ELSEVIER

Thermochimica Acta 318 (1998) 245–249

thermochimica acta

# Measurements of heats of complex association and of solution/substitution in solids by DSC (differential scanning calorimetry)

E.A. Secco*

*Department of Chemistry, St. Francis Xavier University, Antigonish, NS, B2G 2W5, Canada*

Received 28 July 1997; accepted 19 January 1998

## Abstract

Some solid–solid phase transitions yield a structure accompanied by a high conductivity, viz. fast-ion conduction. Our efforts are focused on 'locking-in' or preserving the high conductivity structure by the incorporation of appropriate guest ions. Differential scanning calorimetry (DSC) is used to quantitatively monitor the progress of this structure stabilization or guest–host interaction effects. The DSC data are used to calculate fundamental thermodynamic quantities, viz. heat of transition, heat of complex association, partial molar heat of solution/substitution at infinite dilution $\chi$, the change in heat content/enthalpy of the host lattice $\Delta H_s^0$ and the 'recovered lattice energy', $\Delta H_L^0$. © 1998 Elsevier Science B.V.

*Keywords:* Heat of solution; Heat of complex association; Heat of phase transition in solids

## 1. Introduction

Fast-ion transport/conductivity in a number of solids at ambient or elevated temperatures has been found to be comparable to that of liquid electrolytes and also to be of the same order of magnitude as the electronic conductivity in semiconductors. This phenomenon of solid-state fast-ion conductivity is a rapidly developing field with promising applications for use in electrochemical devices. Some compounds undergo a solid–solid phase transition accompanied by a significant jump in conductivity while attaining fast-ion transport values. In our pursuit of fast-ion composition at lower temperatures, we set out to 'lock-in' or preserve the high-temperature high-conductivity structure by the incorporation of appropriate guest ions.

Differential scanning calorimetry (DSC) is used to screen the compositions for phase-transition behavior and to quantitatively monitor the progress of structure stabilization as a function of guest-ion concentration. The quantitative calorimetric data can be related to aspects of solid–solid interaction and the impact of the guest ion on the host lattice and its eventual correlation with its effect on ion conductivity.

Our studies concentrated on two host compounds, sodium sulfate ($Na_2SO_4$) and thallium iodide ($T\ell I$), possessing contrasting molecular formulas, crystalline structures, ionic masses and ionic radii along with volume effects on phase transition. This report mainly deals with the enthalpic effects of incorporating some guest ions in these two host lattices.

---

*Corresponding author.

*PII* S0040-6031(98)00349-9

## 2. Experimental

$Na_2SO_4$ and its guest components along with T$\ell$I guest components were supplied by Alfa Products (Thiokol/Ventron Division, Danvers, MA) with specified grades between 99.9% and 99.999$^+$%. T$\ell$I with specified grade 99.999% was supplied by Aldrich, Milwaukee, WI. All samples were prepared by fusing in air the requisite composition mixture of the respective compounds, previously well ground manually, at 50–70 K above its reported melting point, or the melting temperature determined by DTA, in a covered platinum crucible. The fused product in each case appeared as a solid solution/reaction product and was confirmed by its DTA effects.

Thermal analyses of the samples were performed on a DuPont 1090B thermal analyzer equipped with disk memory and data analyzer. Calorimetry measurements were carried out using gold or aluminum pans with the DSC cell. The enthalpies of transition were evaluated after calibration with the heats of fusion or transition of different reference materials, viz. In, Sn, Zn.

## 3. Results and discussion

### 3.1. *Thallium iodide (T$\ell$I)*

Yellow, room-temperature β-T$\ell$I, a double-layered orthorhombic structure related to NaCl [1], transforms to red α-T$\ell$I with a *Pm*3*m* CsCl-type cubic structure at 172°C with transition enthalpy $\Delta H_t$=865 K/mol. The high-temperature cubic structure was stabilized/preserved to room temperature by incorporating 5 mol% $Rb^{2+}$ [2] and 7.5 mol% $Cs^{3+}$ [3]. In other words, 5 mol% $Rb^+$ or 7.5 mol% $Cs^+$ provided the energy of 865 J/mol required to stabilize the *Pm*3*m* CsCl cubic structure of T$\ell$I at room temperature. X-ray diffraction patterns confirmed the cubic structure of T$\ell$I at room temperature in both cases.

Solubility of a solute in a solvent is the practical quantity of interest, but the quantity of thermodynamic and more theoretical interest is the heat or energy of solution. That is to say, one considers the heats of solution in terms of $T\ell^+$ rearrangement which attends the incorporation of $Rb^+$ or $Cs^+$ into the T$\ell$I lattice. To obtain the heat of solution, we proceed by determining the heat of reaction in which 1 mol of guest ($Rb^+$, $Cs^+$) dissolves in an infinite amount of host (T$\ell$I); this is the partial molar heat of solution of the guest/solute in the host/solvent at infinite dilution. This quantity of heat leads to the extra energy required to replace the lattice $T\ell^+$ by an $Rb^+$ or $Cs^+$ ion.

The chemical reaction of dissolving $x$ mol of RbI in T$\ell$I is written as

$$x\mathrm{RbI}_{(c)} + (1-x)\mathrm{T\ell I}_{(c)} \rightarrow \mathrm{Rb}_x\mathrm{T\ell}_{1-x}\mathrm{I}_{(c)} + \Delta H \tag{1}$$

When $x$ is small, $\Delta H/x$ is the partial molar heat of solution at infinite dilution which can be rigorously expressed as

$$\left(\frac{\partial(\Delta H)}{\partial x}\right)_{x=0} = \lim_{x\to 0}\frac{\Delta H}{x} \equiv \chi \tag{2}$$

In terms of the heats of formation of the reactants and product, one writes

$$\begin{aligned}\chi &= \lim_{x\to 0}\frac{1}{x}[\Delta H_f^0(\mathrm{Rb}_x\mathrm{T\ell}_{1-x}\mathrm{I}) - (1-x)\Delta H_f^0(\mathrm{T\ell I}) \\ &\quad - x\Delta H_f^0(\mathrm{RbI})] \\ &= \lim_{x\to 0}\frac{\Delta H_f^0(\mathrm{Rb}_x\mathrm{T\ell}_{1-x}\mathrm{I}) - \Delta H_f^0(\mathrm{T\ell I})}{x} \\ &\quad + \Delta H_f^0(\mathrm{T\ell I}) - \Delta H_f^0(\mathrm{RbI}) = \Delta H_s^0 \\ &\quad + \Delta H_f^0(\mathrm{T\ell I}) - \Delta H_f^0(\mathrm{RbI})\end{aligned}$$

or

$$\Delta H_s^0 = \chi - \Delta H_f^0(\mathrm{T\ell I}) + \Delta H_f^0(\mathrm{RbI}) \tag{4}$$

where $\Delta H_s^0$ is the change in heat content of the T$\ell$I lattice per mole of substituted RbI or the heat of the reaction

$$x\mathrm{RbI}_{(c)} + \mathrm{T\ell I}_{(c)} \rightarrow \mathrm{Rb}_x\mathrm{T\ell}_{1-x}\mathrm{I}_{(c)} + x\mathrm{T\ell I}_{(c)} \tag{5}$$

The $\Delta H_f^0$ quantities are taken to be the heats/enthalpies of formation from the elements in their standard thermodynamic states.

Beside the heat/enthalpy of solution of or substitution, since it is the change of T$\ell$I heat content resulting from the substitution of RbI per mole of RbI, one can view $\Delta H_s^0$ as another interesting quantity, the 'recovered lattice energy', $\Delta H_L^0$. If one accepts the solution process as the destruction of 1 mol of RbI lattice and the creation of a new imperfect lattice, we want to know how much new lattice energy has been produced to compensate for the loss of the old, i.e.

$$\Delta H^0_{\mathrm{L}} = \chi - \Delta H^0_{\mathrm{fL}}(\mathrm{T}\ell\mathrm{I}) + \Delta H^0_{\mathrm{fL}}(\mathrm{RbI}) \qquad (6)$$

where $\Delta H^0_{\mathrm{fL}}(\mathrm{T}\ell\mathrm{I})$ and $\Delta H^0_{\mathrm{fL}}(\mathrm{RbI})$ are the heats of formation of the lattice from gas-phase ions, i.e. $U_{\mathrm{L}} = -\Delta H^0_{\mathrm{fL}}$

Knowing that 5 mol% RbI and 7.5 mol% CsI stabilize T$\ell$I in the CsCl cubic structure requiring 865 J mol$^{-1}$, we have

$$\chi = \lim_{x\to 0}\frac{\Delta H}{x} = \frac{+865\,\mathrm{J\,mol^{-1}}}{0.05}$$
$$= +17\,300\,\mathrm{J\,mol^{-1}} = +17.3\,\mathrm{kJ\,mol^{-1}} \text{ for RbI}$$

and

$$\chi = +11\,533\,\mathrm{J\,mol^{-1}} = +11.5\,\mathrm{kJ\,mol^{-1}} \text{ for CsI}$$

Using the appropriate $\Delta H^0_{\mathrm{f}}$ values [4] inserted in Eq. (4), we obtain $\Delta H^0_{\mathrm{s(RbI)}} = -191.1$ kJ mol$^{-1}$ and $\Delta H^0_{\mathrm{s(CsI)}} = -209.7$ kJ mol$^{-1}$. Also inserting the appropriate $\Delta H^0_{\mathrm{fL}}$ values [4] in Eq. (6), we obtain the recovered lattice energy, $\Delta H^0_{\mathrm{L}}$, for each case, viz. $\Delta H^0_{\mathrm{L(RbI)}} = -29.5$ kJ mol$^{-1}$ and $\Delta H^0_{\mathrm{L(CsI)}} = -49.5$ kJ mol$^{-1}$.

In some respects, T$\ell^+$ resembles the alkali metals, especially Rb$^+$ and Cs$^+$ [1]. On this basis, the presence of RbI or CsI in T$\ell$I can be considered an extension of a mixed halide system. Values of $\chi$, $\Delta H^0_{\mathrm{s}}$, $\Delta H^0_{\mathrm{L}}$, and $-\Delta H^0_{\mathrm{fL}}$ for RbI–T$\ell$I, CsI–T$\ell$I, and NaI–KI binary systems are given in Table 1. The $\chi$ and $\Delta H^0_{\mathrm{L}}$ values appear to be consistent within reasonable limits for the three systems. However, the values of $\Delta H^0_{\mathrm{s}}$ for the T$\ell$I crystal are beyond limits of comparison with NaI and KI. In the comparison, one does not take into account the host structure where the NaCl structure is in strong contrast to the CsCl structure.

Table 1
Comparison of Heats of Solution (kJ mol$^{-1}$) of RbI and CsI in T$\ell$I with some mixed alkali iodides

| Solvent (host) | Solute (guest) | $\chi$, solute | $\Delta H^0_{\mathrm{L}}$ | $\Delta H^0_{\mathrm{s}}$ | $\Delta H^0_{\mathrm{fL}}$, solvent |
|---|---|---|---|---|---|
| T$\ell$I | RbI | 17.3 | −29.5 | −191.1 | 663.5 |
| T$\ell$I | CsI | 11.5 | −49.2 | −209.7 | 663.5 |
| NaI | KI | 13.4 | −42.2 | 67.9 | 682.8 |
| KI | NaI | 9.6 | 65.3 | −37.7 | 627.2 |

Studies are now in progress in an effort to stabilize the CsCl structure of T$\ell$I with anions, such as Br$^-$, Cl$^-$, and NO$_3^-$ to obtain $\chi$, $\Delta H^0_{\mathrm{s}}$, and $\Delta H^0_{\mathrm{L}}$ values. Preliminary results indicate a similar trend with interesting secondary effects where anions replace I$^-$ in T$\ell$I crystal [5].

### 3.2. *Na$_2$SO$_4$*

The success of the thermodynamic analysis on the substitution of an impurity/dopant of the same charge in T$\ell$I prompted us to revisit our earlier studies and to analyze the results of the incorporation of K$^+$, MoO$_4^=$, and Cs$^+$ as guest ions in Na$_2$SO$_4$.

The $\Delta H$ values accompanying the III–I phase transformation [6] for pure Na$_2$SO$_4$ and K-doped 0.8 mol% K$_2$SO$_4$ are given in Table 2. The dopant effected a lowering of the transition enthalpy by 0.84 kJ mol$^{-1}$ or 840 J mol$^{-1}$. The difference in $\Delta H$ is interpreted as a contribution to the stability of phase I relative to phase III. In order words, the partial molar heat of solution at infinite dilution, $\chi$, is calculated from Eq. (2) as

$$\chi = \lim_{x\to 0}\frac{\Delta H}{x} \equiv \frac{0.84\,\mathrm{kJ\,mol^{-1}}}{0.008} = +105\,\mathrm{kJ\,mol^{-1}}$$

Inserting the appropriate $\Delta H^0_{\mathrm{f}}$ values in Eq. (4), we obtain the change in heat content of the Na$_2$SO$_4$ lattice per mole of substituted K$_2$SO$_4$, $\Delta H^0_{\mathrm{s}}$,

$$\Delta H^0_{\mathrm{s}} \equiv \chi - \Delta H^0_{\mathrm{f}}(\mathrm{Na_2SO_{4,III}} + \Delta H^0_{\mathrm{f}}(\mathrm{K_2SO_4})$$
$$= 105 - (-1380.7) + (-1433.5)$$
$$= +52\,\mathrm{kJ\,mol^{-1}}$$

In the study on the effects of mixed anion in Na$_2$SO$_4$, we reported [7] that for MoO$_4^=$-doped Na$_2$SO$_4$, 50 mol% Na$_2$MoO$_4$ stabilized the Na$_2$SO$_4$(I) structure. That is, the presence of 0.5 mol MoO$_4^=$ in the SO$_4^=$ sublattice provided 7.03 kJ/mol of energy to stabilize phase I. Using the same approach described

Table 2
Transition temperature and $\Delta H$ (kJ mol$^{-1}$). Data of pure and K-doped Na$_2$SO$_4$

| | $T_{\mathrm{t}}$/K | $\Delta H$ | Transition |
|---|---|---|---|
| Pure Na$_2$SO$_4$ | 514 | 7.03 | III–I |
| K-doped Na$_2$SO$_4$ (0.8 mol%) | 506–508 | 6.19 | III–I |

above, we obtain $\chi$=14.0 kJ mol$^{-1}$ and $\Delta H_{\rm s}^0 = -144.0$ kJ mol$^{-1}$, where $\Delta H_{\rm f}^0(\mathrm{Na_2SO_4, III}) = -1380.7$ kJ mol$^{-1}$ and $\Delta H_{\rm f}^0(\mathrm{Na_2MoO_4, II}) = -1539.3$ kJ mol$^{-1}$. Inserting in Eq. (6) the heats of formation of the lattice from gas-phase ions for $Na_2SO_4$, $K_2SO_4$, and $Na_2MoO_4$, i.e. $\Delta H_{\rm fL}^0(\mathrm{Na_2SO_4})$, $\Delta H_{\rm fL}^0(\mathrm{K_2SO_4})$, $\Delta H_{\rm fL}^0(\mathrm{Na_2MoO_4})$, where $U_{\rm L} = -\Delta H_{\rm fL}^0$, we obtain the 'recovered lattice energy' $\Delta H_{\rm L}^0$.

Almost all the solubility studies, experimental and theoretical, of impurity/guest ions in crystals relating to heat of solution/substitution have been on alkali halides. We are unaware of similar studies on sulfate systems which precludes any comparison with our $\chi$ and $\Delta H_{\rm s}^0$ as with the iodides in Table 1. The $\chi$ and $\Delta H_{\rm s}^0$ involving $\mathrm{MoO_4^=}$ appear to be consistent within reasonable limits for the T$\ell$I case. And the $\Delta H_{\rm s}^0$ values for $K^+$ are consistent within limits for the substitution of $K^+$ in NaI. Are these consistencies genuine or fortuitous? The $\chi$ value for $K^+$ on the other hand seems unreasonably high.

Studies on the $Na_2SO_4$–$Cs_2SO_4$ binary system [8], where both sulfates exhibit polymorphism, reveal novel solid–solid interaction such as cluster formation or complex association. We focus on enthalpy values identified with two endotherms of this system at 250°C and 400°C.

Fig. 1 shows the transition enthalpies $\Delta H_{\rm t}$ at 250°C and 400°C and their dependence on mole fraction of $Cs_2SO_4$. The 400°C endotherm maximum $\Delta H_{\rm t}$ value occurs at 1 : 1 mol ratio, i.e. $NaCsSO_4$ composition. However, $\Delta H_{\rm t}$ values for the 250°C endotherm due to the III→I $Na_2SO_4$ transition exhibit accelerated decline relative to its fractional presence. Also, the $\Delta H_{\rm t}$ values for the 400°C endotherm associated with $NaCsSO_4$ show an accelerated rise relative to this fractional presence. Assigning $\Delta H_{250}^E$ to the difference between the expected enthalpy for fraction of $Na_2SO_4$ III→I transition $\Delta H_{\rm t}$ and the experimentally observed enthalpy for the given composition $\Delta H_2$, i.e. $\Delta H_{250}^E = \Delta H_1 - \Delta H_2$, we calculate the enthalpy for the fraction of $NaCsSO_4$ formed using 2.42 kJ mol$^{-1}$ of pure $NaCsSO_4$ $\Delta H_3$ and also the enthalpy for the association complex between β-$NaCsSO_4$ and excess $Na_2SO_4$I from $\Delta H_{250}^E = \Delta H_3 + \Delta H_4$. These $\Delta H$ values are given in Table 3 and plotted in Fig. 2. The maximum $\Delta H$ for complex association near $x_{\mathrm{Cs_2SO_4}} = 0.25$ suggests a 1 : 1 complex, i.e. $NaCsSO_4 : Na_2SO_4$ indicating preferential reaction with $Na_2SO_4$I. No complex association between $NaCsSO_4$ and excess $Cs_2SO_4$ is evident at 250°C.

The 400°C endotherm is attributed to the combined solid phase transition β→α in $NaCsSO_4$ and a complex association of α-$NaCsSO_4$ with excess $Na_2SO_4$. Taking $\Delta H_1$ as the expected enthalpy for the fraction of $NaCsSO_4$ β→α transition using 4.45 kJ mol$^{-1}$ for pure $NaCsSO_4$ and $\Delta H_2$ as the experimentally

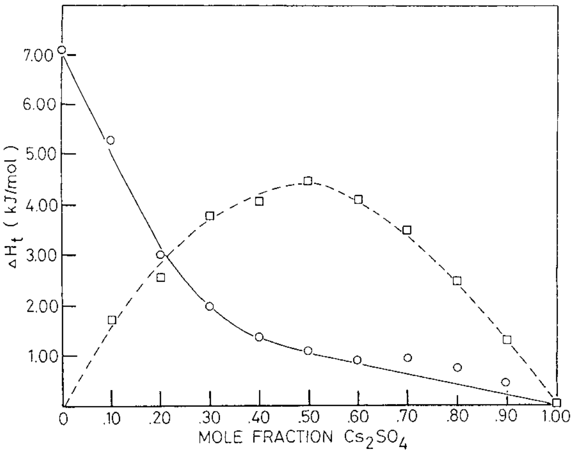

Fig. 1. Plots of $\Delta H$ values vs. $Cs_2SO_4$ mole fraction for observed thermal effects: (○), $\Delta H_2$ from Table 3; and (□), $\Delta H_2$ from Table 4.

Table 3
Enthalpy values (kJ/mol) for transition at 250°C

| Mole fraction $Na_2SO_4$ | $\Delta H_1$ [a] | $\Delta H_2$ [b] | $\Delta H_{250}^E$ [c] | $\Delta H_3$ [d] | $\Delta H_4$ [e] |
|---|---|---|---|---|---|
| 1.00 | 7.03 | 7.03 | — | — | — |
| 0.90 | 6.33 | 5.25 | 1.08 | 0.48 | 0.60 |
| 0.80 | 5.62 | 3.00 | 2.62 | 0.96 | 1.66 |
| 0.70 | 4.92 | 2.00 | 2.92 | 1.44 | 1.48 |
| 0.60 | 4.22 | 1.40 | 2.82 | 1.93 | 0.89 |
| 0.50 | 3.52 | 1.10 | 2.42 | 2.42 | — |
| 0.40 | 2.80 | 0.90 | 1.91 | 1.93 | — |
| 0.30 | 2.11 | 0.85 | 1.26 | 1.44 | — |
| 0.20 | 1.46 | 0.55 | 0.91 | 0.96 | — |
| 0.10 | 0.71 | 0.45 | 0.25 | 0.48 | — |

[a] Expected enthalpy for fraction of $Na_2SO_4$III→I transition using 7.03 kJ/mol for $Na_2SO_4$.

[b] Experimentally observed enthalpy for the composition cited.

[c] $\Delta H_1 - \Delta H_2$.

[d] Calculated enthalpy for fraction of $NaCsSO_4$ formed using 2.42 kJ/mol for pure $NaCsSO_4$.

[e] Enthalpy calculated for the association complex between β-$NaCsSO_4$ and excess $Na_2SO_4$.

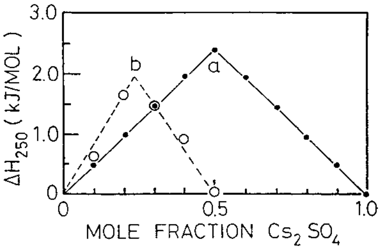

Fig. 2. Plots of $\Delta H$ values vs. mole fraction $Cs_2SO_4$ for thermal effects occurring at 250°C: plot a, $\Delta H_3$, plot b, $\Delta H_4$ from Table 3.

Table 4
Enthalpy values (kJ/mol) for transition at 400°C

| Mole fraction $Na_2SO_4$ | $\Delta H_1$ [a] | $\Delta H_2$ [b] | $\Delta H^E_{400}$ [c] |
|---|---|---|---|
| 1.00 | — | — | — |
| 0.90 | 0.89 | 1.60 | 0.71 |
| 0.80 | 1.78 | 2.90 | 1.12 |
| 0.70 | 2.67 | 3.75 | 1.08 |
| 0.60 | 3.57 | 4.10 | 0.53 |
| 0.50 | 4.45 | 4.45 | 0 |
| 0.40 | 3.57 | 4.10 | 0.53 |
| 0.30 | 2.67 | 3.50 | 0.83 |
| 0.20 | 1.78 | 2.50 | 0.72 |
| 0.10 | 0.89 | 1.25 | 0.36 |

[a] Expected enthalpy for the fraction of $NaCsSO_4$ β→α transition using 4.45 kJ/mol for pure $NaCsSO_4$.
[b] Experimentally observed enthalpy for the composition cited.
[c] Enthalpy calculated for the association complex between α-$NaCsSO_4$ and excess $Na_2SO_4$ or excess $Cs_2SO_4$.

observed enthalpy for the given composition, we calculate the enthalpy for the association complex $\Delta H^E_{250}$ between α-$NaCsSO_4$ and excess $Na_2SO_4$I or excess β-$Cs_2SO_4$, i.e. $\Delta H^E_{250} = \Delta H_2 - \Delta H_1$. These $\Delta H$ values are given in Table 4 and plotted in Fig. 3. The maximum near $x_{Cs_2SO_4} = 0.25$ confirms the existence of the complex $NaCsSO_4 : Na_2SO_4$ and the maximum near $x_{Cs_2SO_4} = 0.75$ indicates the existence of the complex $NaCsSO_4 : Cs_2SO_4$. It is interesting to note the greater stability of the complex β-$NaCsSO_4 : Na_2SO_4$ relative to α-$NaCsSO_4 : Cs_2SO_4$.

Physico-chemical studies of the solid state usually involve impurities in crystals to some degree. A large class of phenomena and useful solid-state devices depend on impurity or the presence of dopant. The sub-solidus portion of phase diagrams of many binary systems is a relatively unexplored area of solid–solid interactions. Our knowledge on such interaction in polymorphic systems and of structurally different simple inorganic solids is somewhat lacking, as evidenced by a number of studies [9–11]. Studies already initiated on other parallel systems are TINO–RbNO, $TINO_3$–$CsNO_3$ and $NH_4NO_3$–$KNO_3$. Knowledge of these interactions and their resultant properties can be rewarding and lead to useful application. This report illustrates a somewhat novel approach by phase-transition studies to obtain pertinent thermodynamic data and to characterize solid interactions by using DSC.

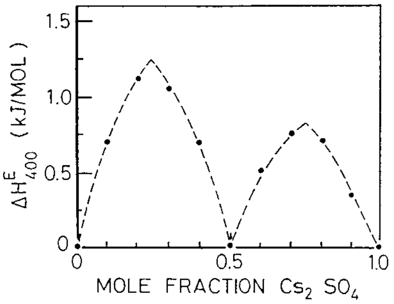

Fig. 3. Plot of $\Delta H^E_{400}$ vs. mole fraction $Cs_2SO_4$ from Table 4.

## Acknowledgements

Support for these studies from the Natural Research Council of Canada, the Natural Sciences and Engineering Research Council of Canada and the American Chemical Society–Petroleum Research Fund is gratefully acknowledged.

## References

[1] N.N. Greenwood, A. Earnshaw, Chemistry of the Elements, Pergamon Press, New York, 1984, p. 272.
[2] P.-N. Huang, E.A. Secco, J. Sol. Stat. Chem. 103 (1993) 314.
[3] E.A. Secco, Anita Sharma, J. Phys. Chem. Solids 56 (1995) 251.
[4] E.A. Secco, J. Phys. Chem. B101 (1997) 1641.
[5] E.A. Secco, Sol. Stat. Commum. 104 (1997) 485.
[6] R. MacL. Murray, E.A. Secco, Can. J. Chem. 56 (1978) 2616.
[7] U.M. Gundusharma, E.A. Secco, Can. J. Chem. 65 (1987) 1205.
[8] K.G. MacDonald, C. MacLean, E.A. Secco, Can. J. Chem. 66 (1988) 3134.
[9] J.M. Rowe, J.J. Rush, D.G. Hinks, S. Susman, Phys. Rev. Lett. 43 (1979) 1158.
[10] K.H. Michel, J.M. Rowe, Phys. Rev. B22 (1990) 1417.
[11] D. Civera García, K. Knorr, A. Loidl, S. Haussühl, Phys. Rev. B36 (1987) 8517.