Ga^+ atom. Thus in principle all three Ga^+ atoms have the same coordination number with respect to the bromine atoms. The polyhedra around Ga(5) and Ga(6) are approximately tricapped trigonal prisms. The Ga–Br distances range from 311 to 389 pm (Ga(5)) and 293 to 376 pm (Ga(6)). A remarkable feature of these coordinations is the close approach of a Ga^+ ion to the central one (300 pm), as compared to a bond length with a bond strength of unity (see below). As the positions of Ga(5) and Ga(6) are only partly occupied, the question might be raised whether this close approach really occurs or is an artifact only present in the averaged structure. Taking into account the occupation factor 0.75 for Ga(5) and Ga(6), the compound Ga_2Br_3 might be formulated as $Ga_4\square[Ga_4Br_{12}]$, according to a general structure type $A_5[B_4C_{12}]$. It is obvious that there is at least a 25% probability of simultaneously occupied adjacent Ga(5), Ga(6) positions leading to the above-mentioned close approach. It is interesting to ascribe some metal-metal bonding to a distance d(Ga–Ga) = 300 pm. Using the Donnay-Allmann bond length–bond strength formalism (*9*) (with a single bond distance d_1(Ga–Ga) = 242 pm, $N = -6$) one calculates a bond order of $n \approx 0.3$ corresponding to the distance of 300 pm.

But obviously this calculation is misleading. If the bond order sum for all Ga–Br bonds is calculated, this sum is identical (deviation less than 0.5%) for Ga(5) and Ga(6) but exceeds the bond order sum for Ga(4) slightly, i.e., the valency of Ga(5) and Ga(6) is exhausted with Ga–Br bonds.

Close nonbonding approaches of ions are not unusual (*16*). In the case of the Ga_2Br_3 the observed short nonbonding Ga–Ga distance yet raises the interesting question, whether the structure may serve as a host for ions, e.g., Cu, Ag, and Au, capable of homonuclear bonding interactions which substitute Ga(5) and Ga(6). On the other hand one should try to replace Br by Se atoms leading to an occupation of the vacancies by Ga^+.

The publication of our crystal structure investigation on Ga_2Br_3 was delayed for quite a long period, because the structure seemed strange with respect to the arrangement of cations and anions and especially with respect to the presence of vacancies, caused by stoichiometry. Evidence for the correct description of the structure of Ga_2Br_3 came from further experiments aimed at a proof of the vacancy structure, which should allow Ga^+ ions to move in the crystal.

Figure 4 shows the conductivity of Ga_2Br_3 as a function of temperature for several samples and various heating and cooling cycles. An Arrhenius-type behavior is observed for the product of the conductivity and absolute temperature which indicates an activated process for the diffusion of the mobile charged species. The activation enthalpy is ~0.8 eV; the preexponential factor is of the order of $9 \times 10^7\ \Omega^{-1}\ cm^{-1}\ K$.

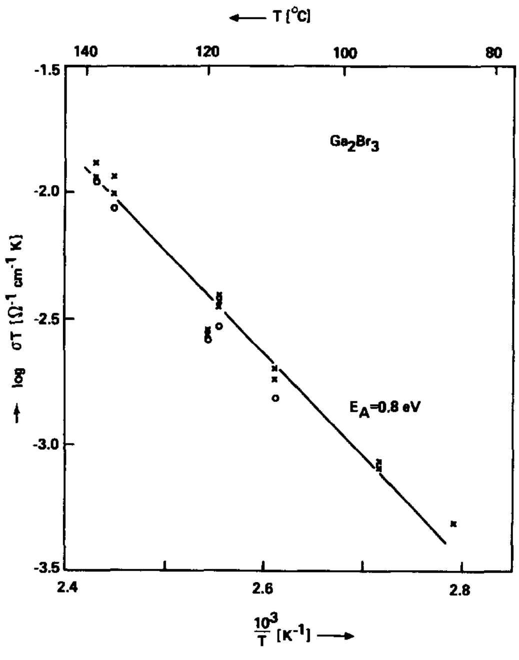

FIG. 4. Logarithmic representation of the ionic conductivity $\sigma \times T$ of Ga_2Br_3 as a function of the inverse absolute temperature T. The symbols × and O represent different samples for multiple heating and cooling runs.

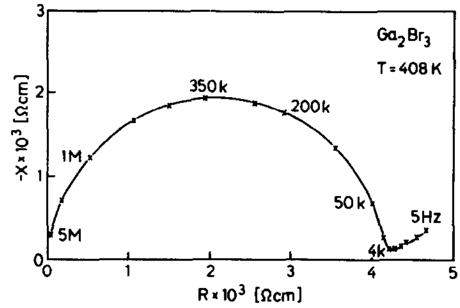

FIG. 5. Impedance spectrum of Ga_2Br_3 at 408 K. The diagram indicates a Debye equivalent circuit.

Ga_2Br_3 is predominantly ionically conducting as indicated by the impedance spectra (Fig. 5). The geometrical capacity of the sample is calculated from the top of the semicircle to be 100 pF. The ionic conductivity is more directly demonstrated by the dc polarization measurements. A plateau of the current as a function of the applied voltage exists below about 0.4 V (Fig. 6). This results in a partial electronic conductivity for Ga_2Br_3 in equilibrium with elemental gallium of $5 \times 10^{-8}\ \Omega^{-1}\ cm^{-1}$ at 413 K according to Wagner's relation (*14*). Compared to the ionic conductivity of $3 \times 10^{-5}\ \Omega^{-1}\ cm^{-1}$ at the same temperature (Fig. 4), the electronic transference number is determined to be $\leq 2 \times 10^{-3}$.

Silver slightly enhances the ionic conductivity. The activation enthalpy remains unchanged within the limits of error. Extrapolation of the linear increase of the polarization current as a function of the applied voltage indicates a decomposition potential of pure Ga_2Br_3 of 0.38 V. The sample is in equilibrium with Ga at the negative electrode and with $GaBr_2$ at the positive

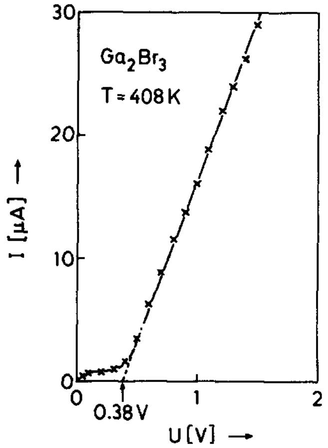

FIG. 6. Polarization measurements of Ga_2Br_3 at 408 K, using a Ga reference electrode and an inert, ionically blocking Pt electrode. $GaBr_2$ is formed at the Pt side at voltages higher than 0.38 V.

electrode. This results in a Gibbs energy of the formation of Ga_2Br_3 from 1.5 $GaBr_2$ and 0.5 Ga of −18 kJ/mole. DTA measurements of the reaction between Ga and $GaBr_3$ indicated an enthalpy of reaction of −20 kJ/mole. The electrochemical and analytical data are consistent with each other (taking literature data for the formation of $GaBr_3$ (*18*)) and confirm the relatively high stability of the trivalent gallium halide.

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