Cation Ordering in the Sillén X₁-Type Oxychloride, BaBiO₂Cl

Mark A. Kennard[1], Jacques Darriet, Jean Grannec, and Alain Tressaud[2]

Laboratoire de Chimie du Solide du CNRS, Université de Bordeaux I, 351 cours de la Libération, 33405 Talence, France

The structure of BaBiO₂Cl has been determined from single crystal X-ray diffraction data. It crystallizes in the orthorhombic space group *Cmcm* with $a = 5.880(4)$, $b = 12.945(18)$, $c = 5.677(3)$ Å, $V = 432.0(3)$ Å³, and $Z = 4$. BaBiO₂Cl is related to a family of bismuth oxyhalides which can be viewed as separate oxygen and chlorine layers stacked along the *b* axis, with bismuth and barium cations located between the layers. The structure differs from other bismuth oxyhalides in that the barium and bismuth cations are found to be ordered in two distinct coordination environments. The cation ordering and fourfold coordination environment of bismuth is seen as a structural expression of the stereochemically active bismuth 6s lone pair of electrons. © 1995 Academic Press, Inc.

INTRODUCTION

A large number of complex bismuth oxyhalides $MBiO_2X$ (M = Ca, Sr, Ba, and Cd) and $M'Bi_3O_4X_2$ (M' = Li and Na; and X = Cl, Br, and I) were discovered and described by Sillén and co-workers. They all contain the common structural motif of a square lattice of close-packed oxygen atoms with metal atoms located in fourfold sites above and below the layers. The metal–oxygen layers are separated by halide layers. Sillén adopted the notation X_n (n = 1,2,3) to indicate the number of halide layers separating the metal–oxygen layers. While the stacking sequence can be complex, the bismuth and M cation are always found to be disordered over a single site, and the overall structure is tetragonal.

In their original paper, Sillén and Gjörling-Husberg (1) reported that BaBiO₂Cl was obtained by reacting BiOCl and BaCl₂ at 960°C for 15 min in a porcelain container. The stoichiometry of the product requires the gain of oxygen and the loss of chlorine, which are likely to originate from water and result in the formation of hydrochloric acid respectively. Based on X-ray diffraction of the polycrystalline product, they reported that BaBiO₂Cl has tetragonal symmetry and is isostructural with other

layered oxyhalides of the X₁ type. They assumed space group *I4/mmm* and determined the unit cell dimensions of $a = 4.019$ Å and $c = 12.98$ Å. A more recent publication has confirmed the unit cell dimensions from X-ray diffraction on powder samples (2).

During our investigation of the system Ba–Bi–Cu–O–Cl we noted that the symmetry of BaBiO₂Cl was lower than tetragonal. The reaction of BaCl₂, BaCO₃, and Bi₂O₃ produces a single orthorhombic phase with composition BaBiO₂Cl. The phase is indeed related to the Sillén X₁-type structure, but the barium and bismuth cations are ordered on two sites which differ in their distance to the oxygen layer and the chlorine layer. In this paper we report the structural determination of BaBiO₂Cl from single crystal and X-ray powder diffraction.

EXPERIMENTAL

BaBiO₂Cl was synthesized by the solid state reaction of stoichiometric mixtures of Bi₂O₃ (Aldrich 99.9% pure), BaCO₃ (Aldrich 99.98% pure), and BaCl₂ · 2H₂O (Ventron ultrapure) at 800°C for 5 days, with several intermediate grindings. The final product was white and had a melting point near 960°C. Heating the product in an alumina boat above 900°C for several days resulted in the partial decomposition to the perovskite BaBiO₃₋δ.

X-ray powder diffraction patterns of ground polycrystalline samples were obtained with a Philips PW 1050 diffractometer and a CuKα radiation source ($\lambda = 1.54178$ Å). Scan parameters were $10° < 2\theta < 120°$, a step width of 0.02° and a slit width of 0.1 mm. Peak positions and intensities were determined by fitting the data to a 60% mixture of Gaussian to Lorentzian functions for both $K\alpha_1$ and $K\alpha_2$. The unit cell indexing and parameters shown in Table 1 were calculated using a least-squares refinement program developed at the Laboratoire de Chemie du Solide.

The original preparation method of Sillén and Gjörling-Husberg was repeated by reacting BiOCl with BaCl₂ · 2H₂O in air in a porcelain crucible at 960°C with reaction times ranging from 5 to 45 min. Evaporation of BiCl₃ was observed resulting from the decomposition of BiOCl giving rise to Bi₂₄O₃₁Cl₁₀ (3, 4). Under these conditions, the

201

TABLE 1
Indexed X Ray Powder Pattern of BaBiO$_2$Cl

h	k	l	d_{calc}	d_{obs}	I	h	k	l	d_{calc}	d_{obs}	I
0	2	0	6.484	6.458	23	3	1	2	1.604	1.600	1
1	1	0	5.367	5.352	13	3	5	0	1.566	1.568	<1
0	2	1	4.276	4.269	1	0	8	1	1.559	1.560	1
1	1	1	3.904	3.900	38	3	3	2	1.514	1.514	2
1	3	0	3.486	3.485	11	1	7	2	1.501	1.502	10
0	4	0	3.242	3.241	6	2	6	2	1.486	1.486	6
1	3	1	2.972	2.973	100	4	0	0	1.474	1.475	3
2	0	0	2.948	2.948	23	4	2	0	1.437	1.436	1
0	0	2	2.844	2.843	21	2	4	3	1.431	1.433	3
0	4	1	2.817	2.818	13	0	6	3	1.425	1.426	2
2	2	0	2.684	2.685	2	0	0	4	1.422 ⎫	1.421	5
0	2	2	2.604	2.602	1	2	8	0	1.420 ⎭		
1	1	2	2.513	2.512	3	1	9	0	1.400	1.400	2
2	2	1	2.427	2.426	1	2	8	1	1.378 ⎫	1.377	2
1	5	0	2.374	2.375	1	1	1	4	1.374 ⎭		
1	3	2	2.204	2.204	5	1	9	1	1.359 ⎤		
1	5	1	2.191 ⎫	2.184	11	2	5	3	1.358 ⎬	1.358	5
2	4	0	2.181 ⎭			3	1	3	1.357 ⎦		
0	6	0	2.161	2.160	7	3	7	0	1.348	1.347	4
0	4	2	2.138	2.136	9	4	4	0	1.342	1.342	1
2	0	2	2.047	2.048	23	1	3	4	1.317	1.315	1
2	4	1	2.037	2.036	10	3	7	1	1.312	1.312	1
0	6	1	2.020	2.020	6	4	0	2	1.309	1.308	5
2	2	2	1.952	1.951	4	4	4	1	1.306	1.305	2
3	1	1	1.839	1.839	6	0	4	4	1.302 ⎫	1.301	9
3	3	0	1.789 ⎫	1.788	5	3	3	3	1.301 ⎭		
1	1	3	1.788 ⎭			1	7	3	1.293	1.294	1
1	7	0	1.767	1.766	8	2	6	3	1.283 ⎤		
2	6	0	1.743	1.742	8	4	2	2	1.283 ⎬	1.282	4
2	4	2	1.731	1.731	5	2	0	4	1.281 ⎦		
0	6	2	1.721	1.722	7	0	10	1	1.264	1.264	5
3	3	1	1.707	1.707	20	2	2	4	1.256 ⎫	1.256	3
1	7	1	1.688	1.687	3	1	9	2	1.256 ⎭		
2	6	1	1.667 ⎫	1.665	25	3	7	2	1.218 ⎫	1.218	5
1	3	3	1.666 ⎭			4	6	0	1.218 ⎭		
0	4	3	1.637	1.637	2	4	4	2	1.214	1.214	2

products contained a mixture of phases, including a Sil-lén-type phase, however it was not possible to distinguish between orthorhombic and tetragonal symmetry.

Single crystals of BaBiO$_2$Cl were grown by heating a portion of the polycrystalline product in a gold crucible in air for 1 hr at 990°C, then cooling to 940°C at a rate of ~10°C/hr, before cooling to room temperature. A mass of clear colorless crystals was obtained.

The composition of several crystals was verified using a Cameca CAMEBAX electron microscope with a Tracor silicon diode and analysis package. BaBiO$_{3-\delta}$ and BiOCl were used as reference standards. The average of several measurements on nine crystals from the same growth gave Ba$_{1.00\pm0.05}$Bi$_{1.01\pm0.09}$Cl$_{0.98\pm0.06}$.

RESULTS

Polycrystalline Sample

BaBiO$_2$Cl prepared at 800°C is a white, nonhygroscopic powder. The X-ray diffraction pattern of polycrystalline BaBiO$_2$Cl is shown in Fig. 1. The X-ray diffraction pattern was indexed with the orthorhombic cell $a = 5.890(2)$, $b = 12.952(3)$, $c = 5.681(3)$. The observed and calculated d spacing and observed intensity are listed in Table 1. The unit cell edges were observed to vary slightly depending on the synthesis temperature. Several lines could not be indexed with a tetragonal cell. The splitting of diffraction peaks arising from the symmetry lowering orthorhombic distortion is clearly seen in the inset of Fig. 1.

Structure Determination

A clear, colorless single crystal, suitable for structure determination was mounted on a glass fiber parallel to its long axis. The crystal resembled a rectangular prism with

TABLE 2
Crystal Data, Conditions of Data Collection, and Structural Refinement for BaBiO$_2$Cl

Data collection	
Symmetry	Orthorhombic
Space Group	Cmcm (No. 63)
Cell Parameters	$a = 5.880(4)$ Å
	$b = 12.945(18)$ Å
	$c = 5.677(3)$ Å
Volume	432.0(3) Å^3
Calculated density (g · cm^{-3})	6.36
Crystal size	0.023 × 0.042 × 0.15 mm
Aperature	Variable, based on $x + y$ tan θ
Scan mode	ω–2θ
Data collection range	$2° \leq 2\theta \leq 90°$
Standard reflections	$\overline{1}3\overline{1}$; 200; $\overline{2}0\overline{2}$
Number of measured reflections	3786
Maximum h, k, l	$-11 < h < 11$
	$-25 < < k < 25$
	$0 < l < 11$
Absorption	501.2 cm^{-1}
Transmission factors: T_{min}, T_{max}	0.736, 0.999
Refinement conditions	
Program used for refinement	SHELX-86 and SHELXL-93
Number of reflections	2994
R_{av}	0.0498
Independent reflections	886 ($I > 3\sigma(I)$)
Number of reflections used in the refinement	886
Number of refined parameters	19
Reliability factors[a,b]	$R_1 = 0.0268$, $wR_2 = 0.0554$
Weighting scheme: $1/w = [\sigma^2(F_0^2) + (0.0207P)^2 + 3.99P]$ $P = $ (Max $F_0^2 + 2F_c^2)/3$	

[a] $R_1 = \Sigma|F_0 - |F_c||/\Sigma F_0$.
[b] $wR_2 = (\Sigma w(I_0 - I_c)^2/\Sigma wI_0^2)^{1/2}$.

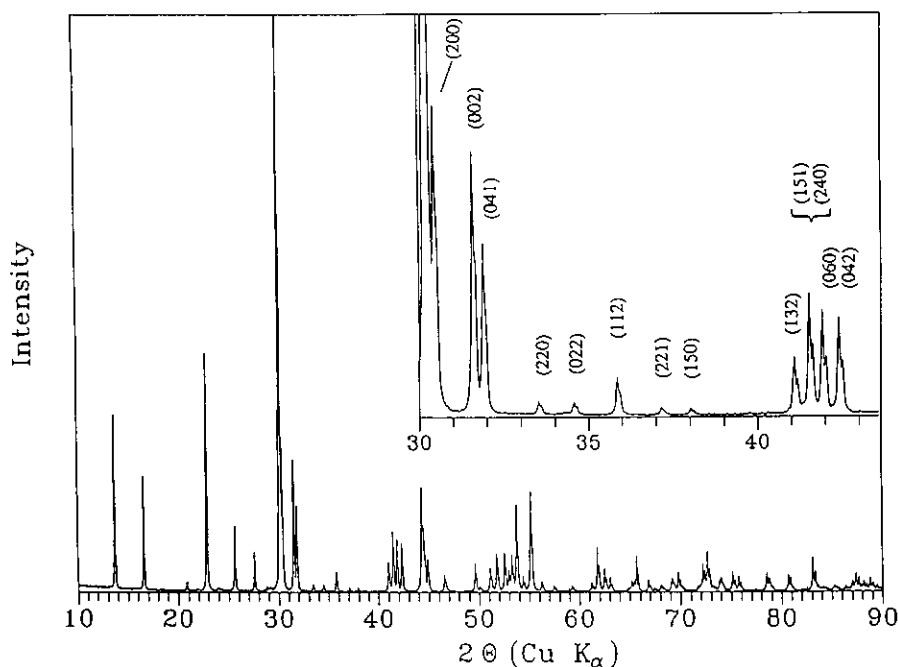FIG. 1. The powder X-ray diffraction pattern of BaBiO₂Cl. The inset clearly shows the separation of diffraction lines which would be coincident if the material possessed tetragonal symmetry.

regular perpendicular faces of 0.023 × 0.042 × 0.15 mm. Preliminary Laüe photographs confirmed orthorhombic symmetry. Weissenberg photographs showed the following extinction conditions: hkl, $h + k = 2n$ and $h0l$, $l = 2n$. These conditions are characteristic of the space groups $Cmc2_1$ (No. 36), $C2cm$ (No. 40), and $Cmcm$ (No. 63).

Intensity data for the structure determination were collected on an automated four-circle diffractometer (Enraf-Nonius CAD4) with monochromated (Mo$K\alpha$) radiation. Intensities were corrected for Lorentz and polarization effects, and an empirical absorption correction with the SDP package of programs was made on the basis of psi-scan data. The intensity collection was carried out under the conditions reported in Table 2. Calculations were per-

formed using SHELX-86 (5) and SHELXL-93 (6). Atomic scattering factors and anomalous dispersion corrections were taken from International Tables for X Ray Crystallography (7).

The structure of BaBiO₂Cl was determined by the interpretation of the Patterson map, which resulted in the positions of the barium and bismuth atoms. Those of the oxygen and chlorine atoms were located in subsequent difference Fourier maps. The final conventional R_1 (based on F_0) and wR_2 (based on F_0^2), including anisotropic thermal motions for all atoms, are respectively 0.0268 and 0.0554 for 886 independent reflections and 19 parameters. The atomic and thermal parameters are listed in Table 3 and the main interatomic distances in Table 4.

TABLE 3

Atomic Parameters, Anisotropic Temperature Factors[a] (U_{ij} × 10⁴ and B_{eq} (Å²)) for BaBiO₂Cl

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	B_{eq}
Ba	4c	0	0.3793(1)	1/4	99(1)	96(1)	111(2)	0	0	0	0.80(1)
Bi	4c	0	0.0761(1)	1/4	102(1)	73(1)	82(1)	0	0	0	0.68(1)
O	8e	0.2255(6)	0	0	93(10)	140(11)	112(14)	15(11)	0	0	0.91(5)
Cl	4c	0	0.7463(2)	1/4	214(8)	171(7)	182(8)	0	0	0	1.49(3)

Note. Standard deviations are given in parentheses.

[a] The vibrational coefficient is relative to the expression

$$T = \exp[-2\pi^2(h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hkabU_{12} + 2hlacU_{13} + 2klbcU_{23})].$$

TABLE 4

Selected Interatomic Bond Lengths (Å) for $BaBiO_2Cl$
(with Standard Deviations Given in Parentheses)

Bi–O	2.178(2) × 4	Ba–O	2.657(3) × 4
Bi–Bi	3.455(2) × 2	Ba–Cl	$\begin{cases} 3.271(2) \times 2 \\ 3.407(2) \times 2 \end{cases}$
Bi–Cl	$\begin{cases} 3.653(3) \times 2 \\ 3.673(3) \times 2 \end{cases}$	Bi–Ba	3.890(3) × 2

No improvement of the R factors was obtained with the noncentrosymmetric space groups $Cmc2_1$ and $C2cm$. Furthermore, if we consider a satistical repartition of barium and bismuth in the two sites, the R factors are very high ($R_1 = 0.0835$ and $wR_2 = 0.2376$), which confirms the proposed model. The list of structure factors may be obtained from the authors upon request.

Description of the Structure

The structure of $BaBiO_2Cl$ is shown in Fig. 2. It is indeed related to other bismuth oxyhalides. Their common structural feature is the presence of metal–oxygen layers which are separated by one or more halogen layers. The oxygen layer is formed by close packing of oxygen ions on a square lattice. Metal atoms lie above and below the oxygen plane in the fourfold coordination sites. The halide layer is offset from the oxygen layer so as to form a cubic antiprism of anions around the metal atoms as shown in Fig. 2b. Table 5 lists the lattice parameters and metal–anion distances of related metal bismuth oxyhalides. In all of these examples the two cations are found to be mixed on the fourfold cation site. $BaBiO_2Cl$ differs from these related phases in that the bismuth and barium atoms order on two sites. The bismuth atoms are found at a distance of 1.02 Å from the oxygen layer whereas the barium atoms are located 1.55 Å from the oxygen layer. A similar structure was described by Sillén and Melander for the mineral nadorite, $PbSbO_2Cl$ (8). Ordering of the two cations lowers the symmetry to orthorhombic and requires a larger unit cell. The
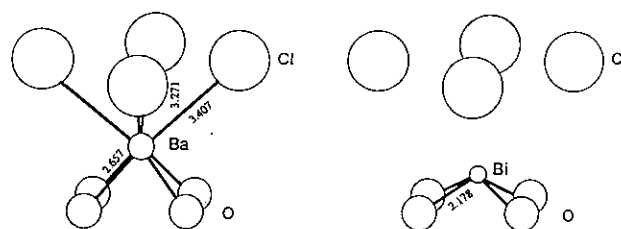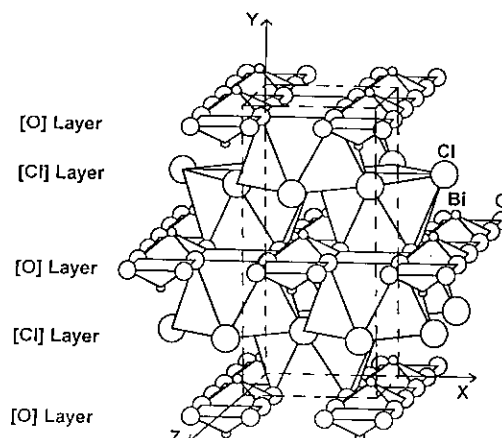

FIG. 2. (top) A polyhedral representation of the structure of $BaBiO_2Cl$. Large circles represent chlorine atoms, medium circles oxygen atoms, and small circles bismuth atoms. Barium atoms are located inside the polyhedra fomed by four chlorine and four oxygen atoms. The unit cell edges are shown with dashed lines. (bottom) A detailed view of the barium and bismuth coordination environments. Metal–anion distances are given in Å. Bismuth is considered to be in a fourfold coordination environment because of the unusually long Bi–Cl distances of ~3.66 Å.

orthorhombic unit cell can be related to the tetragonal cell as $a_0 \cong \sqrt{2}a_T$, $c_0 \sim \sqrt{2}b_T$, $b_0 = c_T$.

There is some precedent for cation ordering in $MBiO_2Cl$ compounds where $M = $ Ba or Pb. In the original structural determination of the mineral perite, $PbBiO_2Cl$, Gillberg (9) found that it was orthorhombic and isostructural with $PbSbO_2Cl$. However later studies by Deschan-

TABLE 5

A Comparison of Cell Parameters and Bismuth–Anion Bond Distances in Related Bismuth Oxyhalides

Formula	Structure type	Space group	a (Å)	b (Å)	c (Å)	Bi–O (Å)	Bi–X (Å)	Reference
$LiBi_3O_4Cl_2$	X_1	$I4/mmm$	3.841		12.03	2.24	3.29	(15)
$NaBi_3O_4Cl_2$	X_1	$I4/mmm$	3.878		12.14	2.24	3.34	(15)
$PbBiO_2Cl$	X_1	$I4/mmm$	3.956		12.63	2.27	3.47	(11)
$BiOCl$	X_2	$P4/nmm$	3.883		7.348	2.32	3.05 + 3.49	(15)
$BaBiO_2Cl$	X_1	$I4/mmm$	4.019		12.98	2.33	3.52	(1)
$BaBiO_2Cl$	X_1	$Cmcm$	5.880	12.945	5.677	2.18	3.65 + 3.67	This work

vres *et al.* (10) on powders and Ketterer and Krämer (11) on crystals of PbBiO₂Cl grown in a sealed quartz tube found that this material is tetragonal and isostructural with Bi₂O₂Se (X₁-type). Furthermore, Rulmont (12) proposed that BaBiO₂Cl has orthorhombic symmetry in order to explain features of the Raman spectrum, but no details of the structure were given.

In order to test whether orthorhombic BaBiO₂Cl transforms to the tetragonal structure, differential thermal analysis was performed on the powder sample. No phase transitions were detected between 25 and 900°C. In addition, attempts to prepare a tetragonal phase by quenching powder samples from 930°C did not change the diffraction pattern.

Bismuth and barium are coordinated by four oxygen atoms and four chlorine atoms which roughly form a archimedean antiprism. The four bismuth–oxygen bond distances of 2.178 Å are reasonable for trivalent bismuth-oxy compounds which are typically between 2.1 and 2.7 Å (13). This is a short bond length however, in comparison with isostructural bismuth oxyhalides in which the metal–oxygen distances are between 2.25 and 2.35 Å. In contrast, the four chlorine atoms coordinating bismuth at distances of 3.653 × 2 and 3.673 × 2 are large compared with other bismuth oxyhalide compounds (see Table 5). Thus bismuth atoms are displaced away from the center of the cubic antiprism to such an extent that they should be considered to be four coordinate.

This displacement of the bismuth position away from the chlorine layer suggests that the bismuth 6s lone pair electrons are stereochemically active. The quality of the X-ray diffraction data was not sufficient to directly determine the position of the lone pair electrons adjacent to bismuth atoms, but it is assumed to be located between the bismuth and four chlorine atoms so as to conserve the fourfold symmetry of the site.

The coordination environment of bismuth is similar to that found in Ba₃BiO₃Cl₃, (14), which has a structure unrelated to the layered Sillén phases. It contains polyhedra joined to form a tunnel structure with the 6s lone pair electrons of bismuth pointing inside the tunnels. In this compound, bismuth has three bonds to oxygen of 2.07 Å and two long bonds to chlorine of 3.61 Å.

CONCLUSIONS

The general structure features of BaBiO₂Cl originally described by Sillén have been confirmed. Our investigation has shown that, in contrast to previous results, the barium and bismuth atoms are not disordered on the same site, as is found with all other MBiO₂Cl compounds, but ordered on two sites. The displacement of bismuth toward the oxygen layer can be seen as a manifestation of the stereochemically active 6s lone pair electrons.

REFERENCES

1. L. G. Sillén and A. S. Gjörling-Husberg, Z. Anorg. Allg. Chem. **248**, 135 (1941).
2. S. S. Lopatin, Russ. J. Inorg. Chem. **32**(7), 1006 (1987).
3. A. E. Arppe, Pogg. Ann. **64**, 246 (1845).
4. L. G. Sillén and M. Edstrand, Z. Krystallogr. **104**, 178 (1942).
5. G. M. Sheldrick, Acta. Crystallogr. Sect. A **46**, 467 (1990).
6. G. M. Sheldrick, "SHELXL-93, Program for the refinement of crystal structures." University of Göttingen, Germany.
7. "International Tables for X-ray Crystallography," Vol. IV. Kynoch Press, Birmingham, UK, 1967.
8. L. G. Sillén and L. Melander, Z. Krystallogr. **103**, 420 (1941).
9. M. Gillberg, Ark. Kemi Mineral. Geol. **B2(44)**, 565 (1960).
10. A. Deschanvres, J. Gallay, J.-M. Hunout, M.-T. Thiault, and C. Victor, C.R. Seances Acad. Sci. Ser. C **270**, 696 (1970).
11. J. Ketterer and V. Krämer, Mat. Res. Bull. **20**, 1031 (1985).
12. A. Rulmont, in "Raman Spectroscopy Linear and Nonlinear, Proceedings from the Eighth International Conference on Raman Spectroscopy, Bordeaux France, 6–11 September 1982" (J. Lascombe and P. V. Huong, Eds.), p. 543 Wiley–Heyden, New York, 1982.
13. A. F. Wells, "Structural Inorganic Chemistry," 5th eds., p. 891. Oxford Science, Oxford, 1991.
14. A. Lentz and Hk. Müller-Buschbaum, Z. Anorg. Allg. Chem. **582**, 25 (1990).
15. L. G. Sillén, Naturwissenschaften **22**, 318 (1942).