

Atomic Contribution to Crystalline Property Temperature Dependence*

S. C. Abrahams

AT & T Bell Laboratories, 600 Mountain Avenue,
Murray Hill, NJ 07974, U.S.A.

Abstract

General atomic locations in crystal structures are temperature dependent: the average thermal change in simple inorganic crystals is of the order of $10^{-3} \text{ \AA K}^{-1}$, with corresponding thermal coefficients of about 10^{-3} K^{-1} . A survey of the thermal coefficients for seven important crystal properties shows that these also have average values of about 10^{-3} K^{-1} , within one order of magnitude. Correlations between microscopic and macroscopic thermal dependence have been developed for the properties of spontaneous polarization and spontaneous strain. Comparable correlations are predicted for the case of piezoelectric strain. Scaling considerations suggest that the remaining dielectric, thermal and optical properties are similarly related to atomic location thermal coefficients. By contrast, the much smaller thermal dependence of such properties as expansivity and refractive index, with coefficients of about 10^{-5} K^{-1} , suggests that these properties are dominated by electronic rather than ionic interactions.

1. Introduction

Numerous solid state properties are temperature dependent, with any major changes generally taking place only at phase transitions. Relationships between the thermal dependence of macroscopic properties far from a phase transition and the underlying atomic or electronic contributions are of fundamental importance. A coefficient of thermal dependence for property X at a temperature T may be defined as $\mathcal{T}(X) = (1/X)dX/dT$. A survey of the average magnitudes of $\mathcal{T}(X)$ as presented in this paper for such macroscopic properties as spontaneous polarization, spontaneous strain, piezoelectric strain, dielectric permittivity, electrostriction, linear electro-optic and piezo-optic effects reveals an unexpectedly narrow range, although the properties themselves have magnitudes (in SI units) that extend over 20 or more orders of magnitude.

A direct relationship between the thermal dependence of atomic location and any of the thermoproperties above has been sought in few materials and found in fewer, despite a range in magnitude for the former, in terms of noncovalently bonded interatomic distances, that is closely comparable with that of the latter. Following a sampling of atomic location thermal coefficients, a brief account is given of each specified macroscopic property together with tables of values of X and $\mathcal{T}(X)$ for

* Dedicated to Dr A. McL. Mathieson on the occasion of his 65th birthday.

representative simple inorganic materials. By contrast, such properties as thermal expansion and refractive index thermal coefficients are shown to be smaller in general by about two orders of magnitude. Relationships found between interatomic distance and spontaneous polarization temperature dependences, and between atomic displacements in ferroelastic transformation and spontaneous strain as a function of temperature, are briefly considered. Universal relationships between atomic displacements and consequent changes in physical properties are not to be expected without also accounting for the electronic contribution: both microscopic effects are retrievable from diffraction measurements, and determination of their temperature dependence in a wide range of materials will provide a sound experimental basis for clarifying their relationships to the macroscopic properties.

Table 1. Atomic location thermal coefficients

Crystal	Point group	Atom ^A	ΔT^B (K)	dr/dT ($10^{-4} \text{ \AA K}^{-1}$)	Reference
Ba(NO ₂) ₂ ·H ₂ O	6	O	-278	4.4(1)	Kvick <i>et al.</i> (1982)
Ba ₃ SrRu ₂ O ₉	2/m	O	-294	3.7(3)	Zandbergen and Ijdo (1984)
CSe ₂	mmm	Se	-182.5	14.0(5)	Powell and Torrie (1983)
K ₂ Cd ₂ (SO ₄) ₃	222	O	119.5	12.7(1.4)	Abrahams <i>et al.</i> (1978)
KClO ₃	2/m	O	-221	1.2(2)	Danielsen <i>et al.</i> (1981)
LiIO ₃	6	O	-275	0.7(1)	Svensson <i>et al.</i> (1983)
LiNO ₃ ·3H ₂ O	mmm	O	-175	2.0(1)	Hermansson <i>et al.</i> (1984)
Mn ₁₁ Ge ₈	mmm	Mn	-179	3.1(1)	Ohba <i>et al.</i> (1984)
Pb ₃ (PO ₄) ₂	2/m	Pb	90	22.0(2.0)	Guimaraes (1979)
Tb ₂ (MoO ₄) ₃	mm2	O	75	15.8(2.4)	Abrahams <i>et al.</i> (1980)

^A Atom with the largest total thermal location displacement r coefficient.

^B Thermal interval between structure determinations with respect to room temperature, except for CSe₂ and Pb₃(PO₄)₂: the higher temperature in these studies was 200 and 443 K respectively.

2. Atomic Location Thermal Dependence

Numerous crystal structure determinations are reported annually, the vast majority having been undertaken at a single temperature. Most of the small number made at two or more temperatures are concerned with the structural rearrangements associated with phase transitions, and relatively few determinations have been made on the same phase as a function of temperature. Results from some recent studies in the latter category are given in Table 1 for a group of simple inorganic materials. In evaluating the coefficient dr/dT , dr is taken as the largest difference between atomic coordinates (in \AA) at temperatures T_1 and T_2 , where $dT = T_1 - T_2$.

Magnitudes outside the range in Table 1 of dr/dT from 0.7 to $22 \times 10^{-4} \text{ \AA K}^{-1}$ are to be expected, although the smallest value is comparable with that found in crystals with all atoms in invariant positions and hence with location coefficients due entirely to the thermal expansion coefficient α as, for example, in f.c.c. Ag with $dr/dT = \alpha a/\sqrt{2} = 0.5 \times 10^{-4} \text{ \AA K}^{-1}$. Larger values are found in organic and organometallic compounds such as $[\text{Ni}_2(\text{C}_2\text{H}_5)_3][\text{BF}_4]$, for which $dr/dT(\text{max}) = 44(7) \times 10^{-1} \text{ \AA K}^{-1}$ (Dubler *et al.* 1983). It is, however, notable that the average atomic location thermal coefficient for simple inorganic crystals is about $10^{-3} \text{ \AA K}^{-1}$, with variations generally less than one additional order of magnitude; since r is of the order of 1 \AA , dr/dT is about 10^{-3} K^{-1} .

3. Pyroelectric Coefficient Thermal Dependence

The spontaneous polarization P , or electric moment per unit volume, is a vector property of all polar crystals that is reversible only in ferroelectric crystals. A small temperature change ΔT produces a proportional change ΔP in the polarization of a pyroelectric crystal such that $\Delta P = p\Delta T$. The pyroelectric coefficients p necessarily conform to the point group symmetry and are nonzero only in the ten non-centrosymmetric groups for which a unique direction exists. Table 2 lists the thermal coefficients of p , i.e. $(1/p)dp/dT$, for a group of typical inorganic pyroelectric crystals together with the value of p corresponding to the mid-temperature interval ΔT . Since the thermal dependence is generally nonlinear, the thermal coefficients listed are necessarily approximate. It may be noted that the thermal coefficient sense for ΔP is indeterminate in nonferroelectric crystals, and also that crystals with point group m and 1 respectively have two and three independent pyroelectric coefficients.

Table 2. Pyroelectric coefficient thermal dependence

Crystal	Point group	p^A (10^{-6} C m $^{-2}$ K $^{-1}$)	T (K)	dp/pdT^B (10^{-4} K $^{-1}$)
Ba(NO ₂) ₂ ·H ₂ O	6	42	240	50 ^C
CdS	6 <i>mm</i>	5	185	-25 ^D
Fe-I boracite	<i>mm2</i>	75	318	340 ^D
K ₂ SbNb ₅ O ₁₅	3 <i>m</i>	25	375	100 ^D
LiNbO ₃	3 <i>m</i>	-60	140	-30 ^E
Li ₂ SO ₄ ·H ₂ O	2	50	220	100 ^E
LiTaO ₃	3 <i>m</i>	145	210	30 ^D
NaNO ₂	<i>mm2</i>	250	390	200 ^D
Tb ₂ (MoO ₄) ₃	<i>mm2</i>	30	255	360 ^D
ZnO	6 <i>mm</i>	5	125	35 ^E

^A Value at the midpoint of ΔT , with an e.s.d. of about 10%.

^B Nonlinear thermal dependence gives e.s.d. values of about 25%.

^C Liminga *et al.* (1982). ^D Landolt-Börnstein (1984). ^E Landolt-Börnstein (1979).

Table 3. Spontaneous strain thermal coefficients

Crystal	Point group	e_s^A (10^{-4})	T (K)	$de_s/e_s dT^B$ (10^{-4} K $^{-1}$)	Reference
BiVO ₄	2/ <i>m</i>	95	335	-14	David and Wood (1983)
K ₂ Cd ₂ (SO ₄) ₃	222	34	325	-19	Abrahams <i>et al.</i> (1978)
KClO ₃	2/ <i>m</i>	2430	435	-5	Wadhawan (1980)
K ₂ TeBr ₆	2/ <i>m</i>	39	295	-190	Abrahams <i>et al.</i> (1984)
RbAlF ₄	<i>mmm</i>	3	102	-22	Bulou and Nouet (1982)
Tb ₂ (MoO ₄) ₃	<i>mm2</i>	18	335	-39	Abrahams <i>et al.</i> (1980)

^A All spontaneous strains have 12 *ij* suffixes.

^B The e.s.d. value is of the order of the final digit.

4. Spontaneous Strain Thermal Dependence

Spontaneous strain e_s is a property of all ferroelastic crystals that is related to the lattice distortion from a higher symmetry prototypic phase. The application of stress along an appropriate direction reproducibly transforms one stable orientational ferroelastic state into another as e_s is simultaneously reoriented (Abrahams 1971,

1979). Lattice constants have been presented for a moderate number of ferroelastic crystals at fixed temperatures, but rather few such measurements have been reported as a function of temperature, as required for the derivation of the spontaneous strain thermal dependence. Spontaneous strain magnitudes and corresponding thermal coefficients for several inorganic crystals are given in Table 3; all are necessarily negative.

Table 4. Piezoelectric strain thermal coefficients

Crystal	Point group	d_{ij} (10^{-12} C N $^{-1}$)	ij	$dd_{ij}/d_{ij}dT^A$ (10^{-4} K $^{-1}$)
Bi ₁₂ GeO ₂₀	23	-33.7(2)	14	1.5 ^C
Ca ₁₂ Al ₁₄ O ₃₃	$\bar{4}3m$	11.3(5)	14	8.7 ^B
KH ₂ PO ₄	$\bar{4}2m$	-20.9(3)	36	-38.1 ^B
LiNbO ₃	3 <i>m</i>	-0.86(2)	31	19.1 ^B
Li ₂ SO ₄ .H ₂ O	2	1.7(1)	23	210 ^B
LiTaO ₃	3 <i>m</i>	-3.0(2)	31	3.3 ^B
NaBrO ₃	23	-2.42(3)	14	26.5 ^B
NaClO ₃	23	-1.74(3)	14	80 ^B
α -quartz	32	-1.0(1)	14	0.166 ^C
Te ₂ V ₂ O ₉	<i>mm2</i>	4(1)	24	-30 ^C

^A Largest magnitude of coefficient only is listed, with e.s.d. of the order of the final digit, at room temperature.

^B Landolt-Börnstein (1979). ^C Landolt-Börnstein (1984).

Table 5. Dielectric permittivity thermal coefficients

Crystal	Point group	ϵ_{ij}	ij	$d\epsilon_{ij}/\epsilon_{ij}dT^A$ (10^{-4} K $^{-1}$)
Ba(NO ₂) ₂ .H ₂ O	6	9	33	6 ^B
CdSe	6 <i>mm</i>	10	11	13 ^C
LiIO ₃	6	7	33	29 ^B
LiNbO ₃	3 <i>m</i>	29	33	7 ^C
Li ₂ SO ₄ .H ₂ O	2	1	13	-40 ^C
LiTaO ₃	3 <i>m</i>	43	33	12 ^C
NaBrO ₃	23	6	11	5 ^C
NaClO ₃	23	6	11	7 ^C
RbD ₂ AsO ₄	$\bar{4}2m$	72	11	-14 ^C
Te ₂ V ₂ O ₉	<i>mm2</i>	15	33	3 ^B

^A Largest ij coefficient for each crystal at room temperature. A single suffix is used for orthorhombic and higher symmetry, for which $i = j$. The e.s.d. value is not stated in compilations.

^B Landolt-Börnstein (1984). ^C Landolt-Börnstein (1979).

5. Piezoelectric Strain Thermal Dependence

A crystal is piezoelectric if a small applied stress σ_i produces a proportional electric polarization P_i , with $P_i = d_{ij}\sigma_j$. The piezoelectric coefficients d_{ij} are nonzero only in the 21 non-centrosymmetric point groups, excluding 432, and may have other restrictions imposed by the particular point group as given, for example, by Landolt-Börnstein (1979). Magnitudes of the thermal coefficient $dd_{ij}/d_{ij}dT$ for a

group of inorganic piezoelectric crystals are collected in Table 4, which also gives the corresponding piezoelectric strain coefficient (usually at room temperature) and suffix identification.

6. Dielectric Permittivity Thermal Dependence

The relative dielectric permittivity of a material is given by $\epsilon_r' = C_x/C_0$, where C_0 is the capacitance of a cell without the material and C_x is the corresponding capacitance with the dielectric, in the direction of the electric field across the cell. The thermal dependence of the permittivity is a function of the overall polarization change produced by relative movements within the unit cell. The ϵ_{ij} coefficients form a symmetric 3×3 array, with six independent constants in triclinic crystals at a given temperature and fewer in the higher symmetry crystal systems. Dielectric permittivity thermal coefficients for a group of ten inorganic crystals are given in Table 5, together with the corresponding permittivity. It should be noted that all given values are frequency dependent: most were measured at 1 kHz or a higher frequency.

Table 6. Electrostriction thermal coefficients

Crystal	Point group	Q_{ij} ($10^{-12} \text{ m}^4 \text{ C}^{-2}$)	ij	T (K)	$dQ_{ij}/Q_{ij} dT^A$ (10^{-4} K^{-1})
$\text{Ba}_{1/4}\text{Sr}_{3/4}\text{Nb}_2\text{O}_6$	4 <i>mm</i>	2.4	33	373	0.4 ^B
BaTiO_3	4 <i>mm</i>	3.9	13	303	-17 ^C
$\text{Fe}_3\text{B}_7\text{O}_{13}\text{I}$	<i>mm2</i>	0.9	13	313	12 ^C
$(\text{NH}_4)_2\text{SO}_4$	<i>mm2</i>	6.3	23	133	36 ^D
NaNO_2	<i>mm2</i>	-0.2	23	298	153 ^D
$\text{Pb}_3\text{MgNb}_2\text{O}_9$	<i>m3m</i>	1.5	11	286	90 ^B
SbSI	<i>mm2</i>	0.2	33	293	-5 ^D
SrTiO_3	<i>m3m</i>	1.4	13	140	22 ^C

^A Largest magnitude of ij coefficient. Nonlinear thermal dependence gives e.s.d. values of about 20%.

^B Landolt-Börnstein (1984). ^C Landolt-Börnstein (1981). ^D Landolt-Börnstein (1982).

7. Electrostriction Thermal Dependence

In the converse piezoelectric effect, an applied electric field E produces a proportional strain $\epsilon = d_{ij} E$ in a non-centrosymmetric crystal. As the strains increase, a quadratic field dependence becomes appreciable due to the additional term $Q_{ij} E^2$, in which Q_{ij} is the electrostriction coefficient. Unlike the piezoelectric effect, electrostriction may be exhibited by all solids: the property is generally temperature dependent. Values of Q_{ij} together with the thermal coefficients $dQ_{ij}/Q_{ij} dT$ for a group of inorganic crystals are given in Table 6.

8. Linear Electro-optic Thermal Dependence

The application of an electric field E across a crystal changes the refractive index* n_0 to n , as given by $n = n_0 + r_{ij} E + R_{ij} E^2 + \dots$, where r_{ij} is the linear and R_{ij} the quadratic electro-optic effect. Linear electro-optic effects are nonzero only in

* The change in refractive index is given by the change in shape, size and orientation of the optical indicatrix (Nye 1957).

non-centrosymmetric crystals, whereas quadratic and higher even-order effects exist in centrosymmetric crystals and indeed in liquids. The magnitudes of both effects are frequency and temperature dependent. Values of r_{ij} and $dr_{ij}/r_{ij}dT$ are given in Table 7 for several inorganic crystals. Since the thermal dependence of r_{ij} is generally nonlinear, the values are necessarily approximate.

Table 7. Linear electro-optic thermal coefficients

Crystal	Point group	r_{ij} (10^{-12} m V $^{-1}$)	ij	$dr_{ij}/r_{ij}dT^A$ (10^{-4} K $^{-1}$)
CsCuCl ₃	622	1	41	39 ^B
CuCl	$\bar{4}3m$	-5	41	-17 ^B
GaAs	$\bar{4}3m$	1	41	42 ^B
Gd ₂ (MoO ₄) ₃	$\bar{4}2m$	3	63	-7 ^C
KH ₂ PO ₄	$\bar{4}2m$	40	63	-60 ^C
LiNbO ₃	3m	31	33	5 ^C
Pb ₅ Ge ₃ O ₁₁	3	11	13	82 ^C
α -quartz	32	1	11	-17 ^C
ZnSe	$\bar{4}3m$	2	41	15 ^B

^A Largest magnitude of ij coefficient, at room temperature, except $T=445$ K for Gd₂(MoO₄)₃. The e.s.d. values are of the order of the final digit.

^B Landolt-Börnstein (1984). ^C Landolt-Börnstein (1979).

Table 8. Piezo-optic thermal coefficients

Crystal	System	q_{ij} (10^{-12} m ² N $^{-1}$)	ij	$dq_{ij}/q_{ij}dT^A$ (10^{-4} K $^{-1}$)
KCN	Cubic	-23	11	8 ^B
KH ₃ (SeO ₃) ₂	Orthorhombic	50	55	-79 ^C
MgO	Cubic	1	44	5 ^C
NaCl	Cubic	-1	44	13 ^C
NaF	Cubic	-1	44	4 ^C
NaNH ₄ (C ₄ H ₄ O ₆).4H ₂ O ^D	Orthorhombic	2	55	-80 ^B
NH ₄ Cl	Cubic	4	44	42 ^C
NH ₄ H ₂ PO ₄	Tetragonal	8	44	-52 ^C

^A Largest magnitude of ij coefficient at room temperature. The e.s.d. values are of the order of the final digit.

^B Landolt-Börnstein (1984). ^C Landolt-Börnstein (1979). ^D Ammonium Rochelle salt.

9. Piezo-optic Thermal Dependence

The application of stress σ also changes the refractive index of a crystal, resulting in $n = n_0 + q_{ij}\sigma + \rho_{ij}\sigma^2 + \dots$, where q_{ij} is the linear and ρ_{ij} the quadratic piezo-optic effect. Second and higher order effects are generally small. Unlike the linear electro-optic effect, the piezo-optic effect may be nonzero in all crystal classes: it is both frequency and temperature dependent. Values derived from the thermal dependence are given in Table 8 together with the value of q_{ij} at the mid-temperature interval.

10. Thermal Expansion

This section and the next present two crystal properties with thermal dependence coefficients that, on average, are two orders of magnitude smaller than the coefficients

in the preceding seven sections. Crystals of all symmetry are subject to thermal expansion. Values of the coefficient $dl_i/l_i dT$ (where l_i is the crystal length along the i th direction) have been reported for a very large number of materials (cf. Touloukian *et al.* 1977; Krishnan *et al.* 1979). In Table 9, the largest magnitude of the i coefficient reported along a principal axis is given, where $i = 1, 2, 3$ represents the a, b or c crystal axis.

Table 9. Thermal expansion coefficients

Crystal	System	i	$dl_i/l_i dT^A$ ($10^{-6} K^{-1}$)	Reference
Ba(NO ₂) ₂ ·H ₂ O	Hexagonal	3	60	Kvick <i>et al.</i> (1982)
LiIO ₃	Hexagonal	3	46	Abrahams <i>et al.</i> (1983)
LiNbO ₃	Trigonal	1	14	Touloukian <i>et al.</i> (1977)
Li ₂ SO ₄ ·H ₂ O	Monoclinic	2	39	Lundgren <i>et al.</i> (1984)
LiTaO ₃	Trigonal	1	16	Krishnan <i>et al.</i> (1979)
NaBrO ₃	Cubic	1	38	Touloukian <i>et al.</i> (1977)
NaClO ₃	Cubic	1	43	Touloukian <i>et al.</i> (1977)
NH ₄ H ₂ PO ₄	Tetragonal	1	39	Krishnan <i>et al.</i> (1979)
α -quartz	Trigonal	1	14	Touloukian <i>et al.</i> (1977)
ZnO	Hexagonal	1	5	Touloukian <i>et al.</i> (1977)

^A Largest magnitude of i coefficient at room temperature. The e.s.d. values are about 5% or less.

Table 10. Refractive index thermal coefficients

Crystal	System	n	$dn/n dT^A$ ($10^{-6} K^{-1}$)	λ (nm)
Ba ₂ LiNb ₅ O ₁₅	Tetragonal	2.2	35	515 ^B
CdS	Hexagonal	2.6	100	546 ^B
CuCl	Cubic	2.0	70	633 ^B
CuGaS ₂	Tetragonal	2.8	62	550 ^C
LiIO ₃	Hexagonal	1.9	43	700 ^B
LiNbO ₃	Trigonal	2.6	45	310 ^B
NaBrO ₃	Cubic	1.6	-34	633 ^B
NH ₄ H ₂ PO ₄	Tetragonal	1.5	29	405 ^C
ZnSe	Cubic	3.1	30	633 ^C

^A Largest magnitude of coefficient at wavelength λ and room temperature, with e.s.d. values of about 5–10%.

^B Landolt-Börnstein (1984). ^C Landolt-Börnstein (1979).

11. Refractive Index Thermal Dependence

The optical indicatrix is defined by $x_1^2/n_1^2 + x_2^2/n_2^2 + x_3^2/n_3^2 = 1$, where x_1, x_2, x_3 are the principal axes of the dielectric permittivity tensor and $n_1 = K_1^{1/2}$, $n_2 = K_2^{1/2}$, $n_3 = K_3^{1/2}$ are the principal refractive indices with K_1, K_2, K_3 the principal dielectric permittivities at optical frequencies. In cubic crystals we have $n_1 = n_2 = n_3$; hexagonal, trigonal and tetragonal crystals have $n_1 = n_2 = n_o$, $n_3 = n_e$ and are uniaxial; orthorhombic, monoclinic and triclinic crystals are biaxial and without indicatrix restrictions. The refractive index n_i is c/v , where c is the velocity of light with wavelength λ in a vacuum and v is the velocity along the i th principal axis in the crystal: n is dependent on wavelength and on temperature. The frequency dependence may be large, as in LiNbO₃ for which $dn_o/n_o dT = +37.1 \times 10^{-6} K^{-1}$

at 310 nm and $-0.4 \times 10^{-6} \text{ K}^{-1}$ at 640 nm. Typical magnitudes for the refractive index thermal coefficients at a given frequency for a group of inorganic crystals are presented in Table 10.

12. Atomic Contribution to Macroscopic Property Thermal Dependence

Spontaneous polarization. The spontaneous polarization change ΔP in a pyroelectric crystal over the temperature range ΔT is readily measurable, whereas the polarization magnitude itself can be determined only in ferroelectric crystals as a consequence of its vanishing at the Curie temperature. Correlations between ΔP and atomic displacements in pyroelectric crystals heated through ΔT have been reported for the first time, in $\text{Ba}(\text{NO}_2)_2 \cdot \text{H}_2\text{O}$ and in the mineral elbaite (Liminga *et al.* 1982; Abrahams *et al.* 1979). In the former, ΔP between 20 and 102 K is $2.7 \times 10^{-4} \text{ C m}^{-2}$ and between 102 and 298 K it is $-26.3 \times 10^{-4} \text{ C m}^{-2}$. By taking the electric dipole moment of NO_2^- as $6 \times 10^{-30} \text{ C m}$ and that of H_2O as $6.2 \times 10^{-30} \text{ C m}$, with unit negative point charge midway between O atoms in the NO_2^- ion and double positive point charge on Ba^{2+} , the calculated polarization at 298 K based on atomic coordinates determined at this temperature is $27.4 \times 10^{-2} \text{ C m}^{-2}$. The corresponding calculated value of ΔP between 20 and 102 K is $-5(10) \times 10^{-4} \text{ C m}^{-2}$ and that between 102 and 298 K is $-30(10) \times 10^{-4} \text{ C m}^{-2}$. In view of the uncertainties in ΔP due to the small change in P over this temperature range, the agreement between macroscopic measurement and atomic contribution is acceptable.

In the case of elbaite (a tourmaline), ΔP between 200 and 300 K is about $4 \times 10^{-4} \text{ C m}^{-2}$, which corresponds to an average ionic displacement by the cations along the c -axis in this structure, with space group $R3m$, of about $(5-10) \times 10^{-4} \text{ \AA}$ (Abrahams *et al.* 1979). The largest significant atomic displacement along the c -axis measured in this temperature range is that of Al^{3+} at $5 \times 10^{-4} \text{ \AA}$ (Donnay 1977). Although small by comparison with the coefficients in Table 1 (i.e. $dr/dT = 0.05 \times 10^{-4} \text{ \AA K}^{-1}$), the experimental magnitude agrees well with expectation. Further study on the correlation of pyroelectric with atomic location thermal coefficients is in progress.

Spontaneous strain. The atomic distribution within the unit cell of a ferroelastic crystal gradually changes, on raising the temperature, until the symmetry of the prototype phase is approached or the crystal becomes chemically unstable. Spontaneous strain reorientation at any temperature is accompanied by an exchange of identity between pairs of pseudosymmetrically related atoms. Chemically identical atoms at $x_1 y_1 z_1$ and $x_2 y_2 z_2$ undergo identity exchange by a displacement Δ in the reorientation process

$$x_1 y_1 z_1 = f(x_2 y_2 z_2) + \Delta,$$

where $f(x_2 y_2 z_2)$ is a pseudosymmetry transformation causing lattice vector reorientation (Abrahams 1971). Displacements Δ have been measured as large as 2.4 \AA (see Abrahams 1979). In the case of $\text{Tb}_2(\text{MoO}_4)_3$, the temperature dependence of the spontaneous strain is identical to that of the normalized spontaneous polarization (Abrahams *et al.* 1980). The MoO_4^{2-} ions in $\text{Tb}_2(\text{MoO}_4)_3$ rotate as much as 8° in the 136 K interval below the high temperature onset of ferroelasticity, as the cations become displaced less than 0.08 \AA , for a thermal coefficient of $5.4 \times 10^{-4} \text{ \AA K}^{-1}$. The decrease in Δ for each atom in $\text{Tb}_2(\text{MoO}_4)_3$ varies considerably over the two measurement temperatures, but the average value is very close to the corresponding decrease

in spontaneous strain and polarization. Similar structural and strain measurements on other ferroelastic crystals as a function of temperature are necessary.

Piezoelectric strain. Investigation of the thermal dependence of piezoelectric strain on atomic location displacement has still to be undertaken successfully. It is expected that application of pulsed electric fields and simultaneous structure factor determination in the course of the converse piezoelectric effect will give more readily interpretable results. A previous study predicted relative atomic displacements of about $(0.1-3) \times 10^{-4} \text{ \AA}$ under a tensile stress of 10^6 N m^{-2} (Abrahams 1978): LiIO_3 , for example, with $d_{33} = 46 \text{ pC N}^{-1}$ at room temperature, has been calculated to have an ionic displacement of $1.9 \times 10^{-4} \text{ \AA}/10^6 \text{ N m}^{-2}$, assuming rigid ions and point charges. Similarly, $\text{K}_2\text{Cd}_2(\text{SO}_4)_3$ with $d_{14} = +7.3 \text{ pC N}^{-1}$ at room temperature (Lissalde *et al.* 1979) is estimated to have an average ionic displacement of $0.4 \times 10^{-4} \text{ \AA}/10^6 \text{ N m}^{-2}$ at this temperature. If these crystals have piezoelectric strain thermal coefficients similar to the average value of about $40 \times 10^{-4} \text{ K}^{-1}$ in Table 4, the resulting ionic displacements would be expected to change by about 40% in magnitude, for the same stress and temperature interval of 100 K. Comparable displacements are predicted for electric fields of about 10^6 V m^{-1} .

Dielectric permittivity. Experimental correlations between dielectric permittivity thermal coefficients, as given in Table 5, and the atomic location thermal coefficients remain to be investigated. Scaling considerations suggest relationships to the atomic location thermal coefficients similar to those for the preceding properties. A series of thermodynamic relationships connect many basic physical properties, as shown by Nye (1957), such as

$$\epsilon_{ij}^T - \epsilon_{ij}^S = -d_{ikl} d_{jmn} c_{klmn},$$

where ϵ_{ij}^T is the dielectric permittivity at constant strain, ϵ_{ij}^S is the permittivity at constant stress, d_{ikl} is the piezoelectric strain coefficient and c_{klmn} is the elastic stiffness, all at constant temperature. Such relationships will provide rigorous tests of any correlations found with atomic location thermal coefficients.

Electrostriction, electro- and piezo-optical properties. Second order effects such as those arising from a permittivity dependence on applied electric fields or stresses can similarly be related thermodynamically. The magnitudes of the thermal coefficients in Tables 6-8 also scale with those of atomic location in Table 1, but experimental studies of the interrelationships remain to be made.

Thermal expansion and refractive index. The decrease in expansion and refractive index thermal coefficients by two orders of magnitude, as compared with those of the preceding properties (see Tables 9 and 10), suggests a difference in origin. In principle, the refractive index temperature dependence is linearly related to that of the dielectric permittivity except for the different frequency ranges in which the properties are measured. Dielectric permittivities are determined well below the optic mode frequency, whereas the refractive index is measured well above. The ionic contribution predominates below the optic mode, the remaining electronic contribution to both properties becoming much less above these frequencies.

13. Conclusions

A fuller understanding of materials possessing structure sensitive properties with notable thermal dependence, such as those given in Tables 1-8, is contingent upon

their structural determination as a function both of temperature and field (electric and stress). Such studies constitute an important, but presently undeveloped branch of structural science. It is predicted that this new branch will shortly burgeon.

Acknowledgment

It is a pleasure to thank Dr D. F. Nelson for a valuable discussion on refractive index and dielectric permittivity thermal dependence.

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