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ON « MECHANICAL » EFFECT OF IONIZING RADIATION IN KCl CRYSTALS

J. Z. DAMM and M. SUSZYŃSKA

Instytut Niskich Temperatur i Badan Strukturalnych, Polska Akademia Nauk, Wroclaw

Abstract. — Potassium chloride crystals of various origin, both as received and plastically deformed, are coloured by hard or soft ionizing radiation. Based on measurements of microhardness and absorption spectra we point out the existence of some secondary effects of ionizing radiation resembling the effects of ordinary plastic deformation. The « mechanical » effect of hard ionizing radiation is found to resemble that of plastic deformation within the easy glide range and the effect of soft radiation is found to be comparable with that of plastic deformation within the strain hardening range. A mechanism responsible for the radiation-induced plastic deformation of crystals is proposed and some experimental data are discussed.

Résumé. — Les cristaux de KCl de différentes provenances, non déformés ou soumis à une déformation plastique, ont été colorés par des rayonnements ionisants durs ou mous. Les mesures de la microdureté et des bandes d’absorption indiquent l’existence de certains effets secondaires des rayonnements ionisants rappelant les effets de la déformation plastique ordinaire. L’effet « mécanique » des rayonnements durs est comparable à la déformation plastique dans le stade de glissement facile et l’effet des rayonnements mous est comparable à la déformation plastique dans le stade de durcissement. Nous avons proposé un mécanisme responsable de la déformation plastique des cristaux, provoquée par l’irradiation. À l’aide de ce mécanisme, certaines données expérimentales sont discutées.

The influence of spectral composition of ionizing radiation on generation of colour centres in alkali halide crystals has not been sufficiently explained so far. The soft x-rays being strongly absorbed by the crystal produce a sharp colouration gradient in a thin layer adjacent to the surface irradiated directly (cp. [1,2]). The concentration of F centres in the vicinity of this surface reaches a value higher than \(10^{18}\) cm\(^{-3}\) even after relatively small radiation dose (cp. [1]). The hard ionizing radiation like \(\gamma\)-rays or filtered x-rays, colours the crystal uniformly in bulk whereby the concentration of colour centres reached even after rather high radiation doses is in general lower than in the former case. In dependence on spectral composition of the radiation used the mechanical properties of crystals are changing in a quite different manner, too (cp. [3-9]).

In this paper there are presented the results pointing to the existence of some secondary effects of ionizing radiation induced in potassium chloride crystals, resembling the effects of plastic deformation.

1. Experimental. — Five different single KCl crystals were used: (i) natural KCl (sylvine); commercial KCl: (ii) Harshaw and (iii) Hilger-Watt; KCl grown in this laboratory by the Czochralski method: (iv) pure and (v) doped with Zn\(^{2+}\) (about 60 ppm). The crystalline slabs were coloured at room temperature by the nonfiltered x-rays from a copper tube (the operation conditions are given in figures), by the x-rays filtered through a 1 mm thick KCl slab, or by \(\gamma\)-rays from a \(^{60}\)Co source. In some experiments, to avoid any larger error which might be due to the differences between the crystalline slabs obtained even from the same single crystal, a thicker slab of the material examined was cleaved into two parts one of which was coloured by the nonfiltered x-rays and the other by hard rays. There was examined the influence of plastic deformation (uniaxial compression [10]) of some crystals on the generation of colour centres. The absorption spectra of coloured crystals were measured in the range of 200-1 000 nm in a Hilger spectrophotometer (H 700). The changes of hardness in both irradiated and plastically deformed crystals were followed in a microhardness tester (Zeiss-Hanemann type D 32), the indentation diagonals being oriented along \(< 100 >\) directions. The mean dislocation density was appreciated by the etch pit method using an etchant of the composition: 13.3 g BaBr\(_2\) in 100 ml CH\(_3\)OH cp. [11]. If not other-
wise stated, the microhardness and dislocation density were measured on inner surfaces of the coloured or deformed crystals, revealed by cleaving.

2. Results. — The growth curves of F centres, microhardness curves and absorption spectra in u-v range of irradiated crystals are presented. The effect of plastic deformation on the microhardness of crystals and the generation of V₂ centres is shown.

2.1 Action of hard ionizing radiation. — Single KCl crystals used in this work considerably differ between each other, among others, in respect to their colourability. In figure 1 there are shown the growth curves of F centres in some nominally pure crystals (i), (ii) and (iii). The shape of these curves implies that the concentration of initial vacancies in (i) and (ii) is practically of the same magnitude while in (iii) it is considerably higher. In spite of the different colourability of crystals (ii) and (iii) the changes of microhardness followed along with irradiation bear the same character (Fig. 2). In the initial colouration stage a temporary softening of both crystals is observed whereby the relative microhardness drop is larger in vacancy rich material (iii). At higher radiation doses the microhardness rapidly reaches a limiting value higher than that of the nonirradiated material. The microhardness curve for crystal (iv) proceeds similarly. The remaining two materials behave in a different way. In natural KCl (i), the purity of which is not lower than the purity of crystals (ii) and (iii) the microhardness does not change at all with irradiation and in the doped KCl (v) it changes insignificantly.

It should be noticed that the microhardness measure-ments give some information on the gliding ability of dislocations present in crystal. In figure 3 there are compared the microhardness values of KCl crystals used in this work. It is noticeable that the three softer crystals (ii), (iii) and (iv) behave under irradiation in a different way from the harder ones (i) and (v). Based on the results presented one may expect that the eventual changes of microhardness induced in crystal by irradiation are dependent in some way on the initial state of dislocations present in crystal, and most probably are related with their ability of gliding.

The softening effect of the hard ionizing radiation observed in crystals (ii), (iii) and (iv) seems to result, as it has been suggested by Andronikashvili et al. [6, 7], from the radiation induced dispersion of original vacancy clouds pinning the dislocations.
To obtain some more information on the hardening effect of radiation, observed at higher doses (late colouration stage), the dislocation density of the crystals exhibiting specific changes of hardness was estimated. The mean values of dislocation density were appreciated from the observations on the inner surfaces of irradiated crystals. The original surfaces being themselves the two-dimensional defects may fasten the emerging dislocation ends sufficiently strongly to make them immobile and to obscure the eventual changes induced by the radiation inside the crystal. Additionally, the superficial defects produced by radiation may considerably differ from those present beneath the surface. Quite fruitful were the results obtained for crystal (iii), the initial dislocation density of which was sufficiently low (about $10^5$ cm$^{-2}$). It has been found that the mean dislocation density is practically kept constant for the lower radiation doses at which the microhardness reaches the minimum value. For higher radiation doses at which a distinct increase of microhardness was observed: the mean dislocation density was by an order higher (about $10^6$ cm$^{-2}$). The measurements of dislocation density in natural (i) and doped (v) KCl have not revealed any noticeable changes even after a prolonged irradiation.

2.2 ACTION OF SOFT IONIZING RADIATION. — It has been shown in numerous papers that the soft radiation being strongly absorbed by the crystal produces a colouration gradient accompanied by an expansion gradient cp. [1, 2]. Hence, at the same irradiation time at various depths of crystal various colouration stages should predominate. For this and some other reasons the growth curves of $F$ centres bear in general the same character independently of the material used. It has been shown in many papers that the microhardness measured on the directly irradiated surface of the crystal continually increases and may reach a value even by 100 $\%$ higher than the initial one [3]. As it is shown in figure 4 the microhardness of crystals (ii) (iii) and (iv) increases from the very beginning of irradiation. The microhardness increments for the above crystals are rather high and do not differ very much among each other. The behaviour of crystals (i) and (v) considerably differs from that of the above ones. In natural KCl the microhardness does not change at all with irradiation and in the doped KCl it increases in a much lower degree than in samples (ii) (iii) and (iv). The etch pit patterns observed on the inner surfaces of irradiated crystals cleaved perpendicularly to the irradiated surface have revealed that in (ii), (iii) and (iv) the dislocation density is the largest at the directly irradiated surface. In irradiated crystals (i) and (v) the distribution of dislocations has not shown any definite changes when compared with the nonirradiated samples.

Further information on activity of the soft radiation was obtained from the measurements of absorption spectra in the $\nu$-$\nu$ range followed with increasing radiation dose. It has been found that the $V$ bands observed in crystals (ii), (iii) and (iv) irradiated by the nonfiltered x-rays considerably differ from those observed in the same materials («twin» slabs) coloured by hard radiation (Fig. 5 and 6). Based on some earlier data one should expect that the $V$ band shift towards the longer wavelengths is related with the increased contribution of the $V_2$ band. It has been found that the $V_2$ band significantly increases in quenched crystals e. g. [12], and as it is shown in this paper (Fig. 8), in plastically deformed ones, too. In both procedures new anion and cation vacancies are introduced into the crystals bringing about an enhancement of the $F$ band and increase of the $V_2$ band contribution. The above data permit us to accept that the soft ionizing radiation produces in crystals new anion and cation vacancies in a process which is virtually absent during irradiation with hard ionizing rays.
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Fig. 5. — Absorption spectra of $V$ bands in KCl slabs (ii) irradiated by $\gamma$-rays (dotted lines) and by unfiltered $x$-rays from copper tube operated at 20 kV and 20 mA (solid lines). Thickness of both crystals — about 1.4 mm.

Fig. 6. — Absorption spectra of $V$ bands in KCl slabs (iv) irradiated by hard or by soft ionizing rays (cp. Fig. 5).

2.3 EFFECT OF PLASTIC DEFORMATION. — The effect of plastic deformation on the microhardness was examined in crystals (iii) and (ii) (Fig. 7). It should be noticed that the changes of microhardness observed along with the strain per cent, resemble the curves obtained for the same materials coloured by the hard ionizing rays (cp. Fig. 2). In the vacancy-poor material (ii) (cp. Fig. 1) no minimum appears and within the easy glide range the microhardness of crystals is kept constant. For higher deformations entering the strain hardening range, the microhardness increases.

In vacancy-rich KCl (iii) a distinct microhardness minimum appears pointing to an increased gliding ability of dislocations.

Similar character of the microhardness curves obtained for crystals either deformed or coloured by hard ionizing radiation does not seem to be formal. In earlier experiments [8] we have found that the microhardness curves obtained from the measurements on original surfaces of the deformed or irradiated crystals (ii) and (iii), possess a peak appearing at the beginning of the easy glide range or at the beginning of the initial colouration stage respectively. The origin of this superficial effect is not clear so far.

The changes of microhardness observed on inner surfaces of the crystals deformed, undoubtedly reflect the changes in gliding ability of dislocations. In the initial deformation stage the dislocations are assumed to break away from their original environment and hence in crystal (iii) a distinct microhardness minimum appears. It has been shown by Davidge and Pratt [13] that at the same time some quantity of new dislocations is also formed in crystal. In the final stage of the easy glide range the moving dislocations impinge on each other affecting the hardening of the crystal. The deformation in the strain hardening range brings about an increased generation of new dislocations and
additionally the generation of new anion and cation vacancies. At this stage the vacancies are most probably produced by intersecting each other dislocations. It has been shown in earlier paper [10] that within the strain hardening range the quantity of new anion and cation vacancies is proportional to the strain percent.

In Fig. 8 there are compared the u-v spectra of two crystalline slabs of KCl (ii) (one as received and the other one plastically deformed) irradiated by hard ionizing rays. In agreement with the increased quantity of new cation vacancies introduced into the crystal, the contribution of the $V_2$ band in the deformed slab is considerably larger than in the nondeformed one.

It is important to note that the hard ionizing radiation does not produce in KCl crystals examined any noticeable quantities of cation vacancies. The above two effects supported by the experimental data presented in 2.1 and 2.3 (cp. Fig. 2 and 7) point to a close relationship between hard ionizing radiation and plastic deformation within the easy glide range. It should be emphasized that the processes leading to the temporary softening of deformed or irradiated crystals, related with the increased gliding ability of dislocations, are in both cases entirely different.

The nonfiltered x-rays with a high contribution of the soft spectrum, bring about:

a) generation of high quantity of new dislocations in vicinity of the surface irradiated directly, and

b) generation of new anion and cation vacancies.

The above effects induced by the soft radiation resemble the effects of plastic deformation within the strain hardening range (cp. Fig. 5 and 8).

The discussed «mechanical» effects of ionizing radiation are, however, not always observed. In natural KCl (i) neither dislocations nor cation vacancies are produced, even after very long lasting irradiation with nonfiltered x-rays. The behaviour of the doped crystals (v) is of an intermediate character, as the radiation-induced plastic deformation is in this material strongly suppressed.

Now let us consider the probable mechanism which might be responsible for the effects described. The softening of the crystals encountered in the early stage of irradiation [5, 6, 7, 8, 9] can be well explained, according to Andronikashvili et al. [6, 7], by the dispersion of vacancy clouds pinning the old dislocations. Experimental data presented in this paper fully confirm such an interpretation. The hardening effect observed in the late stage colouration (cp. Fig. 2) seems to be related with the activity of some strains induced in crystal by the radiation. Convincing experiments pointing to the existence of such strains were reported by Leider et al. [14] who have found that irradiation of a freshly powdered NaCl crystal with x-rays induces an increased crack formation. The authors have concluded that the energy resulting from irradiation is in some way added to the energy introduced into the crystal by grinding. The experimental conditions applied permit to expect that the contribution of the soft radiation strongly absorbed by the crystal, was in the above experiments very low and that the effects observed were due to the activity of hard radiation only. The appearance of some local strains induced by hard ionizing radiation may be

![Absorption spectra of V bands in KCl slabs (ii) irradiated by γ-rays. Dotted line — nondeformed crystal, solid line-plastically deformed by 4.9%](image)

**Fig. 8.** — Absorption spectra of $V$ bands in KCl slabs (ii) irradiated by γ-rays. Dotted line — nondeformed crystal, solid line-plastically deformed by 4.9%.

3. Discussion. — The comparison of the results presented points to the existence of some secondary effects of ionizing radiation, observed in potassium chloride crystals, similar to those induced by plastic deformation. Now let us briefly consider the observations pertinent to the above comparison. The hard ionizing radiation, except of other activities, brings about:

a) unpinning of the old dislocations owing to the radiation induced dispersion of vacancy clouds, followed by.

b) generation of new dislocations.
tenta-tively explained on the basis of the mechanism recently proposed for the late colouration stage observed at room temperature [8, 10, 15]. In this mechanism an essential role is played by the mobility of the holes produced by ionizing radiation. A number of these holes is expected to reach the dislocations and to bring about the segregation of the neutral halogen atoms. Consequently, in the lattice an equivalent number of anion vacancies is left. These vacancies, except of being responsible for further generation of $F$ centres, should affect a local expansion of the lattice leading to the appearance of some local strains operating in the vicinity of the parent dislocations. Under the action of these strains the sources generating new dislocations may become active. The dislocations gliding under the action of these radiation-induced strains should also impinge on each other bringing about the hardening of the crystals. The last two processes are expected to proceed in the late colouration stage, in which the old dislocations are stripped off from the primary vacancy clouds. In the initial colouration stage in which the dispersion of vacancy clouds predominates, the dislocations should not be accessible to the migrating holes and hence the generation of new anion vacancies should be negligible in agreement with the numerous experimental data.

In crystals irradiated with soft ionizing radiation the colouration is not uniform, being the highest at the directly irradiated surface cp. [1]. The thickness of the layer absorbing the soft radiation strongly depends on spectral composition of the radiation used and for longer wavelengths it may be of the order of few hundredths of $\mu$m (cp. Fig. 9). It has been shown by Primak et al. [16] that the expansion gradient induced at directly irradiated surface of an alkali halide crystal may forward plastic deformation leading to the appearance of the strain birefringence bands. It is shown in this paper that the strain gradient induced in KCl crystals except of being responsible for the generation of new dislocations, is high enough to force the dislocations to intersect each other. Consequently, new anion and cation vacancies are produced in a purely mechanical process.

Based on earlier experiments, in which the plastic deformation effect on the generation of colour centres was examined [10], we have appreciated the quantity of vacancies produced by the soft radiation in crystall (ii) (cp. Fig. 5). By assuming that the quantities of anion and cation vacancies produced owing to plastic deformation are practically the same, one might expect that the optical density increase in the $V_2$ band by one unit should correspond to about $5 \times 10^{16}$ cation vacancies per cm$^3$. A rough graphical resolution of the $V$ band formed in KCl crystal (ii) by the soft radiation, permits us to expect that in a rather thin strained layer of the irradiated crystal more than $10^{17}$ cation vacancies per cm$^3$ are formed. Accordingly, an equivalent number of anion vacancies should be produced, too.

The mechanical effect of soft ionizing radiation explains the increased colourability of the crystals in which the concentration of $F$ centres in the superficial layer may reach the value higher than $10^{16}$ $F$ centres per cm$^3$. Moreover, it permits to answer why in plastically deformed crystals coloured by the nonfiltered x-rays a rather small colourability increase is observed [17]. In that case the effect of ordinary plastic deformation seems to contribute but little to the deformation induced by the soft radiation, in contrast to the effect observed in plastically deformed crystals irradiated with hard ionizing rays.

The plastic deformation induced by the soft radiation seems to exert one more effect observable in the u-v absorption spectrum. For not too high radiation doses one observes a distinct raise at the short wavelength side of the $V_2$ band in vicinity of 200 nm (Fig. 5, 6). It should be emphasized that a similar absorption raise is observed in crystals plastically deformed by e. g. uniaxial compression and it is related with the increased dispersion of light in vicinity of the absorption edge.

The mechanism discussed permits us also to explain the lack of the « mechanical » effect in some materials. It is well known that the natural crystals are frequently highly strained [18] and the dislocations in such a
material are expected to be pilled up. For this reason the strains introduced by the radiation may be too weak to force out the dislocations from their surroundings. In agreement with this supposition one can explain the low colourability observed in natural KCl crystals examined (cp. Fig. 1). In the mechanism proposed the dislocations play an important role by acting as the traps for the migrating holes and as the sources of new anion vacancies conditioning the generation of F centres. In artificial, nominally pure crystals (ii), (iii) and (iv), the quantity of dislocations increases with irradiation and hence it is possible to reach a high concentration of F centres in these materials irrespective of the quantity of initial vacancies present in crystal prior to irradiation. In natural crystals under the action of radiation the dislocations are immobile and hence the late colouration stage seems to be limited by the quantity of already existing primary dislocations.

It should be emphasized that the microhardness measurements performed for various materials seem to be useful in predicting the behaviour of the crystals during colouration with ionizing rays. In our experiments the most pronounced mechanical effect of radiation was found in KCl crystals (ii) for which the lowest initial microhardness was observed (cp. Fig. 3). This effect was somewhat weaker in crystals (iii) and (iv). In the doped crystal (iv) the mechanical effect was significantly suppressed. The initial microhardness of this material was higher than that of the above three materials. In natural crystals (i), the microhardness of which was the highest (Fig. 3), no mechanical effect of radiation was observed.

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