The truth of (*b*) and (*c*), although they are counter to generally held views,* has been demonstrated for some examples.

I am grateful to Professor B. G. Hyde for helpful discussions and a critical reading of the manuscript.

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* In addition to the texts already cited, one might quote Bernal (1969) 'In all coherent structures there is a tendency to arrive at minimal volumes'.

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Structural Mechanism of Pyroelectricity in Tourmaline

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Pyroelectricity in tourmaline, known since antiquity, was ascribed by S. von Boguslawski to a charged, asymmetric, anharmonic oscillator based on the Einstein model of a crystal. His predicted values of the pyroelectric coefficient k were in good agreement with Ackermann's measurements in the range 200–400 K. We have tested Boguslawski's model by refining the structure, at 193 and 293 K, on a sphere of gem-quality elbaite. The pyroelectric effect is due primarily to the asymmetric anharmonic vibrations of O(1), the oxygen atom of point symmetry $3m$ which has a polar environment. Its centre of gravity moves 0·005 Å from 193 to 293 K. It is the only atom with a displacement well above experimental uncertainty. Its large thermal parameters, which are ten times their standard deviation at both temperatures, clearly invalidate the assumption of an ellipsoidal thermal movement. This probably holds for Na and O(2), which also have abnormally large temperature factors, but show no significant displacement.

Introduction

Pyroelectricity, the development of electric charges of opposite signs at the opposite ends of a crystal that undergoes a change in temperature, is one of the earliest recorded properties of crystals. Theophrastus (372–287 BC) reported, probably of tourmaline, that 'it has the power of attraction, just as amber has, and some say that it not only attracts straws and bits of wood, but also copper and iron' (Lang, 1974).

Pyroelectricity was rediscovered in tourmaline, and first described in Europe in 1707 by Johann George Schmidt in a book entitled *Curiose Speculationen bey schlaflosen Nächten*. Schmidt mentions that the Dutch in 1703 brought, from Ceylon, a precious stone called tourmaline, which attracts ashes when a tip of its

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elongated prismatic shape is placed in a fire, but repels them on cooling.

In the second half of the 18th century, there followed a period of various experimental studies in Europe. Again from 1820 to 1900 extensive work was done on pyroelectricity, in England as well as on the continent. Lord Kelvin (1894), for example, worked out an approximate theory of pyroelectricity for molecular crystals. All the results were incorporated by Voigt in 1910 in his classic textbook on crystal physics (Voigt, 1966).

At the time of Voigt's writing (*cf.* 1966, pp. 228–260) the distinction between pyroelectricity and its subclass ferroelectricity had not yet been recognized. Since World War II ferroelectricity has received a great deal of attention because of its practical importance in the electronics industry. The only application of pyroelectricity, however, that has aroused mild interest (Lang, 1974) is its use as a highly sensitive and accurate thermometer over large temperature ranges, but because of practical problems this possible usefulness has not been extensively exploited. The distinction between 'true' and 'false' pyroelectricity was known to Voigt and is correctly interpreted in his book. In the present study we deal with the sum of the two effects on an elbaite crystal ground into a sphere. No attempt is made to maintain the originally spherical specimen at constant volume and shape when it is cooled from room temperature to liquid-nitrogen temperature, a step that would be necessary if only 'true' pyroelectricity were to be measured.

Boguslawski's theory

While working in Göttingen, Germany, the Russian S. von Boguslawski published an elementary theory of pyroelectricity, in three consecutive papers entitled: (1) *Zur Theorie der Dielektrika. Temperaturabhängigkeit der Dielektrizitätskonstante. Pyroelektrizität* (1914*a*); (2) *Pyroelektrizität auf Grund der Quantentheorie* (1914*b*); (3) *Zu Herrn W. Ackermann's Messungen der Temperaturabhängigkeit der Pyroelektrischen Erregung* (1914*c*). The last paper was submitted from his summer-vacation place, Noordwijk-aan-Zee, on 29 July 1914. It happened to be followed in *Physikalische Zeitschrift* by a statement that Fritz Haber had announced his synthesis of ammonia. Germany was ready for World War I; it started six days later. Boguslawski retired to the Black Sea for health reasons (E. Ewald, private communication) and was never heard of again.

Let us begin the summary of Boguslawski's theory with the definition of the spontaneous polarization $\Delta\mathbf{P}=\mathbf{K}\Delta T$, where $\mathbf{P}$ is the pyroelectric polarization vector and $\mathbf{K}$ is a polar vector whose components are the pyroelectric coefficients k_1, k_2, k_3. All three coefficients are different from zero for a triclinic pyroelectric crystal, but they are of the form 0, 0, k_3, with $\mathbf{P}$ parallel to $\mathbf{c}$, for rhombohedral tourmaline (space group $R3m$). Boguslawski derives the following expression* for the change of P with temperature T:

$$\frac{\mathrm{d}P}{\mathrm{d}T}=-\frac{3beNk}{4a^2}\left\{\frac{\dfrac{h^2\nu_0^2}{k^2T^2}\exp(h\nu_0/kT)}{[\exp(h\nu_0/kT)-1]^2}\right\}$$

where a and b are explained below, e is the electronic charge, N the number of charges per unit volume, h is Planck's constant, $\nu_0=(1/2\pi)(2a/m)^{1/2}$, where m is the charge-carrying mass, k is the Boltzmann constant, and T the absolute temperature. The function enclosed between braces is the Einstein function, derived for a crystal model consisting of a set of independent linear oscillators (Table 1, Fig. 1).

Table 1. *Comparison of experimental and theoretical pyroelectric moment dependence on temperature for 'pinkish-red' tourmaline* (*Boguslawski*, 1914*c*)

$\nu_0=10{\cdot}57\times10^{12}$, $3ebNk/4a^2=1{\cdot}660$.

T (K)	Ackermann's experimental values $\frac{\mathrm{d}P}{\mathrm{d}T_{\mathrm{exp.}}}\times3\times10^5$ (Cm^{-2} deg^{-1})	Boguslawski's calculated values $\frac{\mathrm{d}P}{\mathrm{d}T_{\mathrm{theo.}}}\times3\times10^5$ (Cm^{-2} deg^{-1})
23	0·08	0·000
88	0·300	0·166
198	0·982	0·977
253	1·219	1·190
274	1·270	1·251
293	1·313	1·288
352	1·404	1·393
372	1·426	1·424
408	1·460	1·457
488	1·544	1·513
578	1·723	1·556
648	1·943	1·597

Boguslawski's theory considers the electron cloud to remain spherical about the oscillating nucleus, thus ignoring electronic polarization; it also ignores lattice vibrations and zero-point energy. Refinements of the theory are obviously possible and desirable, but better experimental data are needed before the theoretical improvements become essential in the 200–400 K temperature range.

In present-day language Boguslawski's formula predicts that one or more atomic point positions in a pyroelectric crystal perform major anharmonic, asymmetric thermal oscillations. The anharmonic condition implies that the ionic potential V is not proportional to x^2, where x is the displacement from the equilibrium position: its expression includes higher-order terms: $V=ax^2+bx^3+\ldots$ The asymmetric condition, $V(x)\neq V(-x)$, implies that the mean amplitude

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* The complete derivation is to be found in English in Fortier (1975, pp. 7–13). The expression is equation (14) in Boguslawski (1914*b*, p. 572).

of vibration is not symmetrical about the equilibrium position. This asymmetry increases with temperature and can lead to an observable displacement of the mean position of the corresponding peak on an electron-density map. The anharmonic asymmetric nature of the thermal vibration, on the other hand, is not observable in the usual least-squares structure refinements, in which the surface of the thermal motion is compelled to be a biaxial ellipsoid. Thus, large thermal parameters must be looked for: they indicate a disagreement between actual and prescribed thermal motions.

In this last paper Boguslawski (1914*c*) compares his predicted curves of pyroelectric coefficient *vs* absolute temperature with the values measured by Ackermann (1915) for a 'blue-green', a 'yellow-green' and a 'pinkish-red' tourmaline. He obtains the needed numerical values for *a* and *b* from Ackermann's measurements. The agreement between theory and experiment is good for all three curves from ~200 to ~400 K; outside this range of temperature, the discrepancies become major.* The experimental pyroelectric coefficients for the three differently coloured, and hence chemically distinct, tourmaline crystals give very different-looking curves when plotted against temperature (Boguslawski, 1914*c*, Table III). Since no two tourmaline crystals are chemically identical – even different regions of a single crystal differ in composition – tourmaline is a poor substance to use as a standard for pyroelectric measurements. Thus we did not expect to obtain, for our pink elbaite specimen from Pala, San Diego County, California, a pyroelectric coefficient that would be identical with that measured by Ackermann on *his* 'pinkish-red' tourmaline.

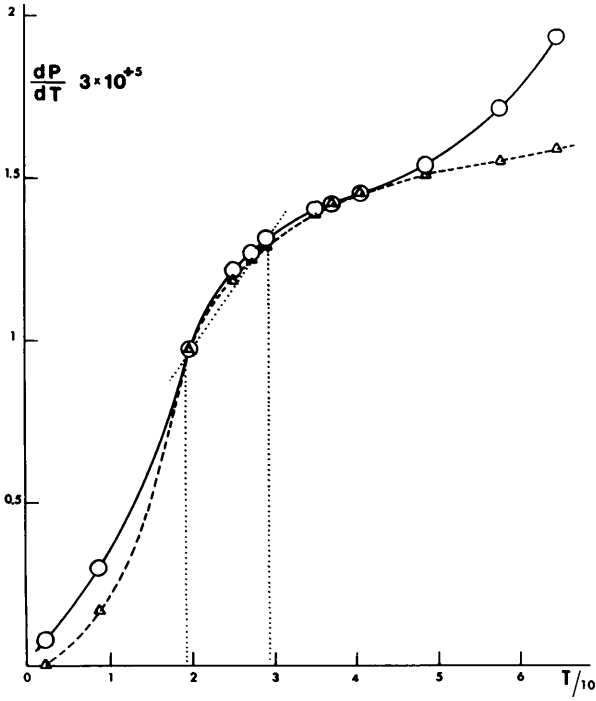

Fig. 1. Observed (circles) and calculated (triangles) values of dP/dT for pinkish-red tourmaline with data taken from Boguslawski (1914*c*, p. 807). Dotted line shown between 193 and 293 K represents slope used in experimental $\Delta P/\Delta T$ value.

In his third paper Boguslawski (1914*c*, p. 805) makes a statement that is perhaps worth translating, because the development of structural crystallography has shown it to be amazingly and totally false. He speculates on being able to connect the Debye temperature with the pyroelectric coefficient and goes on to say, '... should my above assumption prove incorrect, however, pyroelectric investigations will still afford an important means of establishing the structure of pyroelectric matter'. Actually, the structure type of tourmaline was first determined in 1948, and since then the structures of other tourmalines species (dravite, buergerite, elbaite and schorl) have been refined. Optical and Mössbauer spectra have been studied, X-ray topography has shown the inhomogeneity in grain size and orientation, high-resolution electron-microscopy images have shown the structural perfection within a grain. Yet the pyroelectric property has never been mentioned in any of these studies, and Ackermann's painstaking measurements are still the only serious ones in the literature. The only prediction of a structural mechanism for the pyroelectricity of tourmaline came from Wooster (1953) and it was independently repeated by Abrahams (1972). It runs as follows: 'On stretching the SiO_4 tetrahedron along a line running from one corner to the centre of the opposite face, the corner becomes positively charged and the opposite face negatively charged'. Neither of these two authors mentions Boguslawski's theoretical predictions.

Experimental procedure

For the purpose of refining the structure of a given specimen at two widely separated temperatures, it seemed advisable to use a tourmaline crystal as iron-free as possible, so as to minimize electrical conductivity that would instantly dissipate the charges produced during the temperature change. We chose a fragment from a pink elbaite crystal of gem quality, which originally weighed ~5 g, from the US National Museum collection (USNM R-17011). Its optics and structure have already been reported (Wilkins, Farell & Naiman, 1969; Donnay & Barton, 1972), and its average chemical composition has been determined by C. O. Ingamells (referenced in Donnay & Barton, 1972) from wet chemical analysis. The first structure determination, although it produced a final unweighted residual $R=0{\cdot}042$, had not been extended to anisotropic temperature factors because the authors had run out of computing funds.

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* The low-temperature problem was solved by Born (1945) and the high-temperature problem by Lang (1971).

The content of the rhombohedral cell is as follows:

$$(\mathrm{Na}_{0\cdot56}\mathrm{Mn}^{2+}_{0\cdot15}\mathrm{Ca}_{0\cdot14}\square_{0\cdot13}\mathrm{K}_{0\cdot02})_{\Sigma=1\cdot00}$$

$$(\mathrm{Al}_{1\cdot59}\mathrm{Li}_{1\cdot25}\mathrm{Mn}^{2+}_{0\cdot13}\mathrm{Fe}^{2+}_{0\cdot03})_{\Sigma=3\cdot00}$$

$$\mathrm{Al}_{6\cdot00}\mathrm{B}_{3\cdot00}\mathrm{Si}_{6\cdot00}[\mathrm{O}_{27\cdot50}(\mathrm{OH})_{2\cdot87}\mathrm{F}_{0\cdot63}]_{\Sigma=31\cdot00}.$$

A fragment from what little was left of the original crystal was ground to a sphere of radius 0·28 mm in a Bond sphere grinder. This sphere was used throughout the following work. It was mounted in a soft-glass capillary tube and cooled by a copper wire connected to a commercially available cryostatic head. Liquid nitrogen was used as the coolant. The temperature read on the instrument was 193 ± 5 K. (We did not calibrate the temperature scale since the true temperature was not a critical parameter.) Shadowgraphs of the direct beam spot were taken to ascertain the position of the crystal, in the beam, and that of the wire, out of the beam. The low-temperature data were collected first. The crystal then remained untouched and the experimental set-up unchanged, except for turning off the nitrogen, for collecting the room-temperature data. The same region of reciprocal space was measured at both temperatures. Only one-sixth of the total reciprocal volume could be reached, to avoid getting the nitrogen-flow tubing in the way of incident and diffracted X-ray beams. An automated four-circle diffractometer was employed with graphite-monochromated Mo $K\alpha$ radiation. The θ–2θ scan method was used, and the crystal was turned through the angle θ at a rate of 0·05° min^{-1}.

Cell dimensions (Table 2) were based on the least-squares refinement of 12 accurately measured general reflexions with 2θ values about 40°.

Table 2. *Crystal data of elbaite at* 193 (5) *and* 293 (2) K

Space group $R3m$; formula weight 2852·25; r, radius of crystal sphere, 0·28 mm. Linear absorption coefficient for Mo $K\alpha = 9\cdot650$ cm^{-1}; $\mu r = 0\cdot27$

	193 (5) K	293 (2) K	Δ cell dimensions
a (Å)	15·810 (3)	15·830 (2)	0·020 = 0·13%
c (Å)	7·083 (2)	7·098 (1)	0·015 = 0·21%
V (Å^3)	1533	1540	7 = 0·46%
D_x (g cm^{-3})	3·083	3·069	0·014 = 0·46%
D_m (g cm^{-3})	—	3·05 (1)	

The only other available data on the thermal expansion of tourmaline date back to Pfaff (1859, referenced in Voigt, 1915). He measured the increase in cross-section and length of a large tourmaline crystal of unspecified chemical composition, when its temperature was raised from 293 to 373 K. Our own values are twice his in a and are the same in c. Considering the probable difference in composition and in experimental procedure, the agreement is not bad.

For data collection the 2θ values ranged from 5·14 to 114·08° at the low temperature and from 5·14 to 114·96° at 293 ± 2 K (the thermostatically controlled temperature of the laboratory). The indices h and k ranged from 0 to +31 at both temperatures, l ranged from −14 to +16 at 193 K, but only from −12 to +16 at 293 K. Of the 3884 symmetry-independent reflexions contained in the Mo sphere at low temperature, 3746 showed integrated intensities at least 3σ above background, where σ is based on counting statistics only. At room temperature, of a possible 3620 independent reflexions, only 3550 fulfilled the above requirement; about twice as many had to be omitted at the higher temperature.*

Experimental results

Lorentz and polarization factors were applied with the *DATRDN* program of the XRAY 72 program (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). The small value of μr, 0·27 (Table 2), permits us to omit the absorption correction since the ratio of the transmission factors at $2\theta = 120°$ and $2\theta = 0$ equals 1·02 (*International Tables for X-ray Crystallography*, 1959, Table 5.3.6*A*), whereas symmetry-related reflexions and calibration reflexions agree only within 3%. Scattering factors for all atoms were taken from Hanson, Hermann, Lea & Skillman (1964). Anomalous dispersion corrections were applied to Fe, Mn, Ca, K, Si, Al, Na, F and O (*International Tables for X-ray Crystallography*, 1962, p. 215). From the coordinates published for elbaite by Donnay & Barton (1972), both structures refined quickly, with anisotropic temperature factors and unweighted structure factors, to R values of 0·041 at low temperature and 0·042 at room temperature. The fact that the R values are not lower is ascribed to the uncertainty of the composition of the particular sphere used, since the chemical composition is only known as the average of a 2–3 g sample that was needed for the complete analysis. In addition, the particular cryostatic goniometer head that we used did not permit collection of all the symmetry-related reflexions so as to obtain a lower mean deviation of the square root of the observed intensity; we would not use this cryostat arrangement again for work of high accuracy.

Since Boguslawski predicts abnormality in the thermal behaviour of one or more atoms in the pyroelectric crystal structure, let us first scrutinize the anisotropic temperature factors at low temperature (Table 3) and at room temperature (Table 4). We notice that the u values of atom O(1), with site symmetry $3m$, are at least one order of magnitude larger than those of all other atoms, with the exception of cation X and anion O(2) whose u values are both somewhat less than half the values of O(1). It is not surprising that the predicted anisotropic anharmonic thermal vibration

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32793 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 3. *Anisotropic temperature factors* (× 10⁴) *of elbaite at* 193 (5) K

The components u_{ij} represent the tensor that expresses the ellipsoid of mean-square amplitude of the vibration of the atom:

$$\exp\left[-2\pi^2(h^2a^{*2}u_{11}+\ldots+2klb^*c^*u_{23}+\ldots)\right].$$

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
X	202 (6)	202 (6)	161 (11)	101 (3)	0	0
Y	63 (3)	63 (3)	93 (5)	24 (3)	11 (2)	−11 (2)
Z	41 (2)	52 (2)	37 (2)	28 (2)	3 (2)	6 (2)
B	37 (5)	37 (5)	49 (8)	14 (6)	3 (3)	−3 (3)
Si	32 (1)	28 (1)	43 (2)	15 (1)	−1 (1)	−3 (1)
O(1)	512 (31)	512 (31)	142 (27)	256 (15)	0	0
O(2)	206 (9)	206 (9)	123 (10)	191 (10)	2 (3)	−2 (3)
O(3)	95 (4)	95 (4)	44 (7)	−32 (6)	5 (3)	5 (3)
O(4)	55 (4)	55 (4)	68 (7)	−2 (5)	−9 (3)	9 (3)
O(5)	58 (4)	58 (4)	63 (7)	−2 (5)	3 (3)	−3 (3)
O(6)	57 (4)	72 (4)	34 (4)	27 (3)	9 (3)	−9 (3)
O(7)	38 (3)	40 (3)	51 (4)	5 (3)	1 (3)	−10 (3)
O(8)	36 (3)	74 (4)	64 (4)	28 (3)	12 (3)	29 (3)

Table 4. *Anisotropic temperature factors* (× 10⁴) *of elbaite at* 293 (2) K

	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
X	225 (8)	225 (8)	145 (12)	113 (4)	0	0
Y	59 (4)	59 (4)	113 (6)	22 (5)	12 (2)	−12 (2)
Z	34 (2)	47 (2)	34 (2)	23 (2)	−23 (2)	42 (2)
B	42 (7)	42 (7)	56 (11)	26 (8)	2 (2)	−2 (4)
Si	27 (2)	26 (2)	33 (2)	13 (2)	−1 (2)	−3 (2)
O(1)	460 (37)	460 (37)	369 (52)	230 (19)	0	0
O(2)	202 (11)	202 (11)	132 (12)	188 (11)	2 (4)	−2 (4)
O(3)	92 (6)	92 (6)	42 (8)	−39 (8)	4 (4)	−4 (4)
O(4)	56 (5)	56 (5)	73 (8)	−5 (6)	−6 (4)	6 (4)
O(5)	57 (5)	57 (5)	77 (9)	−5 (7)	−5 (4)	5 (4)
O(6)	51 (5)	71 (6)	47 (5)	25 (4)	2 (4)	−7 (4)
O(7)	42 (5)	37 (5)	49 (5)	7 (4)	2 (4)	−12 (4)
O(8)	29 (4)	75 (5)	66 (5)	27 (4)	9 (4)	29 (4)

Table 5. *Atomic coordinates of elbaite at* 193 (5) *and* 293 (2) K *and their differences*, Δ

		293 (1) K	193 (5) K	$\Delta \times 10^4$
X	*x*	0	0	–
	y	0	0	–
	z	0·2341 (5)	0·2338 (4)	3 (6)*
Y	*x*	0·1229 (1)	0·1230 (1)	−1 (1)
	y	*x*/2	*x*/2	−1 (1)
	z	0·6354 (3)	0·6349 (2)	5 (4)
Z	*x*	0·2966 (1)	0·2967 (1)	−1 (1)
	y	0·2600 (1)	0·2599 (1)	1 (1)
	z	0·6092 (1)	0·6097 (1)	−5 (1)
B	*x*	0·1088 (1)	0·1090 (1)	−2 (1)
	y	2*x*	2*x*	−4 (2)
	z	0·4542 (5)	0·4537 (4)	5 (6)
Si	*x*	0·1920 (1)	0·1920 (1)	0 (1)
	y	0·1898 (1)	0·1899 (1)	−1 (1)
	z	0	0	–
O(1)	*x*	0	0	–
	y	0	0	–
	z	0·7839 (16)	0·7788 (12)	51 (20)
O(2)	*x*	0·0601 (1)	0·0602 (1)	−1 (1)
	y	2*x*	2*x*	−2 (2)
	z	0·4892 (5)	0·4891 (4)	1 (6)
O(3)	*x*	0·2659 (1)	0·2656 (2)	3 (2)
	y	*x*/2	*x*/2	1 (1)
	z	0·5084 (4)	0·5077 (3)	7 (5)
O(4)	*x*	0·0936 (1)	0·0932 (1)	4 (1)
	y	2*x*	2*x*	8 (2)
	z	0·0733 (4)	0·0742 (3)	−9 (5)
O(5)	*x*	0·1858 (1)	0·1864 (1)	−6 (1)
	y	*x*/2	*x*/2	−3 (1)
	z	0·0961 (4)	0·0966 (3)	−5 (5)
O(6)	*x*	0·1954 (1)	0·1954 (1)	0 (1)
	y	0·1847 (1)	0·1847 (1)	0 (1)
	z	0·7749 (3)	0·7742 (2)	7 (4)
O(7)	*x*	0·2866 (1)	0·2866 (1)	0 (1)
	y	0·2860 (1)	0·2863 (1)	−3 (1)
	z	0·0781 (3)	0·0791 (2)	−10 (4)
O(8)	*x*	0·2093 (1)	0·2094 (1)	−1 (1)
	y	0·2697 (1)	0·2698 (1)	−1 (1)
	z	0·4389 (3)	0·4392 (2)	−3 (4)

* The standard deviation, σ, on Δ was calculated as $\sigma = (\sigma_1^2 + \sigma_2^2)^{1/2}$, where σ_1 = standard deviation of the 293 (1) K data and σ_2 = standard deviation of the 193 (5) K data.

cannot be observed, since the least-squares refinement forces an ellipsoidal shape on every thermal parameter. The magnitudes of the thermal values for O(1) and, to a lesser degree for *X* and O(2), point to abnormalities in the thermal vibrations of these atoms, so that shifts in their equilibrium positions might be expected with change in temperature.

From the atomic coordinates at the two temperatures and their differences (Table 5), it is evident that, while neither *X* nor O(2) have shifted significantly, O(1) has. It has moved in the positive **z** direction with increase in temperature, which leads to the prediction of an accumulation of negative charge at the positive, antilogous pole on heating. This prediction is borne out by observation. The steeper trigonal pyramid $\{10\bar{1}1\}$, which points in the positive **c** direction, becomes positive on cooling; the less steep one, $\{10\bar{1}\bar{2}\}$, indicates the analogous pole, which becomes positive on heating.

The small absolute value of the O(1) displacement, 0·0051 ± 0·0020 Å, should not surprise us. A temperature change of 100° at more than 1200° below the decomposition temperature of tourmaline could not affect the structure substantially. We had intended to duplicate the structure refinements at liquid helium temperature and at 1073 K, but we were unable to obtain the necessary time in the two laboratories that are set up to perform this work. Undoubtedly atoms *X* and O(2) also contribute to the pyroelectric effect, but a larger difference in temperature is needed to show their atomic displacements.

Discussion and conclusions

No standard deviation of any atomic coordinate at either temperature has as large a value as that of the *z* of O(1) (Table 5). It is another indication, in addition to the high values of the thermal parameters and their standard deviations, that O(1) atoms are not behaving in a normal fashion.

Let us calculate the average pyroelectric moment ΔP for the temperature range between 193 and 293 K, in order to compare it with Ackermann's experimental value. The absolute charge of

$$\mathrm{O(1)}=(\mathrm{F}^{-}_{0\cdot60}\mathrm{OH}^{-}_{0\cdot20}\mathrm{O}^{=}_{0\cdot20})$$

will be assumed equal to 0·5e (P. Coppens and R. F. Stewart, private communications). With three O(1) atoms per cell and the cell volume assumed to change linearly with temperature we have a charge per unit volume of 1·5/1536 e Å^{-3} (Table 2). The displacement of charge per unit volume is $1\cdot5\times0\cdot0051/1536$ e Å^{-2} for a temperature difference of 100 K. To express it in coulombs per square metre per degree, we multiply by 16·02 and divide by 10^2, so that $\Delta P/\Delta T=8\cdot0\times10^{-7}$ C m^{-2} K^{-1}. To compare this value with Ackermann's findings on the 'pinkish-red' tourmaline (Table 1), we must approximate the given values of $\mathrm{d}P/\mathrm{d}T$ between 198 and 293 K to the line of best fit which gives a slope of $1\cdot1\times10^{-7}$ C m^{-2} K^{-1} (Fig. 1). Thus the calculated displacement Δz of O(1) by itself, which we know to be the principal if not the only pyroelectric ion in tourmaline, gives a value of $\Delta P/\Delta T$ 7·3 times larger than the experimental measurement. This is not surprising. The colour description of Ackermann, 'pinkish-red', implies the presence of more iron than is found in our pale-red elbaite. The measured specimen would have been a relatively poor insulator giving low measured pyroelectric coefficients. On the other hand, accepting Ackermann's value $\Delta P/\Delta T=1\cdot1\times10^{-7}$ C m^{-2} K^{-1} and assuming O(1) to be the only ion responsible for the measured pyroelectric coefficient, we find the residual charge on each O(1) to be only 0·07e.

Useful application of the present type of study might place the absolute charge associated with a single 'pyroelectric ion' at the centre of the investigation. Two structure refinements at widely differing temperatures and two accurately determined pyroelectric coefficients at these temperatures and for the same specimen are required to yield the absolute charge association.

Perhaps Dr Boguslawski's wishful thinking that '... die pyroelektrischen Untersuchungen auch an und für sich ein wichtiges Mittel zur Ergründung des Baues der Materie geben' was not so wrong after all. We shall obtain interesting crystal-structure information from his correct interpretation of pyroelectricity.

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