Deformation-induced phonon scattering by debris defects in alkali halides

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Abstract. A number of investigations have shown that the thermal conductivity of alkali halide crystals is markedly affected by crystalline defects, chiefly in the low temperature region, say below around 10 K. The effects are very prominent after plastic deformation, where the conductivity is reduced by more than a factor of 10 after deformation by several percent already. Albeit a considerable amount of data and respective models have been elaborated, the correspondence between models and the body of experimental results still needs improvement, especially in the temperature range between around 1 and 5 K. As will be shown for the case of NaCl, where most of the experimental results exist, a satisfactory description of the thermal conductivity properties can be obtained when relying on, instead of dislocations and/or vacancy defects, a debris defect as suggested by transmission electron microscopy.

1. Introduction
Revisiting work on phonon scattering obtained at temperatures below approximately 25 K from plastically deformed alkali halide single crystals, one realizes a difficulty existing for decades in joining scattering and plasticity properties. Plastic deformation causes an increase in scattering by a factor of more than 15 (as compared to the undeformed state) in a temperature range between 1 and about 10 K [1,2]. The offered explanations are based, of course, on the defects introduced during deformation, i.e. dislocations and point defects. Unfortunately, however, all applied models, be it coherent or incoherent, dynamic or static scattering, have been insufficient in this temperature range, because of either wrong sizes of the computed scattering cross-sections or wrong temperature dependence of the thermal conductivity.

This paper will relieve this unsatisfactory situation based on a deformation-induced defect typical of deformed alkali halide crystals. Discussions concerning this defect date back to the so-called memory effect which describes the capability of an alkali halide crystal to 'remember' the passage of a dislocation through a volume even if this dislocation has left the crystal in the course of the deformation [3]. In metals for example this effect has not been observed. Models for the underlying defect structure, afterwards coined 'debris', have been suggested assuming edge dislocation dipoles [4] or distributed vacancies and vacancy clusters [5]. These models failed by not being able to explain the deformation-induced volume expansion [5]. With alkali halide crystal's defect structures becoming accessible by transmission electron microscopy, the nature of the debris defect could be modelled essentially as a microcrack [6] which model is applied here to the phonon scattering properties.
In the following, by focusing on NaCl single crystal properties, we first collect the appropriate phonon scattering results, then the relevant debris aspects. The discussion will bring together both fields.

2. The state of the research

2.1. Phonon scattering in NaCl single crystals

The typical result for the thermal conductivity of a variety of alkali halide and specifically of NaCl crystals is depicted in Fig. 1. The thermal conductivity of the undeformed specimen shows a strong increase with $T^3$ dependence – as expected from boundary scattering of phonons [7] - from very low temperatures, $T$, a maximum at around 10 K and a decay towards higher temperatures. Very important results have to be noted here. The defects introduced by plastic deformation (here to a length reduction of $\varepsilon=4\%$, i.e. plastic shear in the primary glide system $\gamma = 8\%$) reduce the thermal conductivity by a factor of around 15 in the very low temperature range, say between approximately 1 and 5 K, whereby the $T^3$ dependence of the thermal conductivity is kept. It is also important for the discussion that this part of the curve corresponds to a defect-induced relaxation time (i.e. scattering cross-section) that is independent of the phonon frequency ($1/\tau = 1.1 \times 10^7$ sec$^{-1}$) [1]. Experiments to recover the thermal conductivity loss are shown in Fig. 2a, where the thermal resistivity values (normalized with the respective values of the undeformed state) as measured at 2, 3 and 4 K after isochronal anneals (15 minutes at each annealing temperature) are plotted. One recognizes complete recovery in an annealing range from 450 to 770 K. For comparison reasons to be used below we also have added sketches for the isochronal annealing of the dislocations (Fig. 2b) and of the deformation-induced volume expansion for NaCl crystals (Fig. 2c).

![Fig. 1. Thermal conductivity, $\kappa$, as a function of the temperature for NaCl single crystals in annealed (graph A) and compressed state (4%) (graph B). Measurement and compression along $<001>$. After Taylor et al. [1].](image-url)
Fig. 2. Comparison of isochronal annealing behaviours.

a) Recovery of the thermal resistivity $r$ (inverse of conductivity) for the temperatures 2, 3 and 4 K, plotted as relative values normalized with the respective values of the undeformed crystal. Isochronal annealing steps 15 minutes each. After Taylor et al. [1].

b) Recovery of the dislocation density as measured with etch pits. Dashed line describes the additional density by dislocation dipoles (interpretation of the authors, after Taylor et al. [1]). Annealing steps 15 minutes.

c) Recovery of the deformation-induced volume expansion, normalized to the initial volume expansion. Annealing steps 60 minutes. After Davidge and Pratt [2] and modified by Strunk [6].
2.2. The debris defect in plastically deformed NaCl single crystals

The transmission electron microscope (TEM) investigations of NaCl single crystals, although hampered initially by their irradiation sensitivity, have clarified to a large extent the deformation-induced defect structure. First, the total dislocation densities as determined by TEM corroborate those determined by etch pitting \[8,9,10\] and X-ray measurements \[11\] in all three work-hardening stages of the deformation along \{001\}, ref. 11 concerns deformation along \{110\}. The square root of the total dislocation density, \(\sqrt{\rho}\), is proportional to the resolved shear stress \(\tau\) (see also Fig. 4). Secondly, an additional class of deformation-induced defects has been detected. In the following we restrict ourselves on Stage I work hardening that is characterized by easy glide on one \(-\langle 101\rangle\\{101\}\) glide system only. Figure 3 shows a respective micrograph in which, in addition to a few edge dislocation dipole segments, a high density of damage clusters is present. These clusters have formed due to the extensive electron irradiation during observation in the electron microscope. Careful inspection shows that the clusters are aligned parallel to these dislocation dipoles. Obviously linear defects not visible otherwise have been decorated by the irradiation damage clusters.

![Fig. 3. Defect arrangement in the glide plane of a NaCl crystal deformed along \(\langle 001\rangle\). Transmission electron micrograph, weak-beam dark field with \(g/-3g\), \(g\): diffraction vector. Visible are a few dislocation dipole segments (bright lines, partly both dislocations visible) and a high density of electron irradiation damage clusters that are aligned parallel to the dislocation dipoles (best seen at glancing angle). Deformation data: resolved strain 1.7 MPa, resolved strain rate \(3.7 \times 10^{-4}\) s\(^{-1}\), deformation temperature 220 K, debris density (=density of microcracks) \(\rho_{\text{debris}} = 3.2 \times 10^{12}\) m\(^{-2}\).](image)

Before discussing the possible structure of the debris defect, we consider the dependencies of both the dislocation and debris densities on the resolved flow stress, \(\tau\). Figure 4 shows for three deformation temperatures that the square roots of the densities depend linearly on the flow stress. One notices one important difference (apart from the excessive densities of the debris at all deformation temperatures): The dislocation densities extrapolate to the origin of the coordinate system in agreement with earlier work \[8,9,10\], but the debris densities extrapolate to the respective critical resolved flow stress, \(\tau_0\). This fact indicates that debris form as a consequence of macroscopic slip. In addition we can infer from the similar slopes that the functional dependence of the debris densities on the flow stress is, in a first approximation, the same for all temperatures, at least for the rage covered by the experiments, i.e. the density depends only on the work hardening, \(\Delta \tau = \tau - \tau_0(T)\). Seen this way, since the flow stress
squared is proportional to the work done to the crystal during deformation, the density of debris is proportional to the work done during macroscopic deformation.

\[ \sqrt{\rho} \propto \text{work done} \]

\[ \rho \propto \text{work done} \]

Fig. 4. Plot of the square root of the density, \( \rho \), of both dislocations and debris for three different deformation temperatures \( T \) as a function of the flow stress, \( \tau \). Each debris defect is counted two dislocations (see model in Fig. 5). \( \tau^c_0 \) denotes the critical resolved flow stress at deformation temperature, \( T \).

For the consideration of the possible atomic structure of the debris defect, the observation is important that the decorated defects are aligned parallel to the dislocation dipoles. This observation suggests certain relatedness between both defect types. A respective debris model is sketched in Fig. 5 and describes a narrow edge dislocation dipole of vacancy type where the highly strained volume between both dislocation lines has been removed by decohesion along the cleavage plane of type \{100\} connecting both dislocation cores of the original dipole. This model fulfills all requirements [12] that follow from the debris properties, notably it produces a high lattice expansion and is of low energy (no dislocation strain field anymore and only low energy \{001\} internal surfaces). An energy balance between the elastic strain field energy of a dipole to the energy of the internal \{100\} surface shows that dislocation dipoles in NaCl with a dipole width (distance between the two dislocation cores) below 4.7 nm (equivalent to 16 elementary \{001\} lattice plane distances) are prone to the microcrack transformation [12]. We have to note here that interstitial type edge dislocation dipoles cannot convert by a similar process. At most they may break up into segments of dipoles, however the dislocations still exist. Thus they further-on can take part in the deformation process and have therefore a high chance, during glide, to encounter a dislocation suitable to form a vacancy type dipole.

Fig. 5 Model of the debris defect. This defect forms from an edge dislocation dipole (see respective inserted half planes) by decohesion, i.e. cracking, along the plane of the dipole, which is a \{100\} cleavage plane. \( \vec{b} \): Burgers vector.
The annealing properties of the debris and of the dislocations are different. As shown in Fig. 2, the dislocations, during isochronal annealing, anneal in a much broader and higher reaching temperature range [1], see Fig. 2b, than do the debris defects (as measured in density change) [5], e.g. Fig. 2c. TEM observations on annealed crystals, which had been deformed before at 78 K [13], corroborate this interpretation. Anneal at 520 K (see arrow in Fig. 2c) for one hour reduces the debris density to 95% of the initial value and the dislocation dipole density to 40%. After anneal at 620 K (see arrow in Fig 2c) for one hour, the experiments to decorate debris defects failed completely, which fact can be valued to indicate very low or even zero debris density left (or the remaining debris have changed into a structure that cannot be decorated anymore). Only 8% of the dislocation dipole density has survived, the density of free dislocations is still 85% at this annealing stage as compared to the pre-anneal value [13].

3. Discussion

In view of the quantification of debris density and the model of the debris defect as sort of a microcrack, both based on transmission electron microscope observations, two questions arise with regard to the phonon scattering discrepancy mentioned in the introduction. First, can the debris defect population explain the deformation-induced volume expansion in NaCl crystals? Secondly, how and to which degree can the high debris density contribute to the understanding of the phonon scattering dependency on temperature and defect density?

3.1. Debris defect

Concerning the deformation-induced volume expansion of NaCl, all respective attempts based on dislocation densities have failed. As these dislocation data have been confirmed by electron microscopy [9,10] all earlier arguments that rule out dislocations to produce the overall volume expansion (see e.g. [5]) still hold. Moreover, it should be mentioned here without further discussion that the energy stored during plastic deformation in the crystal is too small by a factor of 2 to 4 to explain the observed volume expansion on the basis of vacancies and small clusters thereof [14].

We shall now argue that the debris as discussed here can account for both volume expansion and stored energy. In correspondence to the work of Taylor et al. [1] we have to refer to a resolved shear strain of 8% (strain in compression 4%), where the volume expansion measured by Davidge and Pratt [5] corresponds to 28 g m⁻³. The 8% strain is equivalent to a flow stress at room temperature of 1.1 MPa (see Fig. 3) and Fig. 4 yields a debris density of around 1.8 × 10¹² m⁻³ (mind one debris is counted as two dislocations). Equating now the total debris volume (width × height × total length, i.e. density) times the density (2.1 × 10⁶ g m⁻³) to this volume expansion we obtain a debris height of almost 5 elementary {001}. This number is well below the calculated maximum height of 16 elementary {001} planes and shows that the present debris defect can certainly describe the observed volume expansion.

As regards the stored energy we consider the debris as an internal {001} surface. Unfortunately, however, experimental data on stored energy are sparse and a broad range of values for the {001} surface energy exist. Therefore we restrict ourselves here to show that the debris defects can principally explain the deformation-induced stored energy. Referring to Gurov et al.’s data [14], one finds for a compressive deformation rate (5 × 10⁻⁴ s⁻¹, similar to ours of ~2 × 10⁻⁴ s⁻¹ [13]) for stage I deformation a stored energy of approximately 13 × 10³ J/m³ at an (extrapolated) 4% compressive strain. On the other hand, we have derived above for these deformation conditions a debris density of 1.8 × 10¹² m⁻³. The total surface energy contained in the debris can be calculated from the debris circumference of the cross-section (see fig. 5) × total debris length × surface energy. A very helpful collection of theoretical and experimental surface energy values can be found in ref. [15], according to which the energies range from 144 to 384 mJ/m² (9 to 24 meV/Å²). (The discussion of the question whether free surface energy values can be used for the internal surfaces of the debris is beyond the scope of this paper.) Equating stored energy and debris surface energy yields for the debris height a span between 31 and 87 elementary {001} planes. This result is somewhat larger than the theoretical
maximum debris height of 16 elementary {001} planes. In view of the many uncertainties of this assessment we may take this result as a principal proof for debris to account essentially for the stored energy. In addition we note that the contribution of dislocations and point defects to the stored energy need to be considered of course also.

3.2. Phonon scattering
At this point it appears reasonable to briefly describe the basis of the evaluation of phonon scattering due to crystals lattice defects. In the following, the phonon-dislocation interaction with different lattice defects will be considered, in order to investigate their influence on the lattice thermal conductivity:

i) dislocations
ii) point defects
iii) clusters and debris (as analyzed here)

Phonons are scattered by mobile dislocations and by the elastic distortion field of sessile dislocations (dynamic and static nature of scattering, resp.). From theoretical calculations [16] it is expected that the scattering of phonons by the static strain field of randomly distributed dislocations should produce a thermal resistivity \( W_{ds} \) proportional to \( T^{-2} \), i.e. the thermal conductivity \( \kappa_d = 1/W_{ds} \) varies with \( T^2 \), whereas in the experiment a thermal conductivity proportional to \( T^3 \) is found after plastic deformation [1].

Anderson and co-workers [17, 18] have established that the decrease in thermal conductivity after plastic deformation is primarily due to dynamic scattering of phonons by dislocations. The vibrating string model according to Granato and Lücke [19] has been rather successful in explaining the dynamic behaviour of dislocations as found in acoustic experiments. If phonons induce a dislocation to vibrate, the incident wave will be dissipated as the dislocation radiates elastic waves (reradiation scattering). Especially phonons with frequencies in the vicinity of the resonance frequency \( \omega_0 \) are scattered strongly. In several alkali halides, Anderson and co-workers [17,18] found from thermal conductivity measurements a resonance temperature of about 0.2 K. In order to explain the temperature of the thermal conductivity minimum, it was necessary to assume an average dislocation length of several \( 10^{-8} \) m which is much less than has been determined ultrasonically [20].

Kneezel and Granato [21,22] improved this scattering model by taking into account several additional effects such as phonon focusing and resonance angle scattering and applied it to the scattering of phonons by edge dislocation dipoles. The dipoles were assumed to have a dipole spacing in the range \( 3 b \leq d \leq 300 b \) and a density which is about 100 times the monopole density. In this case high-frequency phonons will excite dipoles into the optical mode of vibration (i.e. the dislocations move in opposite directions). The optical mode resonant frequency is higher than that of independently vibrating dislocations, especially for narrow dipoles. Assuming an average dipole spacing of 60 b, a resonant frequency \( \omega_0 \approx 10^{11} \) Hz was obtained, which corresponds well with the temperature (\( T \approx 0.2 \) K) at which the minimum of the thermal conductivity was observed in deformed LiF [23] and KCl [24] single crystals. Although the model describes the measured thermal conductivity rather good in the temperature range below 1 K, discrepancies become increasingly larger at higher temperatures. At high temperatures high-frequency phonons (\( \omega >> \omega_0 \)) are excited which are out of resonance and hence not scattered. In addition, other scattering processes become effective.

The scattering of phonons by point defects (such as vacancies) increases rapidly with frequency (proportional to \( \omega^4 \)) and gives rise to a thermal resistivity proportional to the temperature \( T \) [16]. Hence the scattering is effective only in the temperature range where the maximum of the conductivity occurs and can be neglected at lower temperatures.

The scattering of elastic waves by inclusions (such as precipitates or clusters) embedded in an elastic medium has been investigated by Truell and co-workers [25,26,27]. In the low-frequency limit (i.e. long wavelengths) the scattering cross-section of spherical obstacles (including a spherical cavity) varies with \( \omega^4 \). Thus the long-wavelength scattering cross-section is Rayleigh-like as in the case of point
defect scattering. In the high-frequency limit (i.e. short wavelengths), one has a problem in geometrical optics [28]. A spherical precipitate presents a constant cross section to all incoming phonons, and the scattering cross section is independent of phonon frequency. If the precipitate is not spherical, then its effective size depends on the direction of the incident phonon. However, the cross-section must again be frequency-independent and must contain some average size of the precipitate [28]. The relaxation rate is then given by [28]

\[ \frac{1}{\tau_{pr}} = N_{pr} v \sigma \]  

(1)

where \( N_{pr} \) is the concentration of the scatterers and \( v \) is the sound velocity. In the case of a frequency-independent scattering process the temperature dependence of the thermal conductivity is expected to be proportional to \( T^3 \) as in the case of boundary scattering. The transition from one scattering type to the other occurs for [28]

\[ q d_{pr} \gg 1.5 \]  

(2)

where \( q \) is the magnitude of the wave vector \( (q = 2\pi/\lambda) \) and \( d_{pr} \) the diameter of the precipitates. The influence of precipitates and clusters on the thermal conductivity has been investigated for example in the case of quenched and annealed KCl and KBr crystals containing Ba\(^{++}\) and Sr\(^{++}\) [28], neutron irradiated magnesium oxide [29] and \( \gamma \)-irradiated LiF [30]. In all cases the thermal conductivity below the conductivity maximum was reduced and had a \( T^3 \) temperature dependence down to about 1 K, indicating extended defects. At the lowest temperatures, however, the corresponding thermal resistance fades away, suggesting that the scattering changed from a geometrical like to a Rayleigh like scattering process.

We now attribute the effect of the plastic deformation on the thermal conductivity of deformed NaCl crystals as observed by Taylor et al. [1] to the influence of extended defects in the shape of the present debris model. The dominant frequency of the phonons that contribute mainly to the thermal current is given by \( \omega = 5 \times 10^{11} \, T \, [K^{-1} \, s^{-1}] \) [17,18]. Hence, we obtain in the temperature range above 1 K a dominant wavelength of the phonons smaller than about 40 nm. According to eqn. (2) the effective diameter of extended defects must be larger than about 9 nm and the corresponding scattering cross-section larger than 64 nm\(^2\). As pointed out in section 3.1 the debris have a rectangular shape about 1 \( \mu \)m long and about 5 nm wide. Thus their cross-section is about 2000 nm\(^2\) and hence large enough for geometrical scattering of the phonons. From eqn. (1) we obtain, with a debris density of about \( 1.8 \times 10^{18} \, m^{-3} \), a relaxation rate of about \( 10^7 \, s^{-1} \) similar to that derived for the deformed specimens [1]

4. Conclusions

In this paper we have elaborated for the case of plastically deformed NaCl single crystals that the models based on dislocation content, measured by etch pitting, and produced vacancy density, derived from the deformation-induced volume expansion, cannot satisfactorily describe the available results on the thermal conductivity at low temperatures, specifically in the temperature range between around 1 and around 5 K. Transmission electron microscopy suggested a different deformation-induced defect that in the simplest form can be classified as a conversion of a vacancy type dislocation dipole into an internal crack. This paper shows that this defect can account for all four criteria important to be explained. For the deformation related criteria, it accounts for the deformation-induced volume expansion and for the energy stored during deformation. For the thermal conductivity related criteria, it accounts for the \( T^3 \) dependence of the thermal conductivity and for the relaxation rate that is independent of the phonon frequency (geometrical scattering).

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