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Microhardness studies in ammonium halide crystals

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Abstract. Microhardness studies of NH_4Cl (pure and doped), NH_4Br and alkali halide crystals are presented. The hardness of ammonium halides is found to be less as compared to alkali halide crystals. Doping NH_4Cl crystals with copper (Cu^{2+}) is found to increase the hardness enormously and the results obtained with various concentrations of copper are presented. The results have been analysed and the various factors contributing to the increase in hardness at lower loads have been discussed.

Keywords. Microhardness ; Rosette pattern ; doping; monovalent impurities-divalent impurities; dislocations.

1. Introduction

Considerable work has been done on the mechanical properties of alkali halide crystals. The effect of monovalent and divalent impurities on hardness has been investigated. The experiments showed that small concentrations of divalent metal impurity ions would greatly harden the alkali halides as compared to monovalent ions (Blank and Smekel 1930; Johnston 1962; Dryden *et al* 1965; Newey *et al* 1966; Chin *et al* 1973; Labenets and Startsev 1968). It has also been observed that if the impurity concentration exceeds the solubility limit, visible precipitates are formed and further additions of the impurity will not contribute further to hardness. Microstructural and hardness studies on KCl crystals doped with alkaline earth impurities have shown that dislocations act as nucleation sites for the formation of large visible precipitates and that the state of dispersion of the impurity plays an important role in determining the hardness of crystals (Lakshmipathi Rao and Hari Babu 1978).

On the other hand monovalent ions can be substitutionally dissolved in alkali halide crystals to a much higher extent than divalent ions. Especially, if the difference between the solute and solvent is not large, any content of composition keeps equilibrium at room temperature (Fancher and Borsch 1969). On the strength of the materials some experimental results are available for KCl–KBr (Stoloff *et al* 1963) and NaCl–NaBr (Wimmer *et al* 1963) systems showing a solid solution hardening or softening and for NaCl–AgCl (Stokes and Li 1962) and NaCl–KCl (Wolfson *et al* 1966) systems showing a precipitation hardening. Recent microhardness studies in alkali halide mixed crystals (Subba Rao and Hari Babu 1978) showed that it varies nonlinearly with composition. Kataokov and Yamada (1977) have studied the yield strength and dislocation mobility of KCl–KBr solid solution single crystals. They have proposed an analytical model of the hardening mechanism on the basis of elastic interaction (size misfit) between an edge dislocation and solute atoms. Uematru *et al* (1978) also studied solution hardening and softening in KCl–KBr single crystals at low temperatures. From the analysis of activation volume, they concluded that the dislocation motion in the higher concentration region was impeded only by the solute ions and that in the lower concentration region by Peirerls barriers in addition to the solute ions.

It is thus clear that considerable work has been done in alkali halide crystals and the mechanism of hardening is fairly well understood. However, there is practically no work on the mechanical properties of NH_4Cl crystals. This paper presents results of microhardness studies on NH_4Cl, NH_4Br and NH_4Cl crystals doped with various concentrations of copper chloride. Microhardness results of some alkali halide crystals are also given for comparison. The dependence of microhardness on load has been analysed and various factors contributing to the increase in hardness at lower loads have been discussed.

2. Experimental

Single crystals of pure and copper doped NH_4Cl crystals used in the present investigation are grown by slow evaporation of saturated aqueous solutions containing urea. Alkali halide crystals have been grown from the melt by the Kyroupolos technique (Subba Rao and Hari Babu 1978). Microhardness measurements have been made by Vicker's indentor attached to a microscope as grown crystals. The microhardness is calculated using the expression $H = 1\cdot8544\ P/d^2$ where P is the load applied in grams and d is the length of the diagonal of the indentor impression in microns. All indentations have been made at room temperature and the time of indentation has been kept at 10 sec. On each sample at least ten indentations have been made and the final value of the microhardness is the average value of all such measurements.

3. Results

NH_4Cl crystals cannot be cleaved easily and indentations have therefore been made on naturally grown cubic faces. Smooth surface is selected before indentation. The impressions obtained on NH_4Cl crystals after indenting with 1·25 P and 60 P loads are shown in figure 1. The size of the impression increases with load.

The microhardness values of NaCl, KCl and KBr obtained at a load of 40 P are given in table 1 and those of NH_4Cl, NH_4Br and copper chloride (Cu^{2+}) doped NH_4Cl crystals are given in table 2. The results show that ammonium halide crystals are more soft as compared to alkali halide crystals. Doping NH_4Cl crystals with copper chloride (Cu^{2+}) considerably increases the hardness. The variation of hardness with concentration of Cu^{2+} is illustrated in figure 2, which shows that for small additions of Cu^{2+} the increase in hardness is large and at higher concentration the hardness tends to saturate.

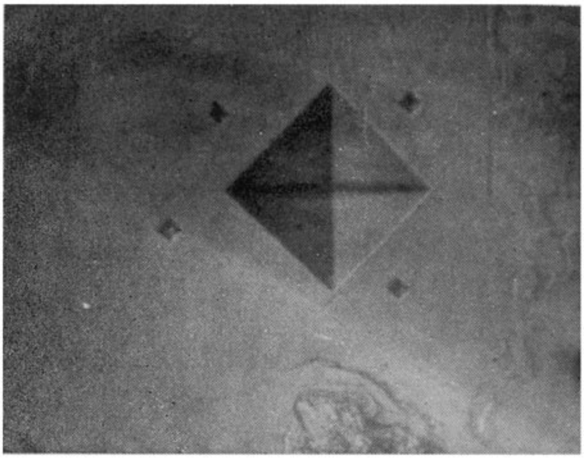

Figure 1. Indentor impressions at lower and higher loads (× 150).

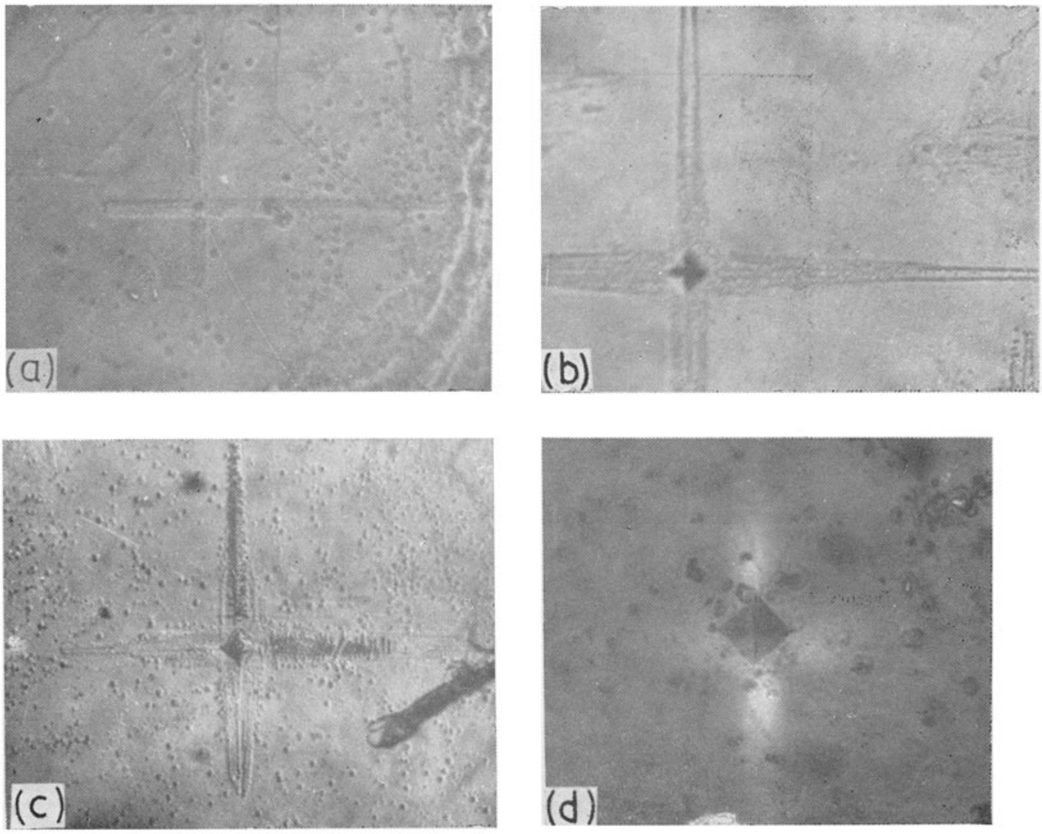

Figure 3. Rosette patterns obtained on undoped and doped NH_4Cl crystals after etching. (a) Indentor Load 1·25 P, (b) Indentor Load 10 P, (c) Load 10 P, (d) Strain pattern obtained after placing the indented copper doped NH_4Cl crystal between crossed nicols.

Table 1. Hardness data for few alkali halide crystals.

Crystal	Hardness (Present work) kg/mm^2	Hardness (Chin *et al* 1972) kg/mm^2	Hardness (Hopkins *et al* 1933) kg/mm^2
NaCl	19·6	18·2	18·5
KCl	10·0	9·3	9·2
KBr	9·37	7·0	..

Table 2. Vickers hardness data for NH_4Cl, NH_4Cl, NH_4Br and copper doped NH_4Cl.

Crystal	Concentration of copper in mol. %	Hardness (kg/mm^2)
NH_4Cl	..	2·5
NH_4Br	..	2·4
Cu–NH_4Cl	0·1	16·2
Cu–NH_4Cl	0·2	20·8
Cu–NH_4Cl	0·4	22·6
Cu–NH_4Cl	0·5	23·6
Cu–NH_4Cl	1·5	28·3
Cu–NH_4Cl	3·0	32·0
Cu–NH_4Cl	5·0	36·4

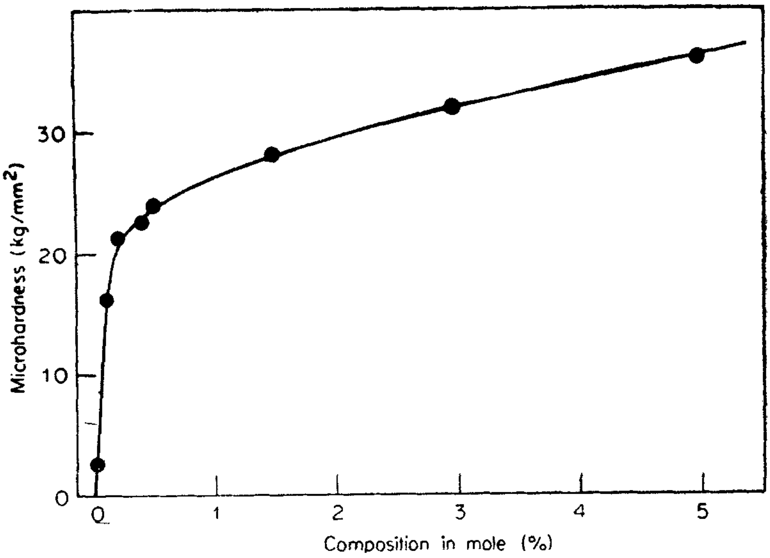

Figure 2. Variation of microhardness with composition of copper (in mol, %) in NH_4Cl crystals,

It was earlier shown that the size of the dislocation of rosette produced around a microhardness indentation is a useful and convenient test for determining mechanical strength of single crystals (Davison and Vaughan 1958). The dislocation rosette around the indentations were revealed by etching the crystals in an etchant consisting of methanol to which cadmium chloride is added as poison. Figures 3 (a) and 3 (b) show the photomicrographs of 'Rosette' patterns obtained on NH_4Cl crystals with 1·25 P and 10 P loads, respectively. The pattern obtained at a load of 10 P in the case of NH_4Cl doped with 1·5 mol% copper chloride (Cu^{2+}) is shown in figure 3 (c). It is seen that the wing lengths which corresponds to the distance travelled by the dislocation decrease as the hardness increases and so in harder crystals the distance travelled is less. The figure also shows that the dislocations in NH_4Cl are propagated along ⟨100⟩ directions. The indentations produce strains in the crystal and these have been observed by placing the crystal in crossed nicols. Figure 3 (d) is a photomicrograph obtained on NH_4Cl crystal doped with 5 mol% copper chloride. It is seen that maximum strains are produced along ⟨100⟩ direction, the direction along which the dislocations have moved.

Upit and Varchenya (1965) and Buckle (1945) have reported earlier that the hardness number gradually increases as load decreases. The microhardness value obtained at different loads for NH_4Cl and NH_4Br are shown in figure 4. The values obtained for NaCl, KCl and KBr are shown in figure 5 and those for NH_4Cl crystals doped with 1·5, 3 and 5 mol% of Cu^{2+} are shown in figure 6.

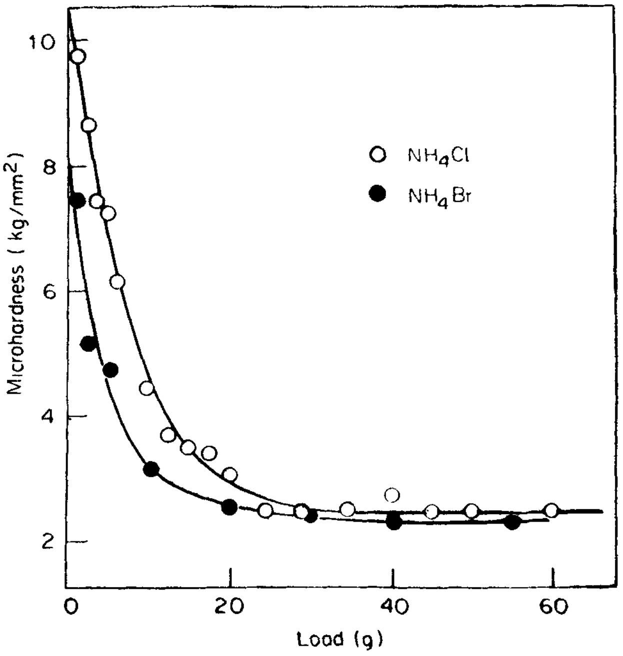

Figure 4. Variation of microhardness with load for NH_4Cl and NH_4Br crystals.

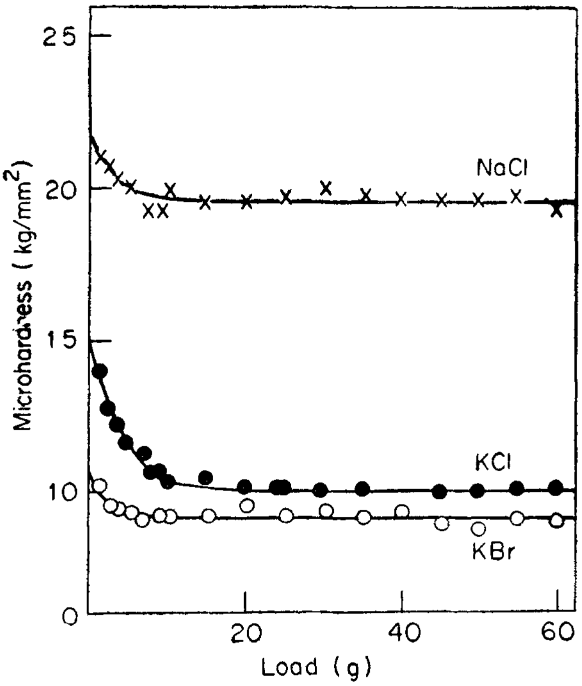

Figure 5. Variation of microhardness with load for NaCl, KCl and KBr crystals.

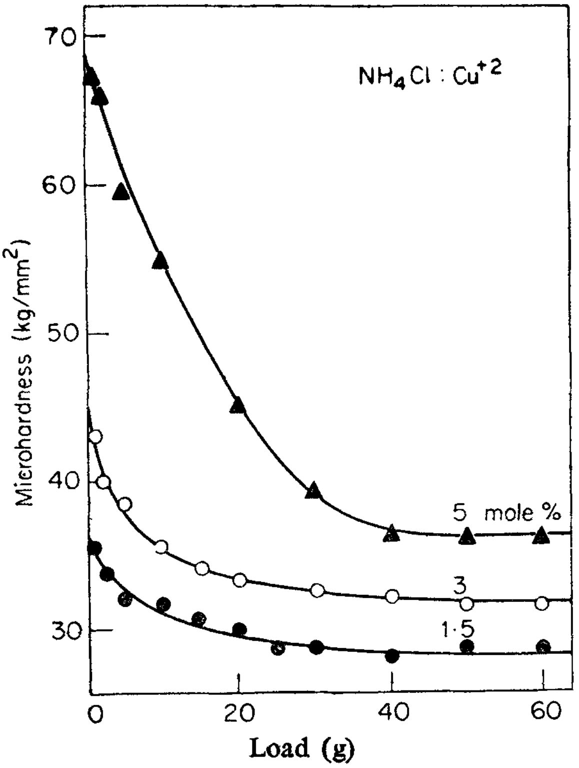

Figure 6. Variation of microhardness with load for copper-doped NH_4Cl crystals,

4. Discussion

The results presented in figures 4, 5 and 6 show that as load decreases, the hardness increases. Upit and Varchanya (1966) have obtained similar results in alkali halide crystals, and they interpreted their results as due to the effect of the surface on the mechanical properties of bulk. On the other hand, Hays and Kendall (1973) who obtained similar results in a number of metals and alloys adopted a different approach to explain their results and this method is used to analyse our results. Earlier Kick (1885) proposed an analysis of hardness and according to this the relation between load P and indentation length d is given as

$$P = K_1 d^n, \tag{1}$$

where P is the applied load in kg, d is the observed length of indentation (mm), K_1 and n are constants. Kick's analysis for hardness postulates a constant value of $n = 2$ for all indentors and for all impressions geometrically similar to each other. Equation (1) was further corroborated (Schultz and Hanemann 1941) when they proposed that Vicker's microhardness and macrohardness values were comparable. However Kick's law (equation (1)) has not been widley accepted due to the fact that n usually has a value less than 2, especially in the low load hardness region. In order to overcome this difficulty Hays and Kendall (1973) assumed that a portion of resistance to deformation could be evaluated by considering it as a Newtonian resultant pressure of the specimen itself. As a load P is applied to a sample, it was assumed that P is partially affected by a smaller resultant pressure W which is a function of the material being tested. According to Hays and Kendall (1973) W represents the minimum applied load to cause an indentation as load W will allow no plastic deformation.

If equation (1) is reconsidered on the basis of the sample's resistance pressure W, it follows that

$$P - W = K_2 d^2, \tag{2}$$

where K_2 is constant, and $n = 2$ is the logarithemic index. In this case n should be equal to 2, since it is proposed that the factor W allows the limiting case to prevail where hardness is not markedly dependent on the load. To evaluate the fraction W for a particular solution, it is feasible to solve the two equations by subtraction, thus

$$W = K_1 d^n - K_2 d^2, \tag{3}$$

$$d^n = W/K_1 + K_2/K_1\, d^2. \tag{4}$$

From this point the analysis is completed by simple graphical methods. A logarithmic study of equation (1) shows that the values of n and K_1 for any set of descrete data can be obtained from a plot of log P against log d. The index n is of course the slope while K_1 is defined as that particular load P which exists at $d = 150 \times 10^{-5}$ mm (figure 7). Similarly a cartesian plot of equation (4) for d versus d^2 yields the slope K_2/K_1 and intercept W/K_1. Since K_1 is known from the previous logarithimic plot, the solution is simplified. All the key data obtained are shown in table 3. Figure 8 is a plot of log $(P - W)$ vs log d, from which $n = 2$ is obtained. This shows that the idea of resistance pressure proposed by Hays and Kendall (1973) can also be applied to alkali and ammonium halide crystals.

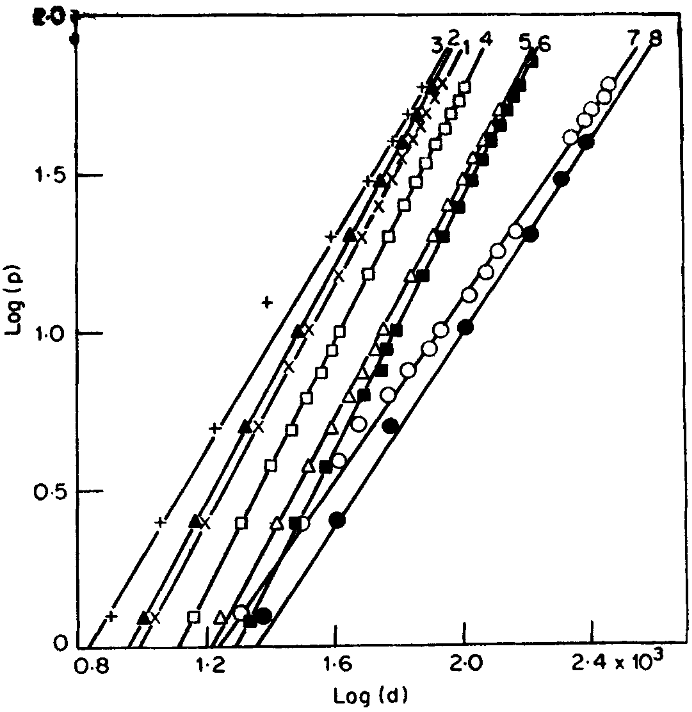

Figure 7. Relationship between the applied load (log P) and the Vickers diagonal (log d) for various crystals.

Table 3. Results of hardness analysis.

Crystal	K_1 (kg)	n	W/K_2	K_2/K_1	K_2 (kg)	$W \times 10^{-6}$ (kg)
Cu–NH_4Cl (5 mole %)	0·01349	1·6666	0·00070	1·8181	0·06340	9·443
Cu–NH_4Cl (3 mole %)	0·01122	1·8518	0·00050	1·3333	0·01495	5·610
Cu–NH_4Cl (1·5 mole %)	0·00933	1·8648	0·00140	4·7000	0·01696	13·062
NaCl	0·00588	1·9608	0·00080	1·2048	0·00709	4·704
KCl	0·00346	1·8693	0·00032	1·9900	0·00689	11·072
KBr	0·00269	1·9608	0·00100	1·2260	0·00330	2·690
NH_4Cl	0·00239	1·4286	0·00600	32·7868	0·07865	14·340
NH_4Br	0·00169	1·5335	0·00480	14·4927	0·02453	8·112

Although hardness has been defined in several ways it is now generally accepted that it is the resistance offered to dislocation motion. There are several contributions to the resistance to dislocation motion and they can be classified broadly into two types (i) the intrinsic resistance and (ii) the resistance due to imperfections.

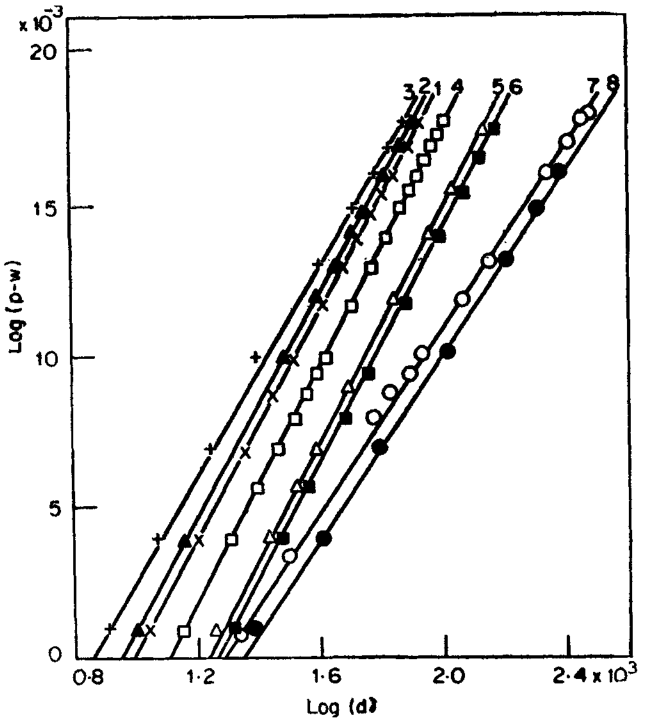

Figure 8. Relationship between true applied load (log $P - W$) and the Vickers diagonal (log d) for various crystals.

It is well known (Blank and Smekel 1930; Johnston 1962; Dryden *et al* 1965; Newey *et al* 1966; Chin *et al* 1973 and Labenets and Startsev 1968) that dilute additions of divalent impurity has an appreciable effect on the hardness of alkali halide crystals. For each divalent ion introduced into the lattice a positive ion vacancy is formed and these defects are distributed in various ways. The impurity ions and vacancies could be present as impurity-vacancy dipoles or as larger aggregates. All these defects act as obstacles to dislocation motion thus increasing the hardness of the crystals. The experimental results show that doping with copper (Cu^{2+}) increases the hardness of NH_4Cl crystals considerably. This dramatic increase has been explained as due to the tetragonal strains introduced into the lattice by the impurity-vacancy dipoles (Fleicher 1962). The large increase in hardness of NH_4Cl crystals doped with Cu^{2+} also may be due to the pressence of impurity vacancy dipoles. At high concentration of impurity, the increase in hardness is not much and this may be due to the association of impurity-vacancy dipoles into larger aggregates as suggested by Dryden *et al* (1965). The formation of impurity-vacancy dipoles and their aggregation is well known in alkali halide crystals. However, the phenomena have to be confirmed in ammonium halide crystals by some other experiments such as dielectric loss and ionic thermo-currents.

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