Recovery of the NMR Signal of Plastically Deformed Alkalijodide Single Crystals

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The annealing process of plastically deformed RbJ- and KJ-single crystals has been studied by means of NMR wide line and spin echo measurements on J^{127}. The mean lattice strain produced by the deformation is correlated with a mean quadrupole perturbation affecting the NMR signal. Resulting from second order quadrupole effects, the wide line measurements lead to a recovery temperature, which is much lower than the "real" recovery temperature given by the spin echo method. Nevertheless the evaluation of both types of measurements results in the same effective activation energy depending on the degree of deformation. The obtained values are probably caused by the migration of positive ion vacancies.

I. Introduction

In a rigid cubic lattice, the shape of the NMR signal of nuclei with spin $I>1/2$ is determined by the magnetic dipole interaction between neighbouring spins and the electric quadrupole interaction between the quadrupole moment Q of the resonant nuclei and the gradient of an electric field (EFG) at their sites.

Since the EFG is caused only by defects in the lattice destroying the cubic point symmetry around the defects, the mean quadrupole perturbation of the NMR signal is correlated with the mean distortion of the lattice [1]. The mean lattice distortion in a non-metallic cubic crystal is mainly due to the mean elastic strain fields of the dislocations produced by the deformation process. Therefore NMR is a good tool for studying the rearrangement of the dislocations during the annealing process, which results in a loss of elastic strain. In spite of that fact there exist only a few wide line measurements, i. e. OHKURA [2] on KBr^{79}, OTSUKA [3] on KJ^{127} and HÖHNE [4] on $AgBr^{79}$ which lead to a recovery temperature much lower than the real recovery temperature which is determined from the recovery of the bulk density, the microhardness and of the flow stress [5]. It will be shown that this discrepancy resulting from second order quadrupole effects vanishes in the case of spin echo measurements.

An evaluation of the annealing measurements according to MEECHAN and BRINKMAN [6] leads to an activation energy for the recovery process, which is independent of the method used if the measured quantity is single valued and monotonic in the mean elastic strain. This is the case in both, the wide line and the spin echo method.

II. Theory

In the case of an inhomogeneous dipolar and quadrupolar broadening the line shape $g(\omega)$ of the NMR wide line signal of nuclei with spin $I>1/2$ can be written as [1]

$$g(\omega)=\sum_{m=-I}^{I-1} c_m \cdot g_{\mathrm{D}}(\omega) * g_{\mathrm{Q}}^{(m)}(\omega). \qquad (1)$$

Here $g_{\mathrm{D}}(\omega)$ is the normalized distribution function of the dipolar frequencies, $g_{\mathrm{Q}}^{(m)}(\omega)$ is the corresponding function of the quadrupolar frequencies depending on state m, c_m is the relative transition probability $m \rightarrow m+1$

$$c_m=\frac{I(I+1)-m(m+1)}{\sum_{m=-I}^{I-1}[I(I+1)-m(m+1)]},$$

and $*$ stands for the convolution operation.

The corresponding expression for the line shape of a spin echo signal after a $\pi/2-\tau-\beta$ pulse sequence is given by [7]

$$E(t)=\sum_{m=-I}^{I-1} C_m(\beta) \cdot D(t) \cdot Q^{(m)}(t) \qquad (2)$$

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where $D(t)$ is the Fourier transform of $g_D(\omega)$ and $Q^{(m)}(t)$ is the Fourier transform of $g_Q^{(m)}(\omega)$, respectively, i. e.

$$D(t) = \mathcal{F}\{g_D(\omega)\} \quad \text{with} \quad D(0) = 1,$$
$$Q^{(m)}(t) = \mathcal{F}\{g_Q^{(m)}(\omega)\} \quad \text{with} \quad Q^{(m)}(0) = 1.$$

Contrary to the wide line signal, the magnitude of the coefficients $C_m(\beta)$ in the spin echo signal depend on the angle β of the second rf-pulse as calculated by MEHRING and KANERT [7].

In first order perturbation, the quadrupole frequency $\omega_Q^{(1)}(m)$ for the transition $m \rightarrow m+1$ can be expressed as

$$\omega_Q^{(1)}(m) = (2m+1)\frac{3eQ}{4I(2I-1)\hbar} V_{zz} f_1(\Theta, \Psi, \eta)$$
$$= (2m+1)\, a_1 \qquad (3)$$

where Q is the nuclear quadrupole moment, V_{zz} is the maximum component of the EEG-tensor produced by the displacement of the neighbouring atoms by elastic strains and $f_1(\Theta, \Psi, \eta)$ is an orientation function given by BEHRSON [8]. In the limit of linear continuum theory the EFG-tensor $\{V_{ik}\}$ is linearly dependent on the elastic strain tensor $\{\varepsilon_{ik}\}$, i. e. in the matrix notation

$$V_{ik} = \sum_1 S_{il} \cdot \varepsilon_{lk} \qquad (4)$$

where the S_{il} are called the gradient-elastic constants [1].

In second order, also the central transition $m = 1/2 \rightarrow -1/2$ is affected by the quadrupole interaction leading to a distortion frequency [8]

$$\omega_Q^{(2)}(1/2) \equiv a_2 = \frac{3}{64}\frac{2I+3}{I^2(2I-1)}\left(\frac{eQ}{\hbar}\right)^2 \frac{1}{\omega_0} V_{zz}^2 f_2(\Theta, \Psi, \eta) \qquad (5)$$

which depends on the Zeeman frequency $\omega_0 = \gamma H_0$ [γ: gyromagnetic ratio of the resonant nucleus, $f_2(\Theta, \Psi, \eta)$: orientation function, given by BEHRSON [8]].

Assuming a Gaussian line shape for the dipolar function $g_D(\omega)$, which is valid to a good approximation in the case of alkalihalide crystals [9] one can write

$$g_D(\omega) = \frac{1}{\sqrt{2\pi}}\frac{1}{\Delta}\exp\left[-\frac{\omega^2}{2\Delta^2}\right] \qquad (6)$$

where Δ^2 is the dipolar second moment, which can be calculated according to VAN VLECK [10].

Supposing a Gaussian distribution for the quadrupole frequencies ω_Q also, as discussed by KANERT and MEHRING [1] the corresponding distribution function can generally be expressed as

$$g_Q(\omega) = \frac{1}{\sqrt{2\pi}}\frac{1}{\langle a^2\rangle^{1/2}}\exp\left[-\frac{\omega^2}{2\langle a^2\rangle}\right], \qquad (7)$$

where the mean quadrupole distortion, represented by the second moment $\langle a^2\rangle$ is determined by first order and second order quadrupole effects, respectively. In first order perturbation, the second moment $\langle a_1^2\rangle$ is a linear function of the second moment $\langle \varepsilon^2\rangle$ of the elastic strain field, according to Eq. (4).

Starting from Eqs. (3) and (5) and using the values of $\langle f_1^2\rangle^{1/2} = 1.033$ and $\langle f_2^2\rangle^{1/2} = 3.31$ [11] the relation between the mean second order perturbation frequency $\langle a_2^2\rangle^{1/2}$ of the central transition and the mean first order perturbation frequency $\langle a_1^2\rangle^{1/2}$ of the satellite transitions is given in a good approximation by

$$\langle a_2^2\rangle^{1/2} = (2I+3)\,(2I-1)\,\langle a_1^2\rangle/\omega_0. \qquad (8)$$

Under these assumptions one can calculate the relative peak intensity f_m/f_{m_0} of the derivative of the wide line signal $g(\omega)$ [Eq. (1)] and the relative width t_E/t_{E_0} of the spin echo signal $E(t)$ [Eq. (2)], respectively as a function of the normalized quadrupole perturbation $w = \langle a_1^2\rangle^{1/2}/\Delta$. Here the echo width t_E is defined by the equation

$$E(t_E) = h_Q(I),$$

where $h_Q(I)$ is an optimized parameter [7].

Results of such a calculation are given in Fig. 1 in the case of J^{127} in KJ which is of interest here ($I = 5/2$, $h_Q = 0.623$, $\beta_{opt} = 40°$, $\Delta = 4.0 \cdot 10^3\ \mathrm{sec}^{-1}$). As expected both NMR parameters decrease with increasing perturbation w. For a certain perturbation w the peak intensity f_m/f_{m_0} of the wide line signal reaches the constant value $c_{-1/2} = 0.257$ whereas the echo width t_E/t_{E_0} is proportional w^{-1}. For large values of w the wide line signal decreases in second order depending on the Zeeman frequency ω_0. The different behaviour of both types of signals results in the different behaviour in recovery measurements.

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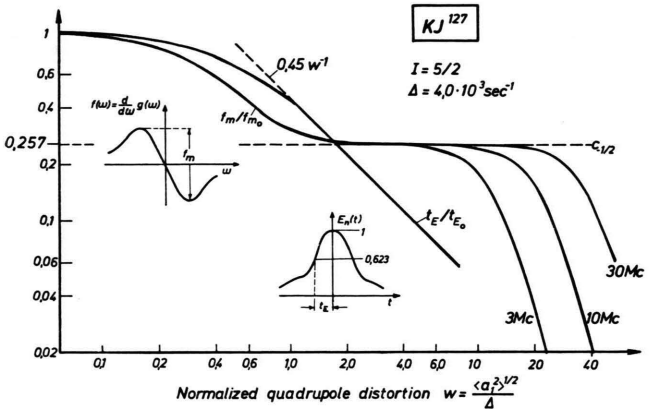

↑ Fig. 1. Calculated plot of the relative peak intensity f_m/f_{m0} of the wide line signal and relative spin echo width t_E/t_{E0} as a function of the normalized quadrupole distortion $w=\langle a_1^2\rangle^{1/2}/\Delta$ for KJ^{127} ($I=5/2$).

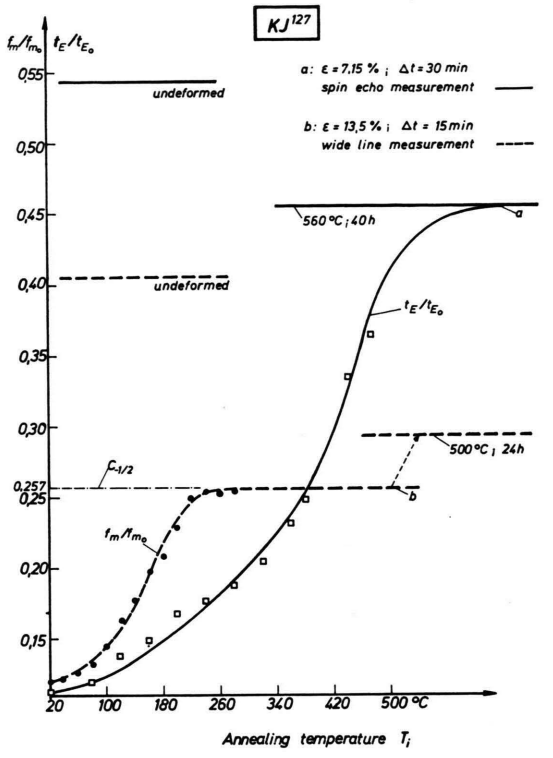

Fig. 2. Isochronal recovery curve of the echo width t_E/t_{E0} (plot a) and the peak intensity f_m/f_{m0} (plot b), respectively of J^{127} in plastically deformed KJ. Detailed data are given in the picture. →

III. Experimental Details

Superpure single crystals of KJ and RbJ (supplied by Dr. K. KORTH, Kiel, Germany) of the size $11\times22\times25$ mm³ were deformed by static compression in ⟨100⟩-direction at room temperature. After deformation every crystal was split into two almost equal pieces which were polished to cylindrical samples of about 8 mm diameter and 20 mm length. Then one of the samples was annealed in isochronic steps, whereas the other was annealed isothermally. Between every annealing step the samples were carefully cooled down to room temperature and the J^{127}-signal (wide line and spin echo, respectively) was measured. The NMR measurements were carried out by means of a conventional wide line spectrometer including an automatic controlled twin T-bridge as spin detector and a coherent pulse spectrometer including a signal averager with a time resolution of 1 μsec (Fabri – Tek 1072) as described elsewhere [12, 13]. In both cases, the resonant frequency was about 10 MHz. To eliminate long time drifts all measurements were referred to a standard-sample measurement and were performed with a constant crystal orientation with respect to the external magnetic field H_0 in order to avoid orientation effects.

IV. Results and Discussion

Figure 2 shows an example of isochronal annealing curves of two deformed KJ single crystals given by spin echo measurements (plot a) and wide line measurements (plot b) on J^{127}, respectively. With increasing annealing temperature, i. e. decreasing elastic strains in the lattice the wide line parameter f_m/f_{m0} increases until it reaches a plateau at 0.257. The plateau is caused by the way one observes the quadrupole effects in a wide line signal, as shown in Fig. 1 rather than a saturation effect in the annealing process. Thus one determines a far too low recovery temperature T_r given by the inflection point of the measured slope, as would be adequate for a saturation effect in the annealing process [2–4]. Consequently, the well annealed sample (500 °C, 24 h) leads to a second increase in the magnitude of the peak intensity in Fig. 1.

Contrary to this, the recovery of the spin echo width t_E/t_{E0} is monotonic in the temperature range of 20 °C – 500 °C. The signal reaches the value of

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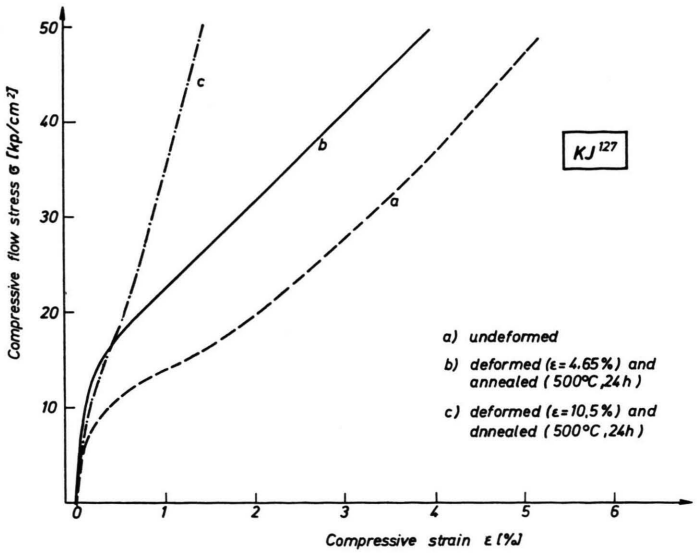

Fig. 3. Stress-strain curve of undeformed (plot a) and deformed and well annealed (plot b, c) KJ single crystals. Deformation axis is ⟨100⟩, deformation temperature is about 300 °K.

the well annealed crystal (560 °C, 40 h) without a second step in the recovery curve.

Both signals never reach the values of the undeformed crystals. This is in agreement with the stress-strain plots of undeformed (plot a) and deformed and well annealed (plot b, c) KJ single crystals as shown in Fig. 3. The deformed and annealed crystals are much harder than the undeformed crystals, showing that the dislocation arrangement is not reduced to the original state.

If the recovery process is activated by a single energy E, the loss in the mean strain $\langle \varepsilon^2 \rangle^{1/2} \equiv \langle \varepsilon \rangle$ is governed by the general rate equation [14]

$$\frac{\mathrm{d}}{\mathrm{d}t} \langle \varepsilon \rangle = -A(\langle \varepsilon \rangle) \exp\left[-\frac{E}{kT}\right] \qquad (9\,\mathrm{a})$$

or if the generalized signal parameter S (peak intensity f_m/f_{m_0} and echo width t_E/t_{E_0}, respectively) is single valued and monotonic:

$$\frac{\mathrm{d}S}{\mathrm{d}t} = \frac{\mathrm{d}S}{\mathrm{d}\langle \varepsilon \rangle} \frac{\mathrm{d}\langle \varepsilon \rangle}{\mathrm{d}t} = -B(\langle \varepsilon \rangle) \exp\left[-\frac{E}{kT}\right]. \qquad (9\,\mathrm{b})$$

By combining the isothermal and isochronal plots, one can eliminate the unknown coefficient $B(\langle \varepsilon \rangle)$ which leads to an Arrhenius equation for the activation energy E [6]:

$$\ln \frac{\Delta \tau_\mathrm{i}}{\Delta t} = -\frac{E}{k}\frac{1}{T_\mathrm{i}} - \frac{E}{k}\frac{1}{T_\mathrm{a}}. \qquad (10)$$

(T_i: step annealing temperature, Δt: step annealing time, T_a: isothermal temperature, $\Delta \tau_\mathrm{i}$: time interval which leads to the same recovery step in the signal as the isochronal step at temperature T_i).

Figures 4 and 5 show two examples (wide line and spin echo, respectively) for such a determination of the activation energy E. In both cases the measured recovery curves lead to a straight line in the Arrhenius plot from which the energy E may be evaluated.

The results of all measurements (including the wide line measurement on KJ^{127} given by OTSUKA [3]) are represented in Fig. 6. The picture shows that both types of measurements lead to the same activation energy for both types of crystals. The magnitude of the activation energy depends on the degree of plastic deformation, i. e. the recovery is not determined by a single activation process.

As found experimentally by DAVIDGE and PRATT [5] there is only a little change in the number of dislocations at annealing temperatures $T \lesssim 400$ °C. Then, the dislocations are rather rearranged in roughly parallel dislocation walls (polygonisation process predicted by CAHN [15]), whereas at $T \gtrsim 400$ °C the number of walls is pretty much reduced and a subgrain structure develops.

In the case of a recovery process by polygonisation the dislocations will move by climbing in order to reduce the elastic energy. The climbing mechanism leads to an anealing process which is governed by Eq. (9 a) according to FRIEDEL [16]. Then the

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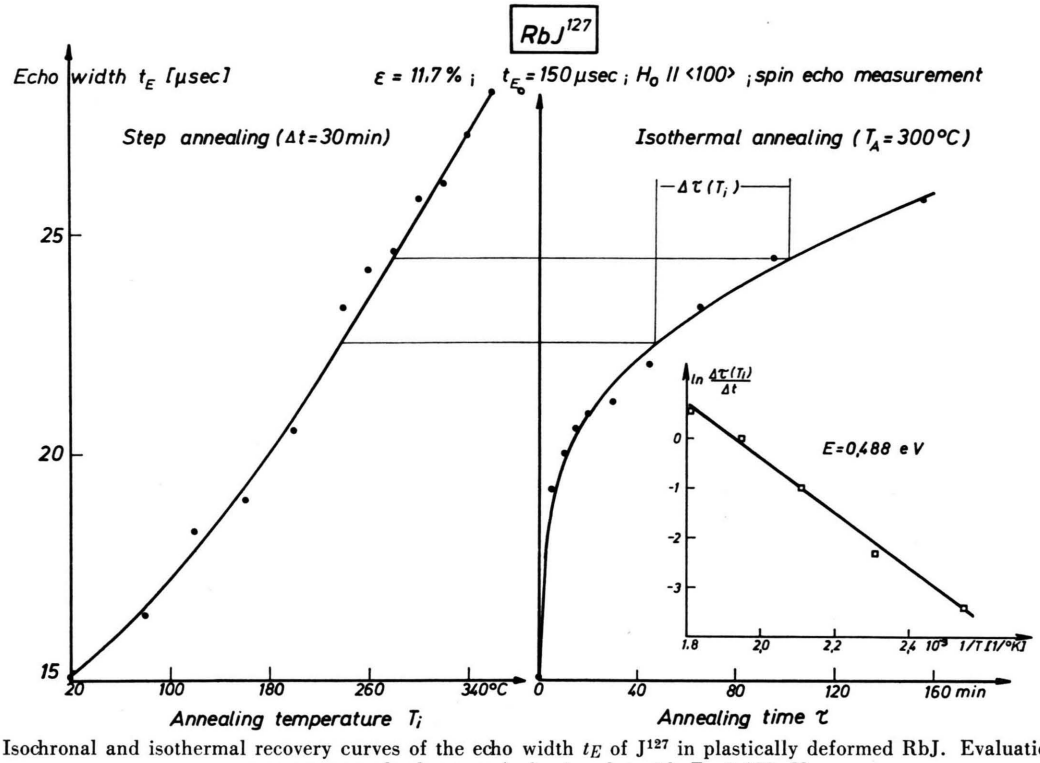

Fig. 4. Isochronal and isothermal recovery curves of the echo width t_E of J^{127} in plastically deformed RbJ. Evaluation of the measurements leads to an Arrhenius-plot with $E = 0.488$ eV.

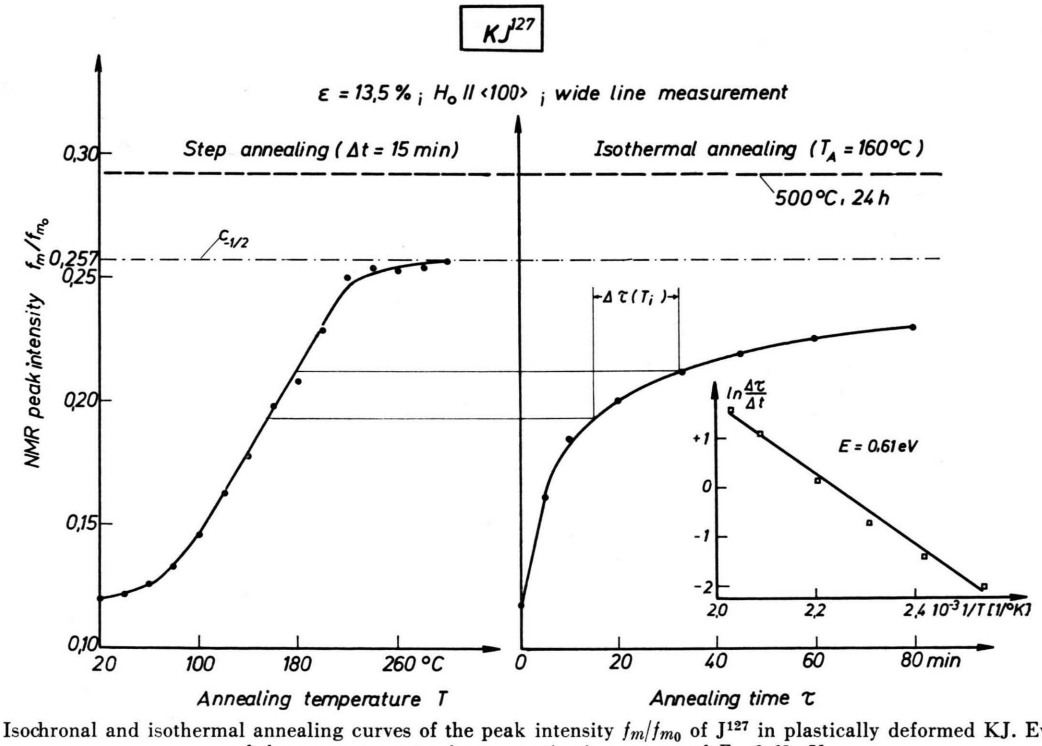

Fig. 5. Isochronal and isothermal annealing curves of the peak intensity f_m/f_{m_0} of J^{127} in plastically deformed KJ. Evaluation of the measurements gives an activation energy of $E = 0.61$ eV.

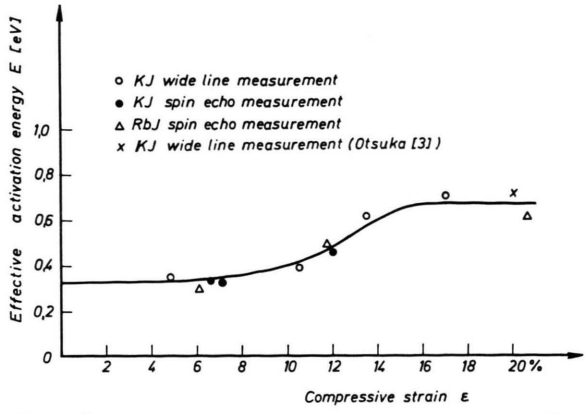

Fig. 6. Dependence of the measured activation energies E on the degree of plastic deformation ε.

activation energy E is obtained for different cases as follows:

a) Dislocation jogs and vacancies at thermal equilibrium:

$$E = E_{fv} + E_{mv} + E_j$$

(E_{fv}: formation energy for vacancies, E_{mv}: migration energy for vacancies, E_j: energy of jog formation).

b) Dislocation jogs at thermal equilibrium, vacancies in supersaturation:

$$E = E_j + E_{mv}\,.$$

c) Dislocation jogs in supersaturation, vacancies at thermal equilibrium:

$$E = E_{fv} + E_{mv} = E_D$$

(E_D: activation energy for self-diffusion).

d) Both types of defects in supersaturation:

$$E = E_{mv}\,.$$

For $\varepsilon \geqq 15\%$ the measured value $E = 0.68$ eV is in agreement with the migration energy of positive ion vacancies in KJ ($E_{mv} = 0.65$ eV), which can be evaluated from the extrinsic part of the measurements given in Ref. [17]. On the other hand, the migration energy of ion vacancies in RbCl and RbBr is of the same order of magnitude as in KCl and KBr [17, 18]. This leads to the conclusion that the migration energy of positive ion vacancies is of the same order as in KJ. In this region of deformation case (d) is valid. During the deformation process an athermal number of vacancies is produced. This is in agreement with density measurements performed on plastically deformed KCl [19] and NaCl [5], which yield a high number of athermal vacancies. A small annihilation rate of the dislocations during the annealing process leads also to more vacancies than at thermal equilibrium. The vacancies diffuse to the supersaturated jogs produced during the deformation. This mechanism results in a climbing speed for dislocation lines leading to a reduction of the mean stress field.

On the other hand, there is not a simple explanation of the low value for the activation energy $E = 0.34$ eV for small ε-values. It may be possible, that in the region of small deformations a large number of vacancies is positioned in the core of the dislocation, as discussed by LOTHE [20] and by NIX et al. [21]. In this case the activation energy for the migration of vacancies is about half the value of the perfect crystal since the stress field in the vicinity of a dislocation constitutes a tube of easy diffusion. The model is in agreement with calculations of BASSANI et al. [22] on NaCl showing that for this type of crystal the migration energy of vacancies is reduced by the stress field of the dislocation by at most 0.4 eV. This would reduce the migration energy in the ideal crystal by about a factor of two, since the migration energy for positive ion vacancies in a perfect NaCl crystal is 0.79 eV [23]. This would explain the values for the activation energy E_D due to the migration of single dislocations as obtained by HESSE [24] on NaCl and by PARIISKII et al. [25] on KBr using the etch pit method. In both cases these values are about half the values for the migration energy of vacancies (NaCl: $E_D = 0.41$ eV, $E_{mv} = 0.79$ eV [22]. KBr: $E_D = 0.35$ eV, $E_{mv} = 0.65$ eV [18]).

Acknowledgements

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