JOURNAL OF MATERIALS SCIENCE 10 (1975) 1154–1156

The structure of precipitates in Mn-doped NaCl

J. A. CHAPMAN*, E. LILLEY
School of Applied Sciences, University of Sussex, Falmer, Brighton, Sussex, UK

Precipitation of a phase identified as 6NaCl.MnCl$_2$ has been studied by X-ray diffraction in slowly cooled single crystals of NaCl doped with MnCl$_2$. The relevance of these observations to other studies of esr, clustering and mechanical properties in this system is discussed.

1. Introduction

Numerous studies have been made of divalent doped alkali halide crystals because the divalent ions lead to the incorporation in a solid solution of an equal number of cation vacancies which can be studied by a variety of techniques. Many systems have been studied but the one most thoroughly studied is probably NaCl/MnCl$_2$. Ionic conductivity studies have been performed by Chapman and Lilley [1], Kirk and Pratt [2], Dreyfus and Nowick [3], and dielectric loss studies by Haven [4], Watkins [5], Cook and Dryden [6, 7], and Symmonds and Kemp [8]. Most important is the fact that the manganese can be studied with spin resonance techniques, and the work of Watkins [5] and Symmonds [9, 10] has yielded information about the occupancy of vacancies of nearest and next nearest neighbour sites to Mn^{2+} and their jump frequency unobtainable with other techniques. It is fortunate that this system exhibits a reasonable degree of solubility [1]. Nevertheless, experimental studies have been performed at or close to room temperature where the solubility limit is exceeded, e.g. Dryden's studies of clustering of divalent ions, Harrison and Newey's studies of the mechanical properties of NaCl/Mn [11], and Chapman and Lilley's ionic conductivity studies [1].

In some of these studies, such as the clustering studies, where the crystals have been quickly cooled then aged, it is quite possible that precipitation has not occurred. However, this is not proven and at the higher ageing temperatures, Mn may well be precipitating. Lilley [12] has found such precipitation in his ageing studies of LiF/MgF$_2$. Whether or not precipitation will occur depends upon the barrier to nucleation which varies from system to system and is a function of the ageing temperature, or cooling rate, and also on the composition. For extremely low compositions precipitation probably becomes impossible.

In the light of these previous studies of NaCl/Mn, a study of the solubility of Mn in NaCl, described elsewhere [1], and of the precipitate structure, to be described here, have been performed.

2. Experimental techniques

Single crystals of Mn doped NaCl were grown with varying compositions by means of a Stockbarger furnace. Care was taken to use high purity starting materials and to encapsulate them under a chlorine atmosphere to avoid OH$^-$ ion contamination. The crystal mainly used for the X-ray examination contained about 0.5 mol % MnCl$_2$ and these were programme-cooled at a rate of 4° C h^{-1} from 400° C to room temperature. Single crystal rotation and oscillation photographs were taken with a Unicam with exposures of about 10 h, using Cu$K\alpha$ radiation.

3. Results

X-ray photographs of single crystals of NaCl/Mn rotated about the $\langle 100 \rangle$ axis revealed extra layer lines between the zero, first, and second NaCl lines. These rotation patterns were analogous to those obtained by Suzuki [13] for NaCl/Cd crystals and by Lilley and Newkirk [14] for LiF/MgF$_2$ crystals. The precipitates are, therefore,

---

*Present address: Mullard Research Laboratories, Redhill, Surrey.

presumed to be $6NaCl.MnCl_2$, like those found by Suzuki of $6NaCl.CdCl_2$, with the same cubic structure. They have a cubic/cubic relationship with the matrix. In this case the precipitates are finely dispersed and only readily visible with electron microscopy [15]. It has been deduced from replica electron microscopy studies [16] that, on the basis of volume fractions, the precipitating phase must be $6NaCl.MnCl_2$.

The precipitate reflections were indexed for the first and third layer lines, the other reflections superimposing on those for NaCl. Estimates of the diffracted intensity were made by comparing with a graded exposure film. These are listed in Table I.

Structure factor calculations must take account of the displacement of the anion next to the vacancy. Consequently [13],

$$F = \{1 + \exp \pi i(h + k) + \exp \pi i(k + l) + \exp \pi i(l + h)\} \cdot \Big[f_{\mathrm{Mn}^{2+}} + 2f_{\mathrm{Na}^+} \Big\{\exp \frac{\pi i h}{2} \cos \frac{\pi k}{2} + \exp \frac{\pi i k}{2} \cos \frac{\pi l}{2} + \exp \frac{\pi i l}{2} \cos \frac{\pi h}{2}\Big\} + 2f_{\mathrm{Cl}^-} \Big\{\cos \frac{\pi}{2}(h + k + l) + \cos 2\pi h x + \cos 2\pi k x + \cos 2\pi l x\Big\}\Big]$$

where h, k, l are the Miller indices of the crystal planes, $f_{\mathrm{Mn}^{2+}}$, f_{Na^+} and f_{Cl^-} are the atomic scattering factors of the ions and $x = (\frac{1}{4} - \delta)$ where δ is the fractional displacement of the Cl^- towards the nearest Mn^{2+} ion. For all odd reflections, the above expression simplifies to

$$F(hkl) = f_{\mathrm{Mn}^{2+}} + 2f_{\mathrm{Cl}^-} \{\cos 2\pi h x + \cos 2\pi k x + \cos 2\pi l x\}.$$

The calculated relative intensities for $\delta = 1/48$ are shown in Table I, after corrections for the absorption factor, the Debye-Waller temperature factor*, the Lorentz polarizing factor, the velocity and multiplicity factors. Owing to the low diffracted intensities the measured values are subject to considerable error. Values of $\delta = 1/32$, 1/48, 1/60, 1/72 and 1/96 were tried; $\delta = 1/48$ was found to give the best agreement.

In addition to the heavily doped crystal, an examination by means of oscillation photographs was made of crystals containing as little as 40 ppm Mn. These also exhibited diffraction from precipitate particles.

TABLE I

(hkl)	Calculated intensity $\delta = 1/48$	Measured intensity
111	48.2	40
311	10	10
331	0.1	N.D.
511	43.2	40
531	15.4	13
551	18.9	18
711	0.7	N.D.
731	0.3	N.D.
751	5.1	4
911	21.1	19
931	10.4	9
771	1.0	N.D.
951	23.0	20
113	10.3	10
313	0.1	N.D.
333	1.1	obscured by (111) streak
513	17.5	20
533	4.5	4
553	10.2	8
713	0.3	N.D.
733	3.2	N.D.
753	0.3	N.D.
913	10.7	12
933	7.7	6
773	3.4	3
953	19.5	12

4. Discussion

The single crystal rotation photographs clearly show that the phase $6NaCl.MnCl_2$ forms in slowly cooled single crystals of NaCl containing about 0.5 mol % $MnCl_2$ down to less than 0.01 mol %. This is supported by the ionic conductivity measurements [1], which indicate that precipitation can occur in slowly cooled crystals containing 0.04 mol % $MnCl_2$. Difficulty, however, has been experienced here in obtaining reasonable diffracted intensities since there is only a small volume fraction of precipitate particles inside an absorbing matrix. Moreover, since the precipitate particles and the matrix have a cubic/cubic orientation relationship the diffracted spots from the $6NaCl.MnCl_2$ planes fall on, and in some cases are obscured by, the NaCl white radiation streaks. Another difficulty is that the diffraction pattern from the precipitated phase is somewhat diffuse.

It has been pointed out [17, 18] that the

---

*The Debye-Waller factor for NaCl was used as the best available approximation.

perfectly ordered model of the crystal structure might need some rearrangement and a modification based on disordering of the cation lattice has been suggested. However, it is not really meaningful to discuss the present diffraction data in any further detail.

The present study indicates that precipitation of $6NaCl.MnCl_2$ can occur in slowly cooled crystals at very low concentrations and so it is possible that it can also occur in the isothermal clustering studies [6-8]. This could account for the post-pleateau kinetic region. To observe precipitation during ageing at temperatures close to room temperature at the low concentrations used in the clustering studies is probably impossible with normal Bragg diffraction, because of the expected small particle sizes. However, precipitation may be observable by small-angle X-ray scattering [19].

Precipitation of $6NaCl.MnCl_2$ has probably occurred in esr studies [5, 8] and appears to correspond to the broad peaks that have been found. Again in the mechanical properties studies of Harrison and Newey [11] it seems likely that precipitation of $6NaCl.MnCl_2$ has occurred in their heavily doped crystals. The cause of hardening of their crystals is then more likely to be precipitation hardening rather than cluster hardening, as proposed by Harrison and Newey.

Acknowledgement

Financial support from AERE Harwell, is gratefully acknowledged.

References

1. J. A. CHAPMAN and E. LILLEY, *J. de Phys. Supplement* **C9** (1973) 341.
2. D. L. KIRK and P. L. PRATT, *Proc. Brit. Ceram. Soc.* **9** (1969) 215.
3. R. W. DREYFUS and A. S. NOWICK, *Phys. Rev.* **126** (1962) 1367.
4. Y. HAVEN, "Defects in Crystalline Solids", (Physical Society, London, 1955).
5. G. D. WATKINS, *Phys. Rev.* **113** (1959) 79, 91.
6. J. S. COOK and J. S. DRYDEN, *Austral. J. Phys.* **13** (1960) 260.
7. *Idem, Proc. Phys. Soc.* **80** (1962) 479.
8. H. F. SYMMONS and R. C. KEMP, *Brit. J. Appl. Phys.* **17** (1966) 607.
9. H. F. SYMMONS, *J. Phys. C* **3** (1970) 1846.
10. *Idem, ibid* **4** (1971) 1945.
11. R. P. HARRISON and C. W. A. NEWEY, *Phil. Mag.* **8** (1968) 525.
12. E. LILLEY, Proceedings of the 6th International Symposium on the Reactivity of Solids (1969).
13. K. SUZUKI, *J. Phys. Soc. Japan* **16** (1961) 67.
14. E. LILLEY and J. B. NEWKIRK, *J. Mater. Sci.* **2** (1967) 567.
15. A. SORS and E. LILLEY to be published.
16. A. R. KAHN, Ph.D. Thesis, Imperial College (1967).
17. K. TOMAN, *Czech. J. Phys.* **12** (1962) 542.
18. E. LILLEY, Ph.D. Thesis, Cornell University (1966).
19. E. LAREDO and E. DARTYGE, *Acta Cryst.* **A27** (1971) 353.

Received 12 November and accepted 2 December 1974.