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X-ray Studies of the NaCl: SrCl₂ System

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High-temperature diffraction experiments have been carried out on the NaCl: SrCl₂ system, both in its poly- and monocrystalline form. These experiments have led us to the determination of the dilution enthalpy of the SrCl₂ precipitates in the NaCl matrix ($h_D = 0.90 \pm 0.05$ eV). Brauer's method was used to calculate the distortion around one defect and Eshelby's model was used to evaluate the resulting change in the lattice parameter due to these perturbing centers. The concentrations of defects calculated from these models are in good agreement with those determined chemically. Small-angle X-ray scattering experiments were performed on the same crystals, with suitable thermal treatments, to follow the clustering of defects as a function of the annealing temperature. It is possible to maintain a large amount of nearly dispersed strontium in the lattice by quenching the crystals from high temperature. The point defects agglomerate by successive annealings from 100 to 300 °C, forming clusters of increasing sizes. A discussion of the composition of those centers is included.

Introduction

The behavior of defects in doped alkali halides has been observed by numerous techniques: ionic conductivity (Dreyfus & Nowick, 1962; Brown & Hoodless, 1967); I.T.C. (Cappelletti & Benedetti, 1967); optical absorption (Cappelletti, 1968); thermal diffusion (Allnatt & Chadwick, 1967); dielectric losses (Cook & Dryden, 1962); e.p.r. (Bergé, Gago, Blanc, Benveniste & Dubois, 1966) and X-rays (Benveniste, Laredo, Bergé & Tournarie, 1965; Lilley & Newkirk, 1967). X-rays studies of defects have been used less frequently than the other techniques since they need a high concentration of defects (~ 1% in molar concentration). We have been able to grow highly doped NaCl crystals with SrCl₂ ($c < 3 \times 10^{-2}$) in which certain zones are single crystals. X-ray diffraction experiments and low-angle scattering experiments have been carried out on these crystals, complemented by ionic conductivity measurements on the same crystals (Laredo & Dartyge, 1970). At room temperature in very slowly cooled crystals, the Sr²⁺ ions exist in two states: as substitutional

ions in the lattice, and as cubic SrCl₂ precipitates in the NaCl matrix. The precipitates have, as in the case of LiF: MgF₂ (Lilley & Newkirk, 1967), an orientation relation with the matrix which in our case is

$$\{100\} \text{ NaCl } \| \{100\} \text{ SrCl}_2$$
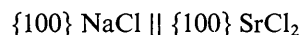
as determined by rotating-crystal photographs of these crystals.

At higher temperatures the precipitates re-dissolve, thus augmenting the number of Sr²⁺ ions in the lattice and the positive vacancies necessary to maintain the electrical neutrality of the crystal. These two types of defects, if they remain next to each other, form the dipole Sr²⁺ $\boxed{\text{Na}^+}$. At the temperatures used in our experiments, the ionic conductivity, which is sensitive to the number of free vacancies, shows that the degree of association Sr²⁺ $\boxed{\text{Na}^+}$ is low. The defects that are present in the matrix give rise to a lattice distortion which can be followed by lattice-parameter measurements in the appropriate range of temperature. More-

over, the amount of $SrCl_2$ present in the $SiCl_2$ phase decreases as the Sr^{2+} enters the NaCl lattice, and the intensity of the reflections due to the $SrCl_2$ decreases proportionally. We can follow this process by making intensity measurements of powdered samples at high temperatures and deducing the increase in the number of point defects in the matrix. At sufficiently high temperatures, all Sr^{2+} ions are substitutional and a rapid quenching to room temperature can maintain the impurities in this state. Low-angle X-ray scattering measurements are sensitive to these heterogeneities of small sizes and to their clustering formed by annealings at different increasing temperatures.

Experimental techniques

The crystals were grown from the melt through a temperature gradient. The strontium concentration was evaluated by colorimetry and by thermal neutron activation analysis.* For the lattice-parameter determination the samples had to be carefully chosen in order to have a single crystalline domain irradiated by the entrance slit of the diffractometer.

The heating device used for powders, single crystals,

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* The thermal neutron activation analysis was performed at the Nuclear Chemistry Laboratory, IVIC.

and the temperature calibration (Benveniste, Laredo, Bergé & Tournarie, 1965) has already been described. Lattice parameters were determined by the method that was used for the pure NaCl crystals (Laredo, 1969). For the low-angle X-ray scattering experiments, a device similar to that described by Levelut & Guinier (1967) was used. By this method the absolute diffusion curve at low angles (3 to 6° in 2θ with Cu $K\alpha$ radiation) can be measured, as well as the state of aggregation of the defects in the crystal. In the case of aggregates where it is possible to define a mean size, the range of the gyration radii that can be determined goes from the point-defect size to a maximum size of 15 Å. The incident beam is made monochromatic and focused (0·5 mm² on the sample) by means of a double-curved LiF monochromator. The scattered intensity is low and must be measured under vacuum and collected by a circular slit. One can sweep the angular range by varying the slit aperture.

The experimental sample was a single-crystal plaquette cleaved to 100μ thickness and with an area of 15 mm². The thermal treatments (annealings of 90 minutes followed by air quenching) were done in nickel crucibles in an open atmosphere. More rapid quenching results in strong scattered intensities. These intensities cannot be attributed to the impurity defects studied in this work, since the pure crystals with the
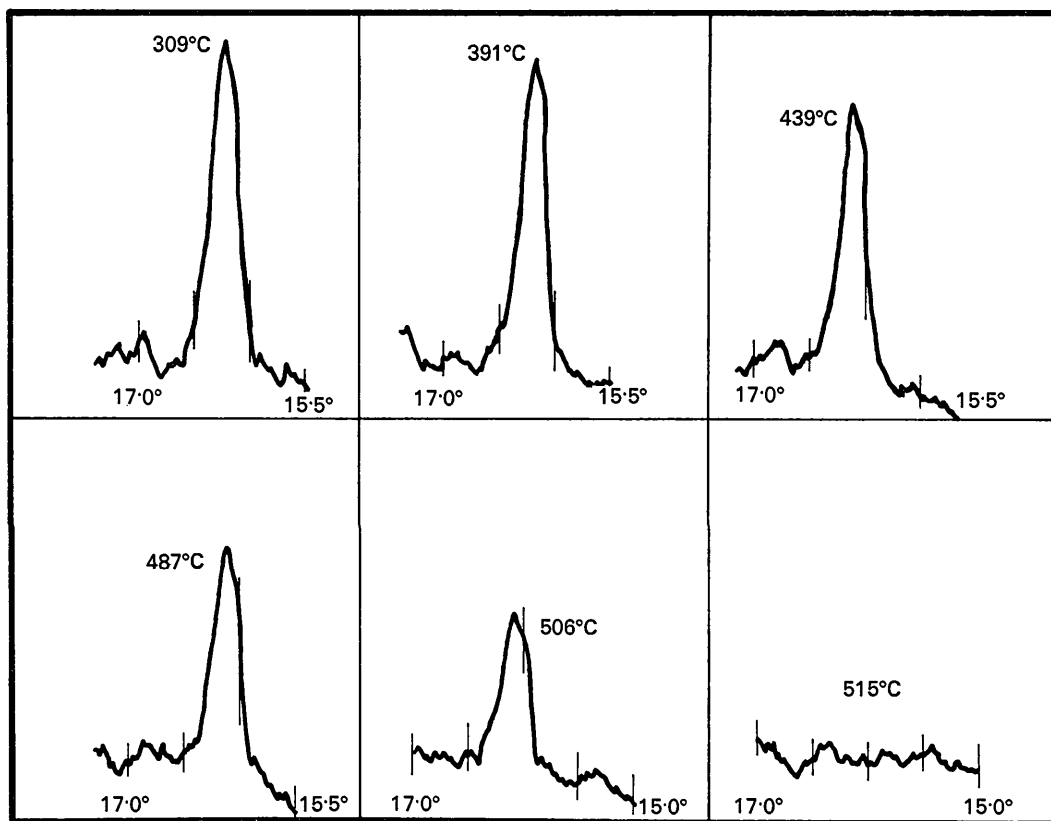

Fig. 1. 220 $SrCl_2$ reflection at different temperatures given by a NaCl: $SrCl_2$ powder with a strontium mole fraction of 7×10^{-2}.

same kind of treatments also showed this effect. They are probably due to the high density of dislocations induced by the quenching, or to double diffraction.

Experiments and results

X-ray diffraction of powders

The powders came either from powdered single crystals or from mixtures of $NaCl : SrCl_2$. $SrCl_2$ is cubic and the most intense reflection of the spectrum is 220. The measured intensity of the 220 reflection is proportional to the concentration of strontium in the $SrCl_2$ phase. Thus, recording the intensity of the $SrCl_2$ 220 reflection at different temperatures gives the amount of Sr^{2+} leaving the $SrCl_2$ phase and entering the NaCl lattice.

The samples had to be previously melted to assure reproducibility. For example, for the sample with a Sr^{2+} concentration of 7·2%, the intensity of the 220 reflection remained unchanged until a temperature of 309 °C was reached. Above this value the intensity decreased until the reflection had a null intensity at 515 °C (Fig. 1). The temperature can be increased either by steps or in a continuous way without any change in the results. However, when lowering the temperature, it was necessary to perform long temperature plateaux to obtain an equilibrium value. Only those runs where the intensity of the 220 $SrCl_2$ reflection at the end of
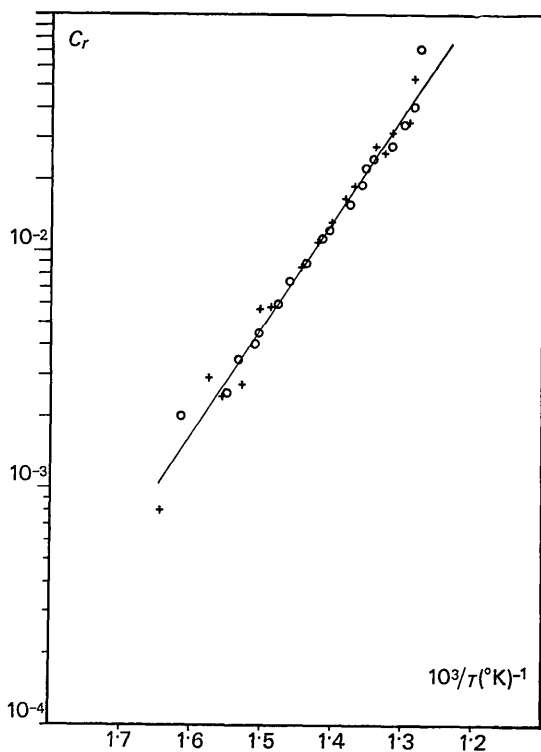

Fig. 3. Variation of the lattice expansion Δa_a with temperature in two single crystals with different Sr^{2+} concentrations: $1·20 \times 10^{-2}$ (+ in Fig.); $2·6 \times 10^{-2}$ (● in Fig.).

the experiment was the same as at the beginning were used. This insured that no strontium was lost during the run. The relative decrease of the 220 reflection as a function of the temperature indicates the relative concentration c_r of Sr^{2+} in the NaCl lattice at each temperature. The absolute concentration c is not known since the precipitates of small size cannot be seen by this method of measurement. It is assumed that either the mass ratio of the small size to the total $SrCl_2$ precipitate is negligible, or the dissolution speed is size-independent. c_r is then calculated at each temperature as the difference between the maximum intensity of the 220 reflection, which is taken as representative of the total concentration of $SrCl_2$, and the intensity of this reflection at the temperature of the experiment. The partial molecular dissolution enthalpy is given by the slope of the plot $\log c_r$ versus $(1/T)$ (Benveniste, Laredo, Bergé & Tournarie, 1965). In Fig. 2 we can see that this plot has a well defined slope, which gives a value of $0·90 \pm 0·05$ eV for the enthalpy of dissolution h_D. The steep increase in the number of carriers ($\boxed{+}$ vacancies), in what is called 'Region IV' of the ionic conductivity plot, is attributed to the dissolution of the precipitated phase present in the alkali halide matrix, since each positive divalent impurity entering the lattice is accompanied by a positive-ion vacancy to maintain the electrical neutrality of the crystal. The activation energy of this process,

Fig. 2. Variation of the relative concentration, c_r, of Sr^{2+} ions in the NaCl lattice as a function of $10^3/T$. Concentration of Sr^{2+}: 5×10^{-2} (○ in Fig.); 7×10^{-2} (+ in Fig.).

deduced from the slope of the plot $\log \sigma T$ versus $(1/T)$, for several NaCl crystals with different amounts of Sr^{2+} doping gives a value of 0.89 ± 0.02 eV. The good agreement found between these two values in the temperature range where this process takes place confirms that the behaviour of the ionic conductivity in 'Region IV' is due to the dissolution of the $SrCl_2$ precipitates.

Lattice-parameter determinations at high temperature of doped single-crystals

At high temperatures the dissolution of precipitates in the crystal gives rise to two types of point defects: Sr^{2+} in a Na^+ position, and a sodium vacancy. These two point defects originate a distortion around them, resulting in a variation of the cubic-lattice constant. Lattice-parameter measurements were made on highly doped single crystals in the range of temperature where it is known that dissolution of the precipitates takes place. It is assumed that the measured increase of the cell constant, Δa, is due to the sum of the lattice expansion caused by the thermal expansion Δa_{te}, and a contribution due to the defects, Δa_d. The variation of Δa_{te} as a function of temperature, measured on pure NaCl crystals, has been reported previously by one of us (Laredo, 1969).

If the two types of defects do not interact then the lattice expansion, Δa_d, is a linear superposition of the expansion due to Sr^{2+} ions occupying Na^+ positions and cation vacancies, which are present in equal number (n) in the lattice.

If n is the atomic concentration of Sr^{2+}, then $\Delta a_d = Kn(T)$, where K is a constant that will be determined later on. The behavior of n with temperature can be written as $n(T) = A \exp -h_D/kT$, where h_D is again the dilution enthalpy of the defects in the lattice.

Fig. 3 shows $\log \Delta a_d$ plotted against $(1/T)$ for the two NaCl crystals studied, with different impurity concentrations. The experimental results can be well approximated by a straight line. However, a temperature (depending on the concentration) is reached where the contribution Δa_d attributed to the defects remains constant. Above this temperature the observed lattice expansion, Δa, can be completely attributed to thermal expansion.

The slope of this plot (Fig. 4) leads to a value of 0.90 ± 0.05 eV for h_D. The agreement of this value with the one determined by ionic conductivity measurements, as well as by powder diffraction experiments, shows that Δa_d is really due to the introduction of point defects in the lattice. To evaluate the effect of these perturbing centers in the lattice, a computer program was written to evaluate the displacements of the first neighbors of each type of defects assuming that they were isolated in the lattice.

The equilibrium distortion around one defect was calculated following Brauer's (1952) method initially used for calculating the energy of imperfections in simple ionic crystals.

Brauer's innovation with respect to existing models (Mott & Littleton, 1938; Reitz & Gammel, 1951) was to introduce for the relative displacement of any ion in an (l, m, n) site, outside the shell of nearest neighbors, an electrical part besides the elastic part

$$\zeta_{elast} = \frac{\zeta}{l^2 + m^2 + n^2},$$

where $\zeta = u_0/a$ is the relative displacement of the nearest neighbor of the defect placed in (000), while u_0 is its absolute displacement.

This absolute displacement of a (100) ion is obtained from the condition that the perturbed lattice is again in equilibrium, i.e. the sum of the forces exerted on the (100) ion is equal to zero: $F_e + F_r = 0$, where F_e is the coulombian force and F_r the repulsive force exerted on it by the 6 nearest neighbors and the 12 next nearest neighbors. The repulsive potential was taken to be of the Born–Mayer form:

$$\omega(r) = bc_{ij} \exp \left(\frac{r_i + r_j - r}{\varrho} \right).$$

Finally, F_e and F_r on the (100) ion can be written as

$$F_e = \frac{2.8955 \times 10^{-4}}{1 + \dfrac{0.3863}{(1+\zeta)^3}} \left\{ \frac{qz_1}{(1+\zeta)^2} + \frac{1.6642z_1^2}{(1+\zeta)^2} \right.$$
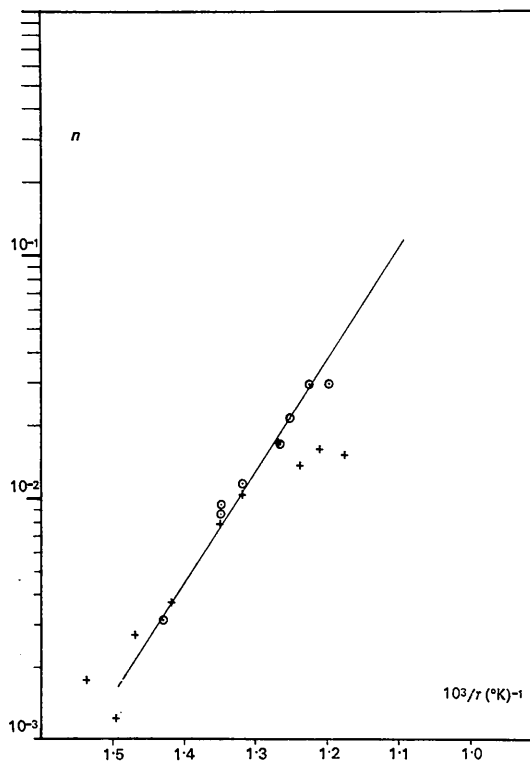

Fig. 4. Variation of the number of the substitutional Sr^{2+} ions in the NaCl lattice as calculated by Eshelby's model.

$$-\frac{4(1+\xi)z_1^2}{[\sqrt{1+(1+\xi)^2}]^3}-\frac{z_1^2}{(2+\xi)^2}-0{\cdot}1253qz_1 \Bigg]$$

and

$$F_r=-\frac{\partial}{\partial u_0}\Bigg\{\omega(a+u_0)+\omega(a-u_0+u_{200})$$

$$+4\omega\sqrt{\left(a+\frac{u_{110}}{\sqrt2}\right)^2+\left(u_0-\frac{u_{110}}{\sqrt2}\right)^2}$$

$$+4\omega[\sqrt2+(a+u_0)]$$

$$+4\omega\left[\sqrt{\left(a+\frac{u_{210}}{\sqrt5}\right)^2+\left(a-u_0+\frac{2u_{210}}{\sqrt5}\right)^2}\right]$$

$$+4\omega\left[\sqrt{\left(\sqrt2+a+\frac{\sqrt2}{\sqrt3}u_{111}\right)^2+\left(u_0-\frac{u_{111}}{\sqrt3}\right)^2}\right]\Bigg\}.$$

The program was run for the corresponding constants of the two types of defects, and the solutions for the equilibrium displacements were found to be

$$\xi_{\boxplus}=+0{\cdot}076 \qquad \xi_{Sr^{2+}}=-0{\cdot}034$$

These two displacements were in opposite directions and of unequal magnitudes. Bassani & Fumi (1954) calculated these two displacements for the same system
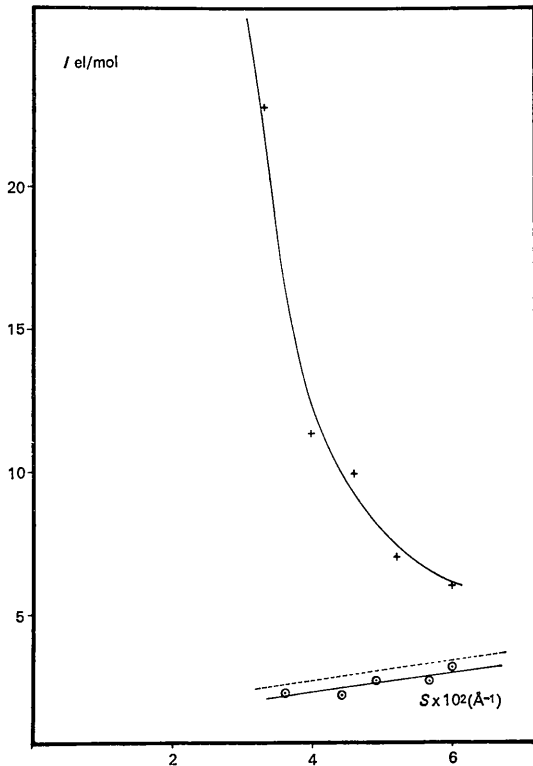

Fig. 5. Diffusion curves of a pure NaCl crystal with different thermal treatments: ○ slowly cooled; + rapidly cooled; --- calculated.

using Mott's model. Their result differs slightly from ours: ($\xi_{Sr^{2+}}=-0{\cdot}030$) due to the different assumptions made for the displacement of the distant ions in Brauer's model. Besides these two local distortions the crystal lattice is uniformly expanded on the addition of defects. To calculate this volume variation, the isotropic approximation proposed by Eshelby (1957) in the sphere and hole model is used here. He related the local distortion to the resultant change in the volume of the crystal approximating the lattice as an isotropic elastic continuum.

A displacement in such a medium can be approximated by the expression

$$\mathbf{u}=\frac{u_0a^2\mathbf{r}}{r^3}.$$

Fukai (1963) evaluated the resulting variation in the lattice constant, due to the introduction of n perturbing centers for monovalent doped alkali halides, assuming a linear superposition of the displacements due to each type of defects:

$$\frac{\Delta a_d}{a_0}=n\,\frac{2\pi}{3}\,\gamma\xi,$$

where γ is given by

$$\gamma=\frac{3(1-\sigma^0)}{1+\sigma^0},$$

σ^0 is an isotropic average of Poisson's ratio (Leibfried, 1953) and n can be taken here as the molar concentration of the Sr^{2+} ions occupying a Na^+ ion position in the lattice. ξ is then the resultant relative displacement due to the Sr^{2+} plus the free vacancy ($\xi=0{\cdot}042$). For NaCl this expression gives:

$$\Delta a_d=0{\cdot}845\times n.$$

It is possible to apply this result to the case of the lattice-parameter high-temperature determinations of NaCl:Sr^{2+} doped crystals. As the temperature increases, the number of active Sr^{2+} ions in the lattice increases, and this number can be calculated from the observed variation of the lattice expansion, which has been attributed to the dissolution of precipitates.

In Fig. 4, n versus $(1/T)$ is plotted for two crystals with different amounts of Sr^{2+} as determined by analysis ($c=1{\cdot}20$ and 2·6%). At high temperatures, when the defects contribution to the lattice expansion remains constant, the number of Sr^{2+} ions calculated by this model should be equal to the strontium concentration obtained by chemical analysis. The theoretical concentration values of 1·50 and 2·98% are in excellent agreement with the chemically determined concentrations.

The isotropic approximation is, as it was in the case of the alkali halides doped with monovalents, a quite adequate description for the calculation of the volume expansion due to the defects.

Low-angle X-ray scattering

(1) *Pure* NaCl *crystals.* The first measurements of scattered intensity were made on pure NaCl crystals in order to subtract this contribution from the total scattering of doped crystals. The intensity scattered by a pure crystal is the sum of the Compton and phonon scattering. The scattering power due to these two effects was evaluated theoretically. The Compton contribution was interpolated from data available in *International Tables for X-ray Crystallography* (1962). The same kind of calculation as Levelut (1968), which is valid in the case of cubic crystals cleaved parallel to (100) and with an [100] axis in the incident beam, was used to determine the intensity scattered by the crystal phonons.

The values of elastic constants reported by Merkulov (1959) were used. Fig. 5 shows the experimental and theoretical angular dependence of the scattering power of a pure NaCl crystal slowly and rapidly cooled to room temperature. The scattering power is calculated for one NaCl molecule and expressed in electrons per molecule: it represents the number of free electrons that should cause the same scattering. The agreement between the experimental determination and the theoretical values is good. The accidental impurities present in the 'pure' NaCl crystal do not give any measurable effect. However, the scattering power depends on the thermal treatment given to the crystals. Slowly cooled crystals give a scattering power very close to the theoretical evaluation, but crystals rapidly quenched from temperatures higher than 500 °C give an important increase of the scattering at the lowest angles. Such rapid quenching is obtained by placing the hot crystal on a copper plate held at 0 °C. This effect can be attributed to double diffraction by the different crystallographic domains created by the quenching. Annealing at temperatures higher than 400 °C followed by slow cooling cures the crystal. The double diffraction effects can be avoided by a slower quenching of the crystal, where the crystal in its nickel crucible is held on a copper plate at room temperature. All the quenching experiments performed in this work were done by this method to avoid the unwanted effects.

(2) *Slowly cooled doped* NaCl *crystals.* Fig. 6 gives the angular depence of the scattering power of a crystal, with 2% of strontium, slowly cooled. In this case we can attribute the variation of the scattering power to the defects whose sizes are not homogeneous. Macroscopic precipitates of SrCl₂ are present in the crystal as has already been shown. These big precipitates do not give any contribution in the range being studied. The small aggregates that originate the scattering could also be small SrCl₂ precipitates. Contrary to what has been observed in other systems such as NaCl:CdCl₂ (Suzuki, 1961), NaCl:CaCl₂ (Miyake & Suzuki, 1954), LiF:NiF₂ (Jehanno & Perio, 1969) and LiF:MgF₂ (Lilley & Newkirk, 1967), no evidence of precipitates of intermediate composition was found.

The explanation could be that since SrCl₂ is cubic the direct precipitation must be easier than in the case of hexagonal or orthorhombic structures such as CdCl₂, MgF₂.

(3) *Quenching experiments on doped crystals.* The samples had a strontium concentration of 1·1%. For higher concentrations we were not able to maintain the Sr^{2+} in the lattice by any quenching technique.

Figs. 7 and 8 show the angular dependence of the scattering power for the same crystal after thermal treatments. The first quenching was done from 500 °C to maintain the Sr^{2+} ions occupying a Na^+ ion position in the lattice. To study the clustering of the impurities at successive temperatures these samples were annealed for 90 minutes followed by quenching in the region of 150–500 °C.

Immediately after quenching from a high temperature, the scattered intensity curve remains parallel to that of the pure crystal, but is it considerably higher. This leads one to believe that the strontium is dispersed as nearly point defects.

Annealing the crystal at 100 °C does not change the plot significantly. For the following increasing annealing temperatures the angular dependence of the scattered intensity $I(s)$ becomes important. The Guinier (1956) approximation is valid in the range of angles used in this work and consequently the logarithm of the
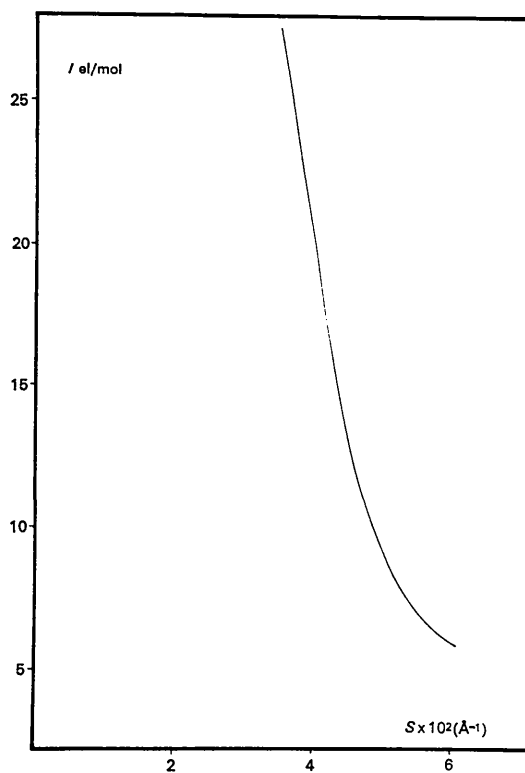

Fig. 6. Diffusion curve of a doped NaCl crystal with 2×10^{-2} of strontium, cooled slowly to room temperature.

scattered intensity attributed to the defects $I_{def}(s) = I_{tot}(s) - I_{pure}(s)$, is proportional to the square of the scattering angle. The defects can then be characterized by a gyration radius R_g, which is the electronic gyration radius of the particle about its electronic center of mass.

Fig. 9 gives the variation of R_g with temperature in the range of 150 to 300°C, showing an increase of R_g from 3·3 to 7·3 Å. After 300°C the intensity scattered in the angular range studied here decreased and R_g decreased simultaneously.

Discussion of the results

Results after the high-temperature quenching

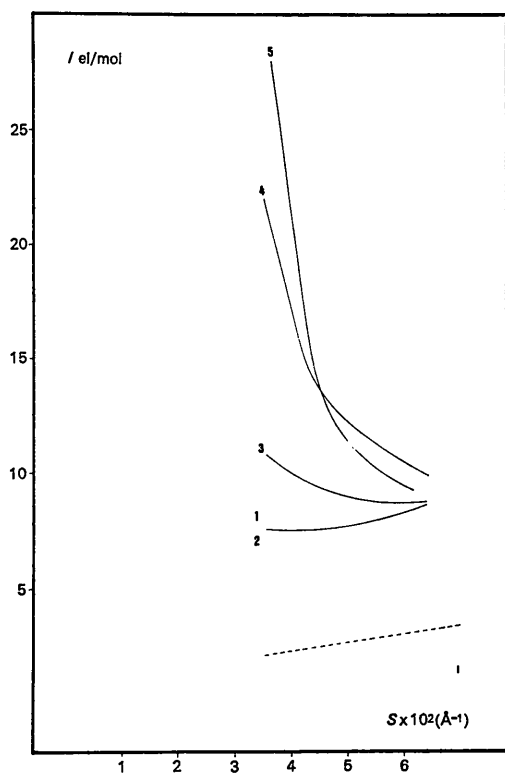The strontium ions are dispersed in the crystal and the Laue law can be applied:

Fig. 7. Diffusion curves of a doped NaCl crystal with 2×10^{-2} of strontium after annealings of 90 minutes at different temperatures followed by quenching. (1) 148°C, (2) 178°C, (3) 230°C, (4) 250°C, (5) 300°C.

$$I(s) = cAf^2 = I(0),$$

where $I(s)$ is the scattering power of the crystal per molecule, c the concentration of strontium per molecule of NaCl and Af the number of additive electrons introduced by a strontium ion substituted for a sodium ion. If the strontium ions were agglomerated in nearly point clusters of p ions ($p < 3$) the Laue formula would become: $I(s) = pcAf^2$.

Af must now be evaluated and it depends on the state of the strontium ions. There are two possibilities:

– The strontium is in the form Sr^{2+} associated with a cation vacancy. In this case the value Af^2 is equal to 230 with the corresponding dispersion corrections.

– The strontium ions are not associated with a sodium vacancy. They can be Sr^+ or Sr^{2+} associated with two OH^- ions which substitute for two Cl^- ions. A structure of this type was previously reported by Laj (1969) in LiF: $MnCl_2$ studied by electronic paramagnetic resonance techniques. In this case, the value of Af^2 is equal to 712 with dispersion corrections applied for the atomic scattering factors of Sr^{2+}, $2OH^-$ or Sr^+ ions.

Experimentally, $I(s)$ was found to be 5·2 el/mol for a crystal in which the atomic concentration of strontium, as determined by thermal neutron activation analysis, was $c = 1·1\%$. For the first hypothesis, $p \sim 2$, the main part of the Sr^{2+} $\boxed{Na^+}$ dipoles should be in clusters of two dipoles. Ionic conductivity measurements were performed on the same crystals with the same thermal treatments. They show that the maximum number of dipoles that could be produced by quenching techniques is 8×10^{-4}, regardless of the strontium concentration in the crystals.

In this interpretation, the remaining Sr^{2+} ions which are in the form of dimers must be considered as unable to generate free vacancies. These vacancies can only be produced by the dissociation of $\boxed{+}$ Sr^{2+} dipoles. To the best of our knowledge, a theory justifying a strong binding of vacancies in dimers does not exist. The presence of dimers in quenched NaCl: $SrCl_2$ crystals is in agreement with the I.T.C. measurements of Cappelletti & Benedetti (1967). They have shown, in the case of NaCl: $SrCl_2$ crystals where the clustering of dipoles is slow, that the first stage of dipole disappearance follows second-order kinetics.

The second hypothesis yields, for the concentration of the dispersed strontium contributing to the scat-

Table 1. *Variation of the cluster sizes and the number of strontium ions in the clusters as a function of the annealing temperature* ($t < 300°C$)

t (°C)	R_g (Å)	$v = 8R_g^3$ (Å³)	$I(0)$ (el/mol)	c_c	n
148	3·30	288	9·8	$1·1 \times 10^{-2}$	3·2
178	3·83	450	10·8	$0·92 \times 10^{-2}$	5
230	4·82	896	20·4	1×10^{-2}	10
250	5·64	1435	32·5	$0·88 \times 10^{-2}$	16
300	7·28	3087	70	1×10^{-2}	

tering, a value of 0.8×10^{-2}, instead of 1.1×10^{-2} as analyzed. The remaining strontium could be present as large precipitates not contributing to the scattering. In this case, it should be easy to explain the low number of free vacancies observed by ionic conductivity measurements in quenched crystals. However, the transition of the strontium from Sr^+, at low temperatures, to Sr^{2+}, which obviously exists at high temperatures, cannot be easily explained. In the case of Sr^{2+} $2OH^-$ centers, the $2OH^-$ concentration should be equal to that of Sr^{2+} which is a highly improbable concentration.

Finally, this work favors the first hypothesis but it must be admitted that the experimental results cannot eliminate the second hypothesis.

(2) *Quenchings from temperatures of* 150 *to* 300°C. The temperature range where the clusters grow in size corresponds to the range where the number of Sr^{2+} $\boxed{Na^+}$ dipoles decreases, as observed by ionic conductivity experiments on the same crystals with the same thermal treatments.

The proportion of agglomerated strontium can be calculated with a knowledge of $I(0)$, the scattering power at zero angle. $I(0)$ can be found by an extrapolation of $I(s)$ to $s=0$ since $I(s)$ follows the Guinier approximation,

$$I(0) = Nn^2,$$

where N is the number of clusters per Na^+ site (or Cl^- ion) and n is the number of extra electrons introduced by one cluster, given by the following expression:

$$n = (\varrho - \varrho_o)v$$

where v is the volume of one cluster, ϱ the electronic density of one cluster and ϱ_o the electronic density of the matrix. The calculations are made in the case of Sr^{2+} ions associated with a cation vacancy

$$\varrho = [c_P f_{Sr^{2+}} + (1 - 2c_P)f_{Na^+}] \frac{4}{V},$$

where $f_{Sr^{2+}}$ and f_{Na^+} are the respective scattering factors of the ions Sr^{2+} and Na^+, V is the volume of the unit cell of NaCl, c_P is the atomic concentration ($[Sr^{2+}]/[Na$ site]) in the clusters, c' the concentration of Sr^{2+} dispersed in the lattice

$$n = \frac{4v}{V} (c_P - c')(f_{Sr^{2+}} - 2f_{Na^+}),$$

$$I(0) = N \frac{16v^2}{V^2} (c_P - c')^2 \Delta f^2$$

and

$$(f_{Sr^{2+}} - 2f_{Na^+})^2 = \Delta f^2.$$

The total amount of Sr^{2+} in the crystal, c_d, was obtained by chemical analysis and is also given by the following expression

$$c_d = c' + \frac{4Nv}{V} (c_P - c')$$

Finally: $I(0) = 4 (v/V)(c_d - c')(c_P - c')\Delta f^2$, where $c' \ll c_P$, as indicated by ionic conductivity measurements which showed that $c' < 8 \times 10^{-4}$. Thus $I(0)$ can be written as:
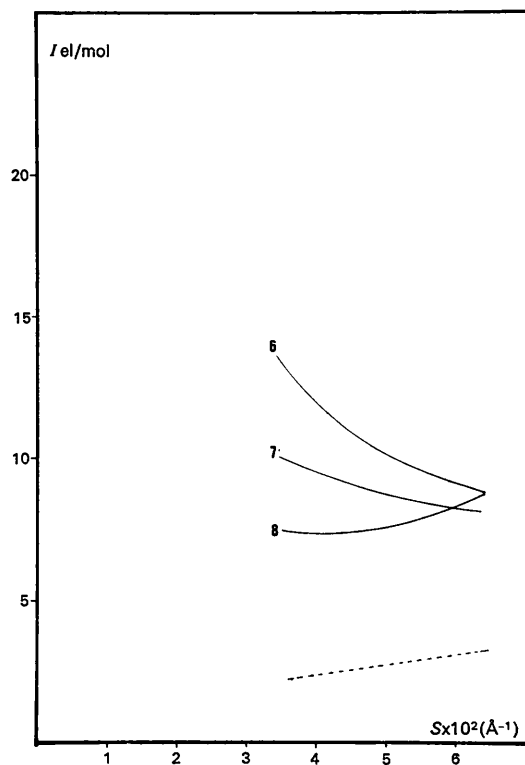

Fig. 8. Diffusion curves of a pure and a doped NaCl crystal with 2×10^{-2} of strontium after annealings of 90 minutes at different temperatures followed by quenching. (6) 350°C, (7) 408°C, (8) 450°C; --- pure crystal.

Table 2. *Variation of the cluster sizes and the number of strontium ions in the clusters as a functions of the annealing temperature* $(t > 300°C)$

t (°C)	R_g (Å)	$v = 8R_g^3$ (Å³)	$I(0)$ (el/mol)	c_c	n
350	4	512	13·3	1×10^{-2}	5·6
408	3·3	288	8·8	$1·2 \times 10^{-2}$	3·2
450	–	—	7	$1·1 \times 10^{-2}$	2·8
527	–	—	5·18	$1·1 \times 10^{-2}$	2

$$I(0) = \frac{4v}{V} c_P (c_d - c') \Delta f^2$$

where c_P and c' are unknown, but in the case of clusters of Sr^{2+} $\boxed{Na^+}$ dipoles $c_P = 0\cdot5$. These clusters have the same chemical composition as the $SrCl_2$ precipitates, but they remain coherent with the matrix. If another hypothesis is assumed where $c_P < 0\cdot5$, which indicates that the clusters are made of Sr^{2+}, Na^+, $\boxed{+}$ (as in the case of the Suzuki superstructure in $NaCl:CdCl_2$), it leads to large negative values for c'; therefore, it is considered that the clusters have the same chemical composition as $SrCl_2$. Table 1 gives the variation of both the total concentration c_c of Sr^{2+} present in those clusters, and n' the mean number of Sr^{2+} ions per cluster, as a function of the annealing temperature. The volume of the clusters has been calculated assuming that the clusters are cubes whose edges equal $2R_g$. Spherical-shaped clusters give the same results.

The amount of strontium in clusters remains constant and practically equal to the total amount of strontium present in the crystal. Growth in size of the clusters with increasing annealing temperature occurs at the expense of cluster dissolution. The isolated dipoles present in the crystal can also contribute to this process since the temperature range of growing corresponds to a decrease in the number of isolated dipoles as observed by ionic conductivity. However, the growing mechanism of clusters cannot only be explained by the disappearance of dipoles as their total concentration is far too low.

(3) *Temperatures higher than* 300°C. At these annealing temperatures a decrease in the scattering power is observed. In the same range of annealing temperatures an increase in the number of isolated dipoles is observed by conductivity experiments performed between −8 and 30°C. Additional conductivity measurements of $NaCl:SrCl_2$ crystals at thermodynamic equilibrium (Laredo & Dartyge, 1969) show that strontium begins to enter the lattice at 300°C. Assuming the clusters to be made of Sr^{2+} $\boxed{+}$ dipoles, it is possible to calculate c_c, as shown in Table 2.

The values found for c_c remain approximately equal to the total amount of strontium in the crystal, which is in agreement with the conductivity measurements, but the observed decrease in R_g requires a supplementary discussion. The usual dilution mechanism in supersaturated solutions is as follows: R_g will still grow as the annealing temperature increases, but N, the number of clusters, will decrease. The observed results of this process are a decrease of c_c and an increase of c'. When the dissolution is nearly achieved, only a very small number of big clusters remains. To check that big clusters do not exist at temperatures higher than 300°C, large-angle photographs were made on a fixed crystal suitably oriented to record the 311 reflection of $SrCl_2$ on the photographic plate. After quenching from 300°C, the photograph presents a large spot of very weak intensity at the position of the 311 reflection. After quenching from higher temperature (350°C), the spot is practically invisible which confirms that big precipitates do not exist in the crystal.

Another type of explanation could be that the clusters still grow above 300°C but their strontium concentration decreases. The observed scattered intensity should be the same. In this case, the Guinier approximation is not valid in the angular domain used here and no calculations of the strontium involved in the cluster can be easily carried out. In both cases the process corresponds to a dilution of the clusters which is in agreement with conductivity measurements.

Conclusions

In $NaCl:SrCl_2$ crystals, it is possible to maintain a large amount of nearly dispersed strontium in the matrix at room temperature by quenching the sample from high temperature. These point defects agglomerate by successive annealings from 100 to 300°C. The contribution of isolated dipoles to the growing of the clusters is negligible. However, the size of the clusters is inversely proportional to the number of isolated dipoles present in the matrix.

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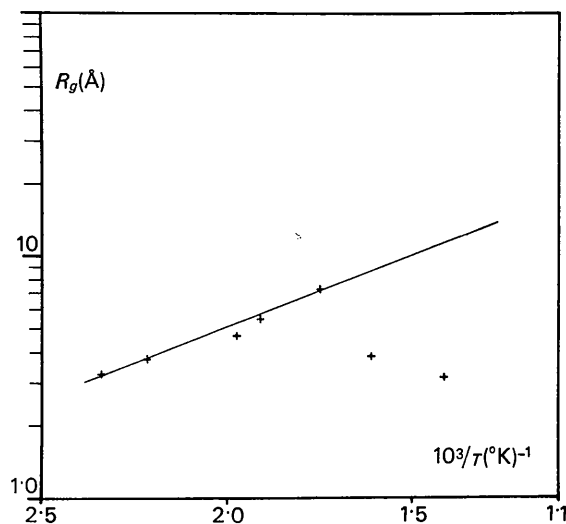BASSANI, F. & FUMI, F. G. (1954). *Nuovo Cim.* **11**, 274.

Fig. 9. Variation of the radius of gyration of the defect with the annealing temperature.

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A Relation Between Structure Factor, Triple Products and a Single Patterson Vector, and its Application to Sign Determination

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The Fourier coefficients D_h of a hypersection of the double Patterson function at a fixed value of U can be written as

$$D_h = (1/V) \sum_{h'} F_h F_{h'} F_{\overline{h+h'}} \cos 2\pi h' \cdot U / \cos 2\pi h \cdot (U/2) \, .$$

It is shown that also $D_h = F_h G_h$, where G_h is the Fourier coefficient of a reduced structure derived from the original structure by positioning an atom with form factor $\sum_{h'} f_i(h') f_j(\overline{h+h'})$ halfway in between those atoms i and j, which are a vector U apart. If U is a single vector between two atoms with form factor $f(h)$, then the reduced structure contains only one atom, at the origin, and $G_h = (1/V) \sum_{h'} f(h') f(\overline{h+h'})$. We obtain the relation $\sum_{h'} F_h F_{h'} F_{\overline{h+h'}} \cos 2\pi h' \cdot U / [\cos 2\pi h \cdot (U/2) \sum_{h'} f(h') f(h+h')] = F_h$. Using this formula with probabilities for the signs of the triple products, the single vectors U are found by a scanning process, as we demonstrate on a heavy atom structure. The signs of the structure factors have thus been calculated directly from the triple products.

Introduction

The double Patterson function (Sayre, 1953) is defined as $T(U,V) \equiv \int \varrho(r)\varrho(r+U)\varrho(r+V)dr$. Its Fourier coefficients are the triple products $F_h F_{h'} F_{\overline{h+h'}}$, divided by V^2. Hypersections* of this six-dimensional function can be synthesized because the phases of triple products show a tendency towards zero. A hypersection at a fixed value of U contains the structure once if U corresponds to a single Patterson vector (Hoppe, 1957) and twice if U is a double Patterson vector, *etc.*

In this paper we relate the Fourier coefficient F_h of a centrosymmetric structure to the Fourier coefficients of a Hoppe section. This leads to a relation between F_h, triple products and a single Patterson vector U. By scanning U through the asymmetric unit of the Patterson space† we expect to find the positions of the single peaks, and the signs of F_h, at values of U where

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* In this paper a coset of the subspace U = 0 (or V = 0) is called a hypersection.

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† Each peak in the linear subspace U = 0 or V = 0 of the double Patterson function corresponds to a peak with the same position but not the same height in the Patterson function. For this reason we will refer to such a linear subspace as a Patterson space.