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Ionic Conductivity of Pure and Ca^{2+}- and Sr^{2+}-Doped Single Crystals of LiCl

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Single crystals of pure and doped LiCl were grown by the Bridgman technique. The ionic conductivity of pure and Ca^{2+}- and Sr^{2+}-doped crystals of LiCl in the temperature range 250–580°C have been reported. The enthalpy of formation of Schottky defects, enthalpy of migration of Li vacancy, and enthalpy of association of (Sr^{2+} ion–Li vacancy) have been calculated by detailed isotherm calculation. The various conductivity parameters are: Enthalpy of formation of Schottky defects: 1.66 ± 0.03 eV; Enthalpy of migration of Li vacancy: 0.59 ± 0.03 eV; Enthalpy of association between Sr^{2+} and Li vacancy: 0.61 ± 0.02 eV.

Introduction

Measurement of ionic conductivity (*1*, *2*) as a function of temperature is an important technique for studying ionic transport in ionic solids. Electrical conductivity has been widely studied with a number of alkali halides, but, due to its extremely hygroscopic nature, the ionic conductivity of lithium chloride has not been investigated in depth. Haven (*3*) in the fifties had studied the ionic conductivity of Mg^{2+}-doped LiCl crystals along with other lithium halides. He used unpurified material for growing crystals and while measuring the conductivity he distorted the crystal by as much as 20%. Further, he did not analyze the conductivity data to evaluate the association parameters (*4*, *5*). Pataloni and Gaune (*6*) have measured the electrical conductivity of Ca^{2+}-doped LiCl and calculated the enthalpy of formation and migration of defects, without doing any isotherm calculation from the conductivity data (*4*). The present work, on the other hand, presents the results of a somewhat detailed study of the ionic conductivity of pure and Ca^{2+}- and Sr^{2+}-doped crystals of LiCl with different dopant's concentrations. The conductivity data have been analyzed by using the general isotherm equation (*7*) to evaluate the various conductivity parameters.

Experimental Procedure

(*i*) *Preparation of single crystals of LiCl*

Anhydrous LiCl (GR Loba Chemicals) was further purified by extracting with 8-hydroxyquinoline (*8*). The solvent-extracted solution was evaporated in a Teflon bottle under vacuum. It was dehydrated in the Teflon bottle for 36 hr at 150°C and then at 200°C in vacuum. This was further dehydrated at 500°C by treating it with anhydrous HCl. Finally it was zone purified (*9*). Zone purification was carried out in an HCl/N_2 atmosphere. The molten zone's

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length was about 2 cm. Five passes were made with a speed 2 cm/hr. No reaction between Pyrex glass and LiCl melt was observed. This was confirmed by the analysis of the material. From the zone-purified material, single crystals were grown by the Bridgman technique in a Pyrex glass container in HCl/N_2 atmosphere. The surface temperature of the Pyrex glass was never allowed to exceed 680°C. Ca^{2+}- and Sr^{2+}-doped LiCl single crystals were prepared by adding the required amount of $CaCl_2$ or $SrCl_2$ respectively to the purified LiCl solution. The resulting solution was evaporated, dehydrated, treated with anhydrous HCl and finally single crystals were grown as described earlier. From the central portion of the bigger single crystal, crystal chips for the conductivity measurement were cleaved. The usual size of the crystal chips used for the conductivity measurements were about $5 \times 5 \times 2$ mm^3. The portion adjacent to the crystal chips selected for the conductivity measurements were used for the determination of dopant's concentration, by atomic absorption spectrometry. A single crystal of pure LiCl showed an absence of any detectable amount of sodium (<0.1 ppm) and was almost free from aluminum (0.1 ppm). This result suggested the absence of any substantial contamination of sodium from the pyrex glass.

(*ii*) *Conductivity Measurements*

The ac conductivity of crystals annealed for 12 hr at 500°C were measured by a simple conductivity bridge at a frequency of 1 KHz (Ajco conductivity bridge, India). The crystal was sandwiched between the two platinum disk electrodes by a spring action. The conductivity was measured (*5*) for several heating and cooling cycles. The crystal containing large concentration of dopant showed some hysteresis. Conductivity results where the hysteresis was apparent were neglected for the conductivity data analysis. The measurements were recorded only when the crystal showed a constant conductivity value for a particular temperature within the experimental error. All the conductivity measurements were made under the continuous flow of dry and oxygen-free nitrogen by bubbling the gas through paragallol solution, $CaCl_2$ (anhydrous), conc. H_2SO_4, and dry KOH pellets. Due to its highly hygroscopic nature of LiCl, the handling of LiCl was always done in a dry nitrogen atmosphere in the drybox. The temperature of the crystal was measured by the two independent chromel/alumel thermocouples, one kept closed and other diagonally opposite to the crystal. Temperatures shown by these thermocouples did not differ by more than 2°C at the highest temperatures. The conductivity values were reproducible for several cooling/heating cycles.

(*iii*) *Analysis of the Results*

The plot of log σT vs $1/T$ for pure LiCl shows a break at 704 K (Fig. 1). At high temperatures (i.e., above 833 K, in the intrinsic region of the conductivity plot) a

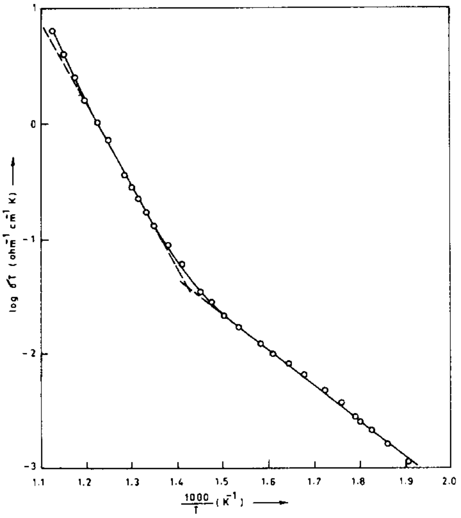

FIG. 1. Logarithm of conductivity multiplied by absolute temperature of pure LiCl single crystal (log σT) as a function of $1000/T$.

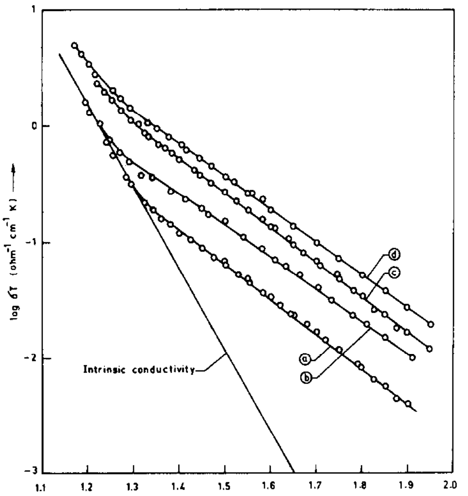

FIG. 2. Conductivity of LiCl single crystals doped with Ca^{2+}: (a) 207 ppm Ca^{2+}, (b) 307 ppm Ca^{2+}, (c) 475 ppm Ca^{2+}, (d) 929 ppm Ca^{2+}.

slight curvature is apparent, but the conductivity data below this temperature in the intrinsic region can be fitted to a very good straight line. From the measurements of conductivity data of four pure LiCl single crystals, the conductivity in the intrinsic region was found to follow the following equation:

$$\sigma T = 5.6 \times 10^8 \exp(-1.42\,\mathrm{eV}/KT).$$

From this equation, conductivities in the low-temperature region (intrinsic) were calculated which were used for the subsequent isotherm analysis. Figures 2 and 3 show the plots of log σT versus $1/T$ for Ca^{2+}- and Sr^{2+}-doped LiCl crystals, respectively. If association between divalent ion and cation is absent, then the slope of the extrinsic region should be equal to the enthalpy of migration of Li vacancy (*10*). To evaluate the enthalpy of migration of Li vacancy from the extrinsic region one should, therefore, confirm the absence of the association complex between the divalent ion and the Li vacancy. This can be done by the methods, discussed here. Plots were made with log σ_C against C (the concentration of dopant) at a constant temperature for Ca^{2+}- and Sr^{2+}-doped crystals (Figs. 4 and 5). All plots with Ca^{2+}-doped crystals are found to give a straight line (Fig. 4). This suggests that in the temperature range, 555–638 K there is no association between Ca^{2+} and Li vacancy. Therefore from the slopes of these linear plots, for this temperature region, an average value of the enthalpy of the migration of cation vacancy was calculated (Table I). The interesting fact of the conductivity isotherms (Fig. 4) is that all

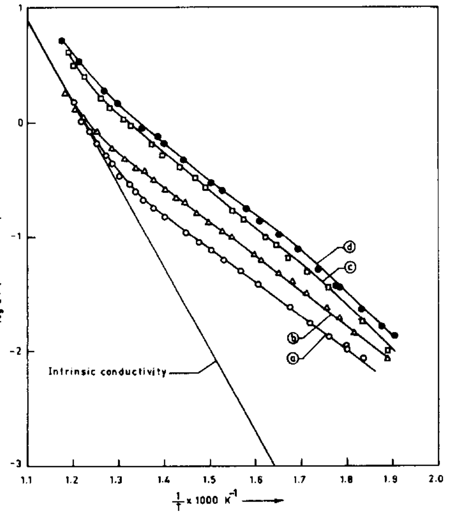

FIG. 3. Conductivity of LiCl single crystal doped with Sr^{2+}: (a) 251 ppm Sr^{2+}, (b) 495 ppm Sr^{2+}, (c) 1175 ppm Sr^{2+}, (d) 1716 ppm Sr^{2+}.

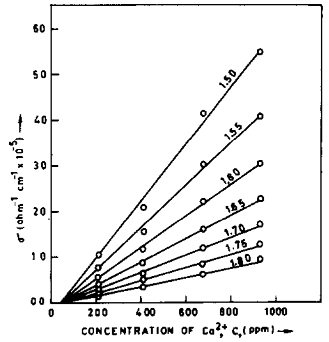

FIG. 4. Isotherms in extrinsic region of Ca^{2+}-doped LiCl single crystal. The number on the isotherms are the values of $1000/T$.

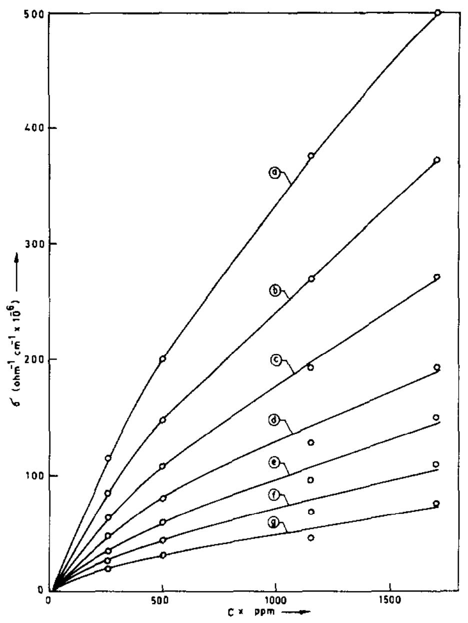

FIG. 5. Isotherms in the extrinsic region for Sr^{2+}-doped single crystals: (a) $100/T = 1.5$ K^{-1}, (b) $1000/T = 1.55$ K^{-1}, (c) $1000/T = 1.60$ K^{-1}, (d) $1000/T = 1.65$ K^{-1}, (e) $1000/T = 1.7$ K^{-1}, (f) $1000/T = 1.75$ K^{-1}, (g) $1000/T = 1.8$ K^{-1}.

the isotherms meet at a positive axis of concentration at 40 ppm of Ca^{2+}. This indicates that the Ca^{2+}-doped crystals contain some aliovalent anion impurities, which associate with the Ca^{2+} ion thereby nullifying the effect of Ca^{2+} impurities equivalent to 40 ppm of Ca^{2+}. For all other analyses, this amount of impurity was, therefore, subtracted from the analytically determined Ca concentration.

TABLE I

ENTHALPY OF MIGRATION OF Li VACANCY IN Ca^{2+}-DOPED LiCl SINGLE CRYSTALS

Concentration of Ca^{2+} (ppm)	Enthalpy (eV)
Pure	0.61
207	0.64
407	0.55
675	0.60
929	0.56
Mean	0.59 ± 0.03

The plots of log σ_C vs C, for Sr^{2+}-doped crystals are all parabolic (Fig. 5) indicating the association between Sr^{2+} and Li vacancy. Here, also, all isotherms meet at a point in a positive axis of concentration at 20 ppm. This indicates that aliovalent anion impurities effectively shield the effect of Sr^{2+} ion by an amount equivalent to 20 ppm of Sr^{2+}.

Since the plots of log σ_C versus C isotherms are parabolic (Fig. 5) it is unrealistic to evaluate the enthalpy of association of cation with Li vacancy by fitting a straight line in the extrinsic region of the conductivity of Sr^{2+}-doped crystals (Fig. 3). In such cases conductivity parameters can be determined by a detailed conductivity analysis using the general isotherm (*7*):

$$\frac{C}{\sigma_C/\sigma_0 - \sigma_0/\sigma_C} = \frac{1}{n-1} x_0(1+\theta) + x_0 \frac{K_1^{-(n-1)1/2} K_n(T)}{(n-1)^n} (1+\theta)\left(\frac{\sigma_C}{\sigma_0}\right)^{n-1}, \quad (1)$$

where

$K_n(T)$ is the association constant at temperature T;

θ is the ratio of mobility of cations and anions;

n is the valence of the dopant;

x_0 is the equilibrium concentration of vacancy defects;

σ_0 is the intrinsic conductivity of the pure crystal;

σ_C is the intrinsic conductivity of the doped crystal with dopant's concentration C;

$\bar{K}_1^1$ x_0^2.

When $n = 2$ and $\theta = 0$ (because at low temperatures, the mobility of cation vacancy is very large compared to the mobility of the anions), Eq. (1) reduces to

$$\frac{C}{(\sigma_C - \sigma_0)/(\sigma_0\sigma_C)} = x_0 + x_0^2 K_2(T) \frac{\sigma_C}{\sigma_0}. \quad (2)$$

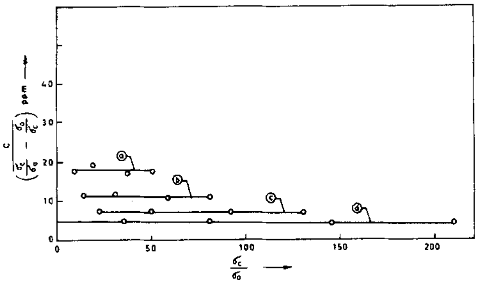

FIG. 6. Conductivity isotherms in the extrinsic region for Ca^{2+} doped LiCl single crystals. Plot of $C/(\sigma_C/\sigma_0 - \sigma_0/\sigma_C)$ vs σ_C/σ_0: (a) $1000/T = 1.55\ K^{-1}$, (b) $1000/T = 1.6\ K^{-1}$, (c) $1000/T = 1.65\ K^{-1}$, (d) $1000/T = 1.7\ K^{-1}$.

According to Eq. (2), a plot of $C/(\sigma_C/\sigma_0 - \sigma_0/\sigma_C)$ vs σ_C/σ_0 should be a straight line with a slope $K_2x_0^2$ and intercept x_0. Such plots for Ca^{2+}- and Sr^{2+}-doped crystals are shown in Figs. 6 and 7, respectively. The slopes of all isotherms obtained with Ca^{2+}-doped crystals (Fig. 6) were almost zero. This can only happen if $K_2 = 0$, which confirms that there is no association of cation Li vacancy with Ca^{2+}-doped crystals in the temperature range 555–630 K. The isotherm plots with Sr^{2+}-doped crystals (Fig. 7) have a positive slope and from the slope and intercept, $K_2(T)$ and $x_0(T)$ were calculated by the method of least-squares fit. Finally, the enthalpy of association and the enthalpy for the formation of Schottky defects were calculated from these values by the method discussed elsewhere (*5*); they are given in Table II.

The equilibrium concentration vacancy defects, x_0, can also be found out from the data of Ca^{2+}-doped crystals by using the Lidiard isotherm equation for the nonassociation region:

$$\frac{\sigma_C}{\sigma_o} = \left(\left(\frac{C}{2x_0}\right)^2 + 1\right)^{1/2} - \frac{C}{2x_0}\left(\frac{\theta - 1}{\theta + 1}\right) \quad (3)$$

If $C \gg x_0$, which is true in the doped crystal in the extrinsic region, then $(C/2x_0)^2 \gg 1$ and Eq. (3) takes the form

$$\frac{\sigma_C}{\sigma_o} = \frac{-C(\theta - 1)}{x_0(1 + \theta)}.$$

If we assume $\theta = 0$ as before, then the plot

TABLE II

THERMODYNAMIC CONDUCTIVITY PARAMETERS FOR LiCl SINGLE CRYSTAL

	Present work (eV)	Haven (*3*) (eV)	Ginning and Phippe (*11*) (eV)	Pataloni and Gaune (*6*) (eV)
Schottky defects				
Formation Enthalpy (h_s)	1.66 ± 0.03	2.14	1.66	1.68
Formation entropy (S_s)	7.8 ± 0.5 K			
Cation vacancy				
Migration enthalpy (h_m)	0.59 ± 0.03	0.41	0.59	0.51
Migration entropy (S_m)	1.7 K			
Association of Sr^{2+} ion and Li vacancy				
Enthalpy (h_a)	0.61 ± 0.02			
Entropy (S_a)	2.6 K			
Enthalpy of formation of defect (h_s) in LiI		1.06 (*17*)		
Enthalpy for migration of defect in LiI (h_m)		0.43 (*17*)		

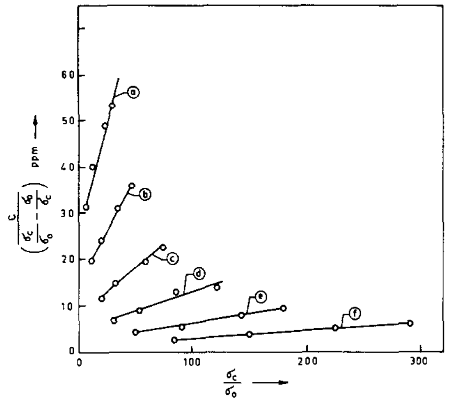

FIG. 7. Conductivity isotherms in the extrinsic region for Sr^{2+}-doped LiCl single crystals. Plot of $C/(\sigma_C/\sigma_0 - \sigma_0/\sigma_C)$ versus σ_C/σ_0: (a) $1000/T = 1.5$ K^{-1}, (b) $1000/T = 1.55$ K^{-1}, (c) $1000/T = 1.6$ K^{-1}, (d) $1000/T = 1.65$ K^{-1}, (e) $1000/T = 1.7$ K^{-1}, (f) $1000/T = 1.75$ K^{-1}.

of σ_C/σ_0 against C should be a straight line with a slope $1/x_0$. The plot of σ_C/σ_0 against C is shown in Fig. 8 for the calcium-doped crystal. From its slope x_0 was calculated as a function of temperature. Then a plot of log x_0 against $1/T$ was made and from the slope of this linear plot, the enthalpy of the formation of Schottky vacancy was calculated (Table II).

The slope of the intrinsic region of the pure crystal gives the value E_1 which is related to the enthalpy of the formation h_s (the value of h_s was obtained from the previous isotherm calculation, Table I) and enthalpy of migration of cation vacancy h_m by

$$E_1 = h_m + 0.5\,h_s. \qquad (5)$$

Using the value of enthalpy of formation h_s and E_1 (experimentally observed value), the enthalpy of migration of cation vacancy h_m, was calculated which was found to be 0.59 ± 0.03 eV. The enthalpy of migration of defects should be independent of the nature of the dopants unless the latter affects the mechanism of conduction process and therefore h_m for Ca^{2+}- or Sr^{2+}-doped crystals should be the same. This is what has been observed in this work.

Discussion

The purity of the crystal has no effect on the conductivity parameters in the intrinsic region and hence it is possible to compare the results of the present work with those published by earlier workers. However, since earlier workers have plotted log σ vs $1/T$, for a better comparison, the present results were also plotted in a similar fashion. From this plot following equation was obtained:

$$\sigma = 3.4 \times 10^5 \text{ mho} \; \exp(-1.38\text{ eV}/KT) \qquad (6)$$

This equation is in agreement with that reported by Ginnings and Phipps (*11*) and Haven (*3*). Haven's value (h_s) is slightly higher which may be due to inclusion of the anionic intrinsic region in their calculation, which has been excluded in our calcula-

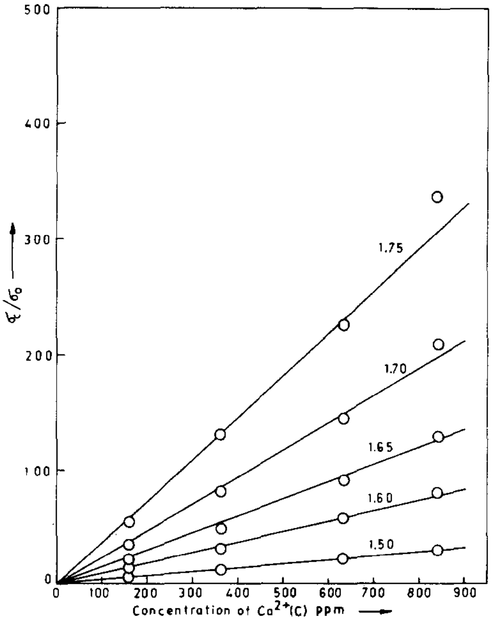

FIG. 8. Plot of σ_C/σ_0 versus concentration C for Ca^{2+}-doped LiCl single crystal.

tions. The enthalpy of migration of Li vacancy is almost same as that observed by others (Table II) with the exception of Haven's (*3*) values. Enthalpy of migration of defects obtained by Haven is normally low with all lithium halides as compared to the recent values (*12*). In the present investigation the enthalpy of migration has been determined from the slope of the intrinsic region of Ca^{2+}-doped crystals as well as from the detailed isotherm analysis of conductivity data of Sr^{2+}-doped crystals and both these methods have yielded the same value for the enthalpy of migration. That is what one would expect to observe.

Until now no one has investigated the effect of Ca^{2+} and Sr^{2+} dopants on the electrical conductivity of LiCl. There is no literature value available on the enthalpy of association between divalent impurity and Li vacancy. When the divalent ion is introduced in the alkali halide crystals, all the divalent ions will not be able to produce free cations vacancies due to association between impurity ion and cation vacancy. Theoretically it has been found that the binding energy should increase as the ionic size of the impurity increases (*13, 14*). In Sr^{2+}-doped crystals, the association between Sr^{2+} ion and Li vacancy is noticeable at the temperature as high as 350°C. And by conductivity isotherm analysis, enthalpy of association was found to be 0.61 eV. This value is slightly higher than the value obtained with NaCl (*15*) and KCl (*16*), which were reported to be equal to 0.53 and 0.58 eV, respectively. On the other hand, enthalpy for formation of defects and enthalpy for migration of defects for LiI (*17*) are reported to be lower than that observed with LiCl (Table II). This is also what one would expect to observe because large anionic size of iodide would ease the formation and migration of cation vacancies.

The size of the Ca^{2+} ion is comparatively smaller than the Sr^{2+} ion and is slightly bigger than the Li^+ ion. The binding energy of the Ca^{2+} ion and Li vacancy therefore should be relatively low compared to that of the binding energy of the Sr^{2+} ion and Li vacancy. It is for this reason, perhaps, that at temperatures as low as 250°C the Ca^{2+} and Li vacancy were found to exist in an unassociated form. At lower temperature there could be some association, but, due to experimental difficulties, no measurements could be made below 250°C. Moreover up to 250°C no steepening of the conductivity plot was also observed (Fig. 2). The analysis of conductivity data also indicated the absence of association between Ca^{2+} and Li vacancy. Hence we conclude that in temperature range from 250°C to near the melting point, there is no substantial association between the Ca^{2+} ions and Li vacancy, whereas there is a substantial association between Sr^{2+} ions and Li vacancy.

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References

1. W. LEHFEDT, *Z. Phys.* **85**, 717 (1933).

2. E. KOCH AND C. WAGNER, *Z. Phys. Chem. B* **38**, 295 (1937).

3. Y. HAVEN, *Recl. Trav. Chim. Pays-Bas* **69**, 1471 (1950).

4. M. SHARON AND A. K. KALIA, *J. Solid State Chem.* **31**, 295 (1980).

5. M. SHARON AND A. K. KALIA, *J. Solid State Chem.* **20**, 53 (1977).

6. J. PATALONI AND P. GAUNE, *C.R. Acad. Sci. Paris Ser B* **270**, 88 (1970).

7. M. SHARON AND A. K. KALIA, *Indian J. Chem.* **15**, 549 (1977).

8. D. HINKS AND S. SUSUMAN, *Mater. Res. Bull.* **9**, 53 (1974).

9. H. GRUDING, *Z. Phys.* **158**, 577 (1960).

10. M. Sharon and A. K. Kalia, *J. Solid State Chem.* **21,** 171 (1977).

11. D. C. Ginnings and T. E. Phipps, *J. Amer. Chem. Soc.* **52,** 1360 (1930).

12. B. J. H. Jackson and D. A. Young, *J. Phys. Chem. Solids* **30,** 1973 (1969).

13. J. R. Reitz and J. L. Gammel, *J. Chem. Phys.* **19,** 894 (1951).

14. M. P. Joshi and G. Airaldi, *Nuovo Chem.* **8,** 584 (1959).

15. N. Brown and I. M. Hodaless, *J. Phys. Chem. Solids* **28,** 2287 (1957).

16. S. Chandra and J. Rolfe, *Canad. J. Phys.* **48,** 412 (1970).

17. B. J. Jackson, and D. A. Young, *J. Phys. Chem. Solids* **30,** 1973 (1969).