

References

1. MUTHUKUMAR, M., SEBASTIAN, K. & PANDIAN, S. J., *J. molec. Structure*, **27** (1975), 117.
2. WATERS, D. N., SHORT, E. L., THARWAT, M. & MORRIS, D. F. C., *J. molec. Structure*, **17** (1973), 389.
3. SANYAL, N. K., GOEL, R. K. & PANDEY, A. N., *Indian J. Phys.*, **49** (1975), 546.
4. CYVIN, S. J., *Molecular vibrations and mean square amplitudes* (Elsevier, Amsterdam), 1968.
5. WILSON, (Jr) E. B., DECIUS, J. C. & CROSS, P. C., *Molecular vibrations* (McGraw-Hill, New York), 1955.

Crystal Data on 12-Heteropoly Nioboantimonate

SALIL KUMAR ROY

Department of Chemistry, Ranchi University, Ranchi 8

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A new heteropoly complex, 12-heteropoly nioboantimonate $K_{11}[SbNb_{12}O_{38}]14H_2O$ has been prepared and the X-ray crystal data recorded.

ONLY a few heteropoly compounds of niobium have been reported¹ in the literature. The present note deals with the preparation, characterization and X-ray crystal diffraction data of a new heteropoly complex, 12-heteropoly nioboantimonate, containing antimony as the hetero atom.

Aqueous solutions of potassium pyroantimonate and freshly prepared² potassium hexaniobate, $K_7Nb_6O_{19} \cdot 13H_2O$, were taken in the molar ratio 1:12, refluxed for 4 hr. After leaving the solution under ambient conditions for three days it was kept *in vacuo* when small needle-shaped crystals separated out which were recrystallized from hot water. Analysis for potassium, niobium and antimony in the compound gave values 17.12, 44.58, 4.86% respectively as against the theoretical calculated values of 17.20, 44.59, 4.87% respectively. The percentage of water and oxygen, calculated by difference, came to 37.44. The individual estimation of hydrogen content in the compound came to 1.12% and hence the percentage of water was 10.02. Thus from these analytical percentage composition data, the compound has been finally represented as $K_{11}[SbNb_{12}O_{38}]14H_2O$, according to the views³ suggested by Lindqvist.

From rotation and Weissenberg X-ray crystal diffraction studies, the cell parameters were found to be: $a = 14.42$, $b = 22.11$, $c = 11.27$ Å and $\alpha = \beta = \gamma = 90$. The system is orthorhombic. The volume V per unit cell was calculated to be 3593.171 Å³. The space group was uniquely established to be I_{41}/a , from the systematic presence of reflections: hkl with $h+k+l = 2n$, ool with $l = 4n$ and hkl with $2k+l = 2n+1$ or $4n$. The last condition gives the number (n) of molecules per unit cell to be 4. The observed density, $\rho_{obs} = 4.61$ g litre⁻¹. From the relation $\rho_{obs} = 1.66 M.n/V$, the molecular weight (M) of the compound came to 2494, against the theoretical value 2499.66.

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References

1. DALE, W. B., BUCKLEY, JANET M. & POPE, M. T., *J. chem. Soc.*, **2A** (1963), 301.
2. MILLER, G. L., *Metallurgy of the rare earth metals*, Vol. VI (Butterworths, London), 1959, 68.
3. LINDQVIST, I., *Chem. Abstr.*, **47** (1953), 728a; **48** (1954), 9782i.

Heats of Formation of Solid Solutions of CsCl with CsBr

S. RAMDAS & A. K. SHUKLA

Department of Chemistry, Indian Institute of Technology
Kanpur 208016

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Substitutional impurity model of Dick and Das [*Phys. Rev.*, **127** (1962), 1053] has been extended to CsCl structure. A statistical treatment has been employed to calculate the heats of formation of solid solutions of $CsCl_{1-x}Br_x$ system. The results are in good agreement with experimental data; discrepancies occur only at high impurity ion concentrations.

FOR substitutional impurities in alkali halides which do not require charge compensation, relaxations in the defect crystal are essentially due to differences in the non-coulombic interaction terms. Studies of substitutional defects in alkali halide crystals employing the Born-Mayer model of ionic solids¹⁻⁶ have shown that the calculated heats of formation, ΔH_f^0 , are not entirely satisfactory in the initial composition range of solid solutions. Fancher and Barsch⁴ have, however, shown that a statistical approach which includes relaxations of ions around impurities in accordance with the model of Dick and Das¹ yields good agreement between theoretical and experimental estimates of heats of formation in the entire range of the solid solutions formed by most of the alkali halides with the NaCl ($Fm3m$) structure (6:6 coordination). Cesium halides which possess the CsCl ($Pm3m$) structure (8:8 coordination) have not been subjected to much theoretical analysis. With our recent success on the calculation of energies of formation⁵ and migration⁶ of defects in these solids, we considered it worth while to employ the Born parameters to estimate the heats of formation of solid solutions of the $CsCl_{1-x}Br_x$ system which retains the CsCl structure throughout the composition range. Experimental heats of formation of solid solutions of $CsCl_{1-x}Br_x$ system are available in the literature⁷.

Method of calculation—We have extended the single substitutional defect model of Dick and Das¹ to the CsCl structure, the details of which are given in the literature^{4,5}. We have allowed four shells of ions to relax in this lattice as shown in Fig. 1.

The $\vec{\xi}_i$ ($i = 1, 2, 3, 4$) represent the displacements of the ions in terms of a , the lattice parameter of the crystal. The displacements $\vec{\xi}_i$ and the electronic dipole moment vectors $\vec{\mu}_i$ (in units of ea) of these polarized ions are assumed to be radially directed. The rest of the lattice is assumed to be undisplaced

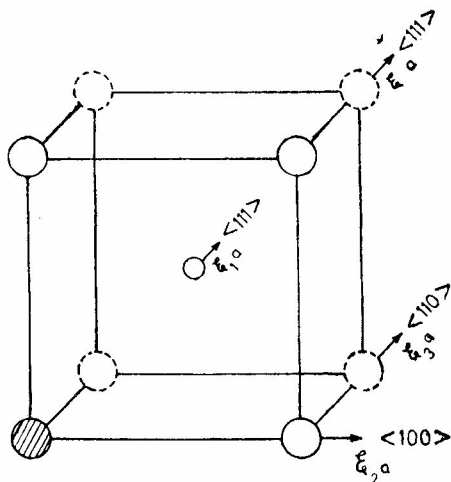


Fig. 1 — Relaxations of the four type of ions around a substitutional impurity

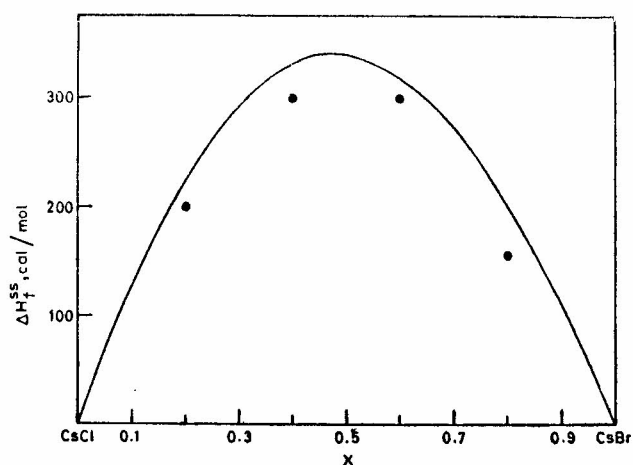


Fig. 2 — Heats of formation of solid solutions of $\text{CsCl}_{1-x}\text{Br}_x$ system [Full circles show the experimental points (ref. 7)]

and unpolarized. The change in the lattice energy, ΔE , due to the introduction of the single substitutional impurity consists of four parts, namely repulsive, electrostatic, electronic dipole self-energy and van der Waals energy. This is minimized, with respect to the displacement and dipole moment variables to get ΔE_{\min} , employing the optimization technique of Fletcher and Powell⁸. Finally, the heats of formation of the solid solution at various compositions are obtained employing the statistical model of Fancher and Barsch⁴. In the present calculations we have employed TKS polarizabilities⁹. The Born parameters, $B_{\text{CsCl}} = 3.0003 \times 10^{-8}$ erg, $\rho_{\text{CsCl}} = 0.293 \text{ \AA}$, $B_{\text{CsBr}} = 2.7589 \times 10^{-8}$ erg and $\rho_{\text{CsBr}} = 0.3067 \text{ \AA}$ were obtained by solving the Hildebrand equations of state employing the lattice constants and compressibilities given by Tosi¹⁰. The van der Waals constants were taken from Hajj¹¹.

The results of our calculations on the heats of formation of solid solutions of $\text{CsCl}_{1-x}\text{Br}_x$ system are shown in Fig. 2. Considering the simplicity of the model employed in the calculation, the results are in good agreement with the recently reported experimental values⁷; discrepancies occur only at

high impurity ion concentrations. There is scope for improvement in the theoretical values in this range of compositions by incorporating some order parameter for the distribution of monovalent impurities as attempted earlier by Wasastjerna¹². We found that the theoretical curve passes through the experimental points once we exclude the van der Waals contributions as was done by Fancher and Barsch⁴. This, however, results in the underestimation of the lattice energies of pure components. The van der Waals contribution to the lattice energies of these halides are important particularly in view of the recent upward revision in the estimated values of these coefficients^{11,13}.

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References

- DICK, B. G. & DAS, T. P., *Phys. Rev.*, **127** (1962), 1053.
- TOSI, M. P. & DOYAMA, M., *Phys. Rev.*, **151** (1966), 642.
- PAUL, S. & SENGUPTA, S., *Phys. stat. sol.*, **68b** (1975), 703.
- FANCHER, D. L. & BARSCH, G. R., *J. phys. Chem. Solids*, **30** (1969), 2503.
- SHUKLA, A. K., RAMDAS, S. & RAO, C. N. R., *J. chem. Soc. (Faraday II)*, (1973), 207.
- SHUKLA, A. K., CHATTOPADHYAY, S. & RAO, C. N. R., *Crystal Lattice Defects*, **6** (1976), 191.
- SHUKLA, A. K., AHLUWALIA, J. C. & RAO, C. N. R., *J. chem. Soc. (Faraday I)*, (1976), 1288.
- FLETCHER, R. & POWELL, J. D., *Computer J.*, **6** (1963), 163.
- TESSMAN, J. R., KAHN, A. & SHOCKLEY, W., *Phys. Rev.*, **92** (1953), 890.
- TOSI, M. P., *Solid State Phys.*, **16** (1964), 1.
- HAIJ, F., *J. chem. Phys.*, **4** (1966), 4618.
- WASASTJERNA, J. A., *Soc. Sci. Fennica, Comm. Phys. Maths.*, **14** (1948), 1; **15** (1949), 1.
- RAO, K. J., RAO, G. V. S. & RAO, C. N. R., *J. Phys. C*, **1** (1968), 1134.

Rate of Dissolution of γ -Irradiated Sodium Chloride Single Crystal Studied by Aquoluminescence

H. J. ARNIKAR, C. D. KALKAR & S. S. SARDESAI
Department of Chemistry, University of Poona
Poona 411007

Received 19 November 1975; accepted 25 April 1976

A new method has been developed for measuring the rate of dissolution of crystals by measuring changes in the intensity of aquoluminescence during their dissolution. The relatively high activation energy of 35.3 kJ/mole observed for NaCl single crystal between 0-60° suggests that its dissolution is not diffusion-controlled.

SOME of the electrons trapped at colour centres in crystals, on receiving the necessary energy, recombine with holes giving rise to thermoluminescence (TL). An alternative mode of releasing the stored energy is observed during their dissolution¹⁻⁵. When the crystal structure breaks down during dissolution the trapped electrons get hydrated and recombine with the holes. In this last process, a faint bluish glow extending into UV is emitted to which the name aquoluminescence (AL) was