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SPECIFIC FEATURES OF STRENGTHENING PHENOMENA IN NaCl:Eu^{2+} CRYSTALS*

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Mechanical strength of europium doped NaCl crystals was studied as a function of both the dopant concentration (c_{2+}) and the kind of obstacles effective in hindering the motion of dislocations. It has been found that the yield strength (σ_0) of solution treated samples is determined by Snoek reorientation of both isolated dipoles and linear dimers within the stress fields of moving dislocations. The deviation of the $\sigma_0(c_{2+})$ plot from linearity is probably due to the presence of quadripoles cutted through the moving dislocations. Also for as- received specimens two precipitation strengthening mechanisms are postulated; these are the Kelly–Nicholson cutting and the Orowan looping, respectively.

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1. Introduction

The purpose of this paper is to demonstrate how the concentration dependence of the yield stress reflects both the state of divalent europium ions in single NaCl crystals and the elementary strengthening processes induced by the presence of these impurities. Divalent europium was selected to make these studies in view of the fact that detailed information concerning the aggregation and precipitation state of these impurities in the NaCl crystals have been recently gathered by using X-ray diffraction and optical techniques [1–6].

It has been evidenced rentgenographically that the following phases are characteristic of as-received (AR) samples:

— regular (CsCl-type) Na_2EuCl_4,

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*The experimental results were partly (as a poster) presented at Colloque International "Mechanismes de Deformation et Resistance des Materiaux Nouveaux", Aussois (France) 1990.

— regular (CaF_2-type) extraordinary $EuCl_2$, and

— orthorhombic ($PbCl_2$-type) normal $EuCl_2$.

On the other hand, absorption studies of these crystals (doped in a wide concentration range) showed that the optical transitions within europium ions embedded in various surroundings result in four types of optical spectra shown in Fig. 1.

In previous works on the hardening induced by europium related obstacles in NaCl monocrystals, the concentration dependence of the yield stress was practically not analyzed [7, 8]. In this sense, the present work extends and completes these pieces of information.

2. Experimental details

The yield stress σ_0 of a series of NaCl:Eu^{2+} crystals was measured as a function of the dopant concentration c_{2+} for both as-received (AR) and solution-treated (ST) samples. If not otherwise stated, the measurements were performed at room temperature (RT). Uniaxial compression along $< 100 >$ direction was realized in the INSTRON machine (Modell 1112) working at the strain rate ε being equal to 3×10^{-4} s^{-1}.

The crystals were grown in our Laboratory by a modified Bridgman method. The modifications made assure both dehydration of the europium salt added (Eu_2O_3) and reduction of the valency state of the dopant ($3+ \rightarrow 2+$). The concentration of Eu^{2+} in the crystals was determined from the optical absorption of ST samples according to the following relationship:

$$c_{2+}[\text{mole ppm}] = 4.5 \times \alpha(e_g)[\text{cm}^{-1}],$$

where $\alpha(e_g)$ is the absorption coefficient of the high energy band [9]. These optical measurements were made parallel with the mechanical ones by means of a SPECORD spectrophotometer (Zeiss). The solution treatment was performed by heating the AR samples at about 893 K for 30 minutes and then putting them on a cold (RT) copper plate.

3. Results and discussion

3.1. ST-state

The A-type absorption spectrum was characteristic for the major part of ST samples. Only for the samples containing more than about 150 mole ppm of europium the spectrum becomes more similar to B-type than to type A (Fig.1, curves A and B, respectively).

Figure 2 shows the $\sigma_0(c_{2+})$ dependences of the ST samples. Reasonably straight line was obtained at RT (curve 1) for the first concentration range (ST–I) which extrapolates to $\sigma_0(0) = 1.5$ MPa; this value of σ_0 is characteristic of our

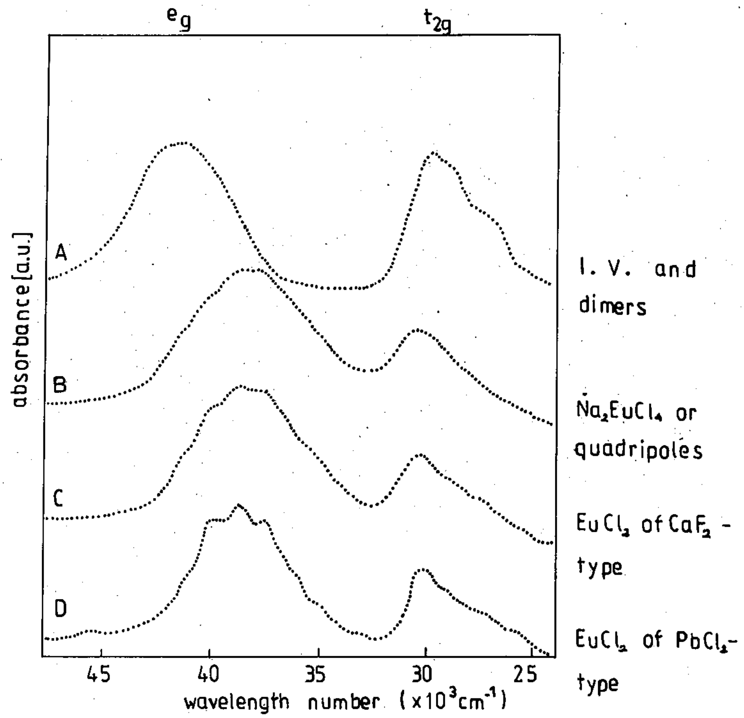

Fig. 1. Optical absorption of NaCl:Eu^{2+} crystals; spectra A,B,C,D and D — correspond to I.V. dipoles and linear dimers — Na_2EuCl_4, $EuCl_2$ (of CaF_2 type) and $EuCl_2$ (of $PbCl_2$ type), respectively.

nominally pure NaCl crystals [10]. In the ST–II range, the RT experimental data deviate from the linearity and may be fitted by a $\Delta\sigma_0(c^n_{2+})$-type of dependence with $n = 0.6$ which resembles the exponent value characteristic of AR–I specimens, cf. Sec.3.2 and Fig. 3(b); for $\Delta\sigma_0$ the difference between the measured σ_0 and the sum of σ_0(ST–I) and σ_0 (nomin. pure) has been considered.

The linear concentration dependence and the relatively low strength of ST–I samples can be understood in the terms of Snoek type interactions between the moving dislocations and the reorientable impurity–vacancy (I.V.) dipoles. With this approach [11] one can use the Frank's formula for the elastic misfit $\Delta\epsilon$ around dipoles in the following form:

$$\Delta\varepsilon = \Delta\sigma_0/2(6.91Gc_{2+}),$$

where $\Delta\sigma_0$ denotes the increase of the crystal strength induced by the dopant, and G — the shear modulus of the system [12]. Assuming that all impurity ions are in the form of I.V. dipoles, i.e. $c_{2+} = c_{\mathrm{I.V.}}$, $\Delta\epsilon$ equals 0.11. However, taking into account that the quenching procedure used after solution treatment is not rapid

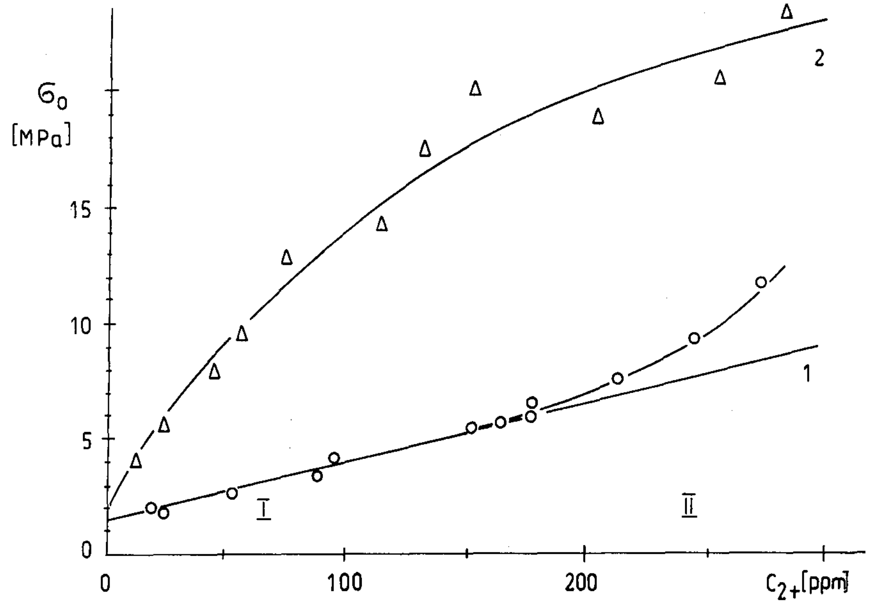

Fig. 2. Concentration dependence of the yield strength of ST samples measured at RT (curve 1) and LNT (curve 2).

enough to quench all the dipoles [8, 9, 13], $c_{\text{I.V.}}$ is smaller than c_{2+} and the correct value of $\Delta\epsilon$ should be a little bit larger.

The fact that all ST–I samples show the same optical spectrum (A) and the linear $\sigma_0(c^{1}_{2+})$ dependence suggests that the first aggregation products influence the structure sensitive properties of NaCl:Eu^{2+} crystals in a way similar to isolated dipoles. This conclusion was additionally supported by the results of mechanical testing performed at LNT, cf. Fig. 2, curve 2. The expected Fleischer type of interactions yield a $\sigma_0(c^{1/2}_{2+})$ plot for both the I.V. dipoles and the linear dimers as well [14].

The deviation of the RT — $\sigma_0(c^{1}_{2+})$ plot from linearity, detected for ST–II specimens, may be related either with further aggregation of dipoles or with a transformation of loosely bound dimers into a more stable configuration, e.g. the planar one. In contrast to aggregates I, the mutual interactions of europium ions embedded within these quadripoles can also influence the optical properties of crystals causing — among others — a shift of both absorption bands towards longer wavelengths and a qualitative transformation of the A-type spectrum into the type B. Moreover, the quadripoles considered cannot reorient either in an electric field or in the stress field of moving dislocations, and the mechanical strength of these crystals should be determined by the elastic type of interactions; more experimental results should be, however, the best proof of this hypothesis.

3.2. AR-state

According to the classification of the optical absorption spectra the increase of $\alpha(e_g)$ in AR samples is accompanied by continuous changes of the europium related phases. Because the nature of these precipitates differs from each other, one has to expect that their interactions with moving dislocations should also be different. In fact, the distinct strengthening observed at the beginning (Fig. 3(a), region I) is followed by a plateau (Fig. 3(a), region between I and II), where σ_0 remains practically unchanged, and finally — a relative softening occurs (Fig. 3(a), region II). The detected strengthening–to–softening transition resembles the effects typical of many *fcc* metal alloys. Hence, the interpretation of these data can be principally done in frames of the well known precipitation hardening mechanisms.

The increase of σ_0 in the initial concetration range (AR–I) (Fig. 3(b)), suggests the operation of a cutting mechanism typical of dislocation interactions with structurally and dimensionally coherent particles [15]. It should be noted that although the requirement of structural coherency is not fulfilled for the *bcc* type of structure, tentatively ascribed to the Na_2EuCl_4 particles [1], the microstructural data are also typical for an ordered array of planar dimers, i.e. the quadripoles [16]. If two such dimers are distributed within the NaCl matrix in a way illustrated in Fig. 4, the coherency and stoichiometry of the Na_2EuCl_4 particles remain preserved. The considered part of the $\Delta\sigma_0(c_{2+})$ dependence corresponds to a power law with n equals either 0.5 or 0.6 for $\Delta\sigma_0$ being equal either to $\sigma_0(\mathrm{AR}) - \sigma_0(\mathrm{ST})]$ or to $[\sigma_0(c_{2+}) - \sigma_0(\mathrm{nomin.pure})]$, respectively. Both values of n are in agreement with the theoretical expectations [14, 15].

At higher concentrations (Fig. 3(a)), the nearly constant crystal strength is accompanied by the appearance of a new type of absorption spectrum (C) ascribed to the transitions within $EuCl_2$ particles with an extraordinary (CaF_2) type of structure which is coherent with the matrix lattice. These metastable $EuCl_2$ particles represent obstacles which are more difficult to be overcome by the moving dislocations than the above discussed Na_2EuCl_4 ones. At this treshold concentration, the NaCl:Eu^{2+} crystals attain their maximal yield strength and the strengthening of material becomes exchanged by a relative softening. These phenomena should correspond to the exchange of cutting by looping of dislocations around some inpenetrable particles of the europium-related second phase. It is necessary that either the structurally coherent Na_2EuCl_4- and CaF_2-type $EuCl_2$ particles became dimensionally incoherent at these concentrations (AR–II) or a new phase appears which is structurally incoherent with the matrix. In favour of the second possibility are the optical absorption data; namely, the spectrum becomes of D-type which corresponds to the $EuCl_2$ phase with the orthorhombic ($PbCl_2$-like) type of structure. On the other hand, however, the observed two $\sigma_0(c_{2+})$ plots suggest that at this precipitation stage the size of particles may be also important. The strong size effect, typical of the Orowan-looping [17] is in contrast to the weak concentration dependence of the crystal strength.

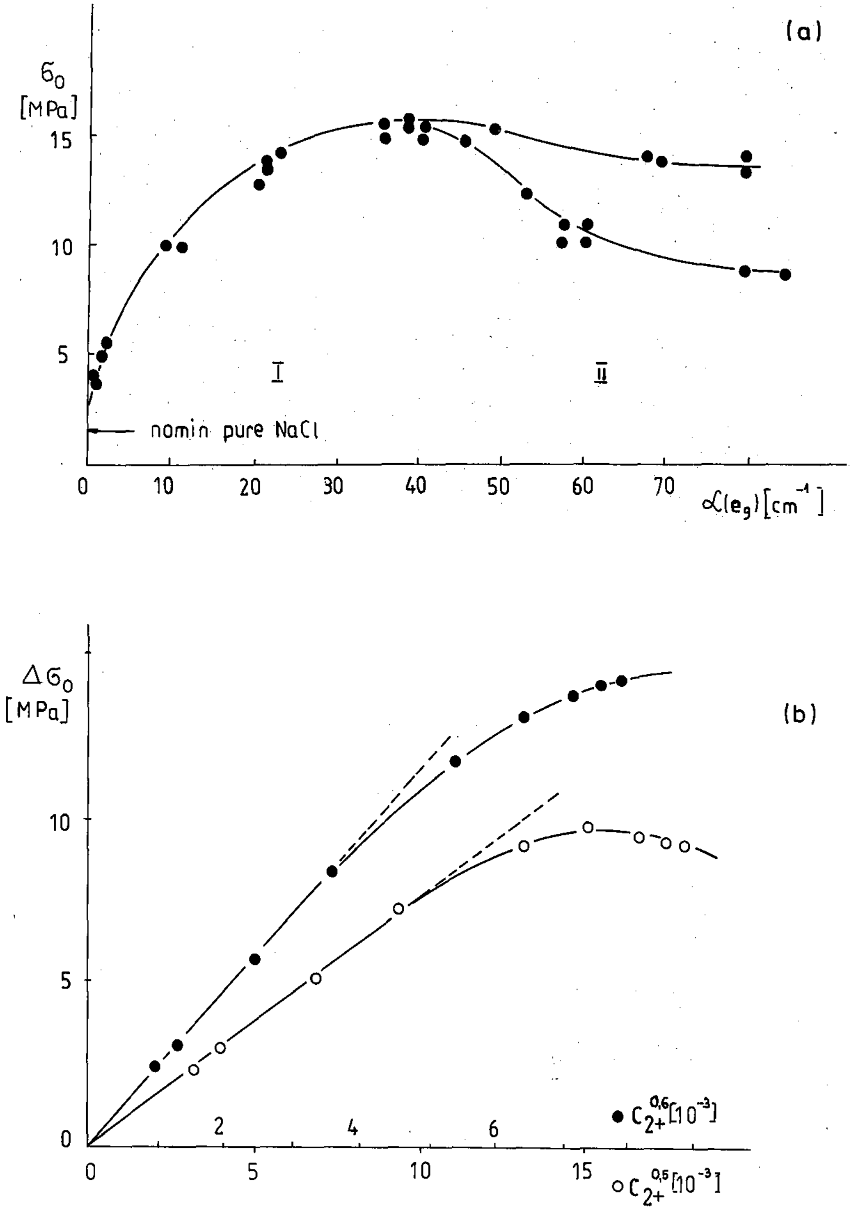

Fig. 3. Concetration dependence of the yield strength σ_0 (a) and the yield strength increments $\Delta\sigma_0$ (b) of AR samples; for region I $\Delta\sigma_0$ is proportional to c_{2+}^{n}, where (•)$\Delta\sigma_0 = [\sigma_0(c_{2+}) - \sigma_0(\text{nomin.pure})]$ yields $n = 0.6$, and (o)$\Delta\sigma_0 = [\sigma_0(\text{AR}) - \sigma_0(\text{ST})]$ relates to $n = 0.5$.

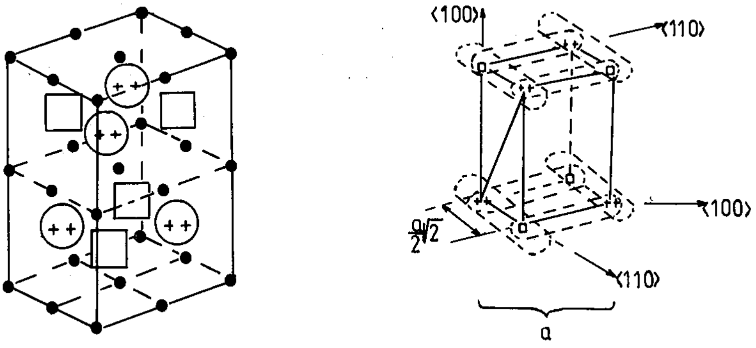

Fig. 4. Structure of the Na_2EuCl_4 precipitates; from among three possible orientations within the NaCl-type cation–sublattice only one is visualized. The marks: (•), (∘), (□) correspond to Na^+, Eu^{2+} and cation vacancies, respectively.

4. Conclusions

It has been confirmed that the yield strength of Eu^{2+}-doped NaCl crystals depends on both the concentration and the dispersion form of the europium-related obstacles effective in hindering of the moving dislocations. Changes in the concentration dependence of the yield stress occur together with changes of the dispersion form. These data also suggest that the particles present in AR-samples containing less than 50 mole ppm of Eu^{2+} exist in ST-specimens containing more than about 150 mole ppm of the dopant. Moreover, it has been ascertained that loosely bound dimers have the same effect on hardening as the isolated I.V. dipoles. This statement is in contrast with some previous results on $NaCl{:}Sr^{2+}$ crystals [10] for which the RT-hardening was considered as a sum of the Snoek contribution due to the dipoles and a Fleisher-type contribution related with the presence of small aggregates. In view of the present results either these aggregates are larger than clusters of 2 I.V. dipoles or the behaviour of dimers in $NaCl{:}Sr^{2+}$ crystals differs from that typical of isolated dipoles.

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