Correlated thermal conductivity and ionic thermocurrents measurements to study lead induced defect in KCl

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M. Locatelli, E. Zecchi

Service des Basses Températures, Centre d'Etudes Nucléaires de Grenoble, France

and R. Capelletti

Gruppo Nazionale di Struttura della Materia del CNR, Istituto di Fisica dell'Università, Parma, Italy

Résumé. — La mesure de la conductivité thermique entre 0,05 et 100 K est utilisée pour étudier la croissance des phases de Suzuki dans KClPb, en fonction du temps de recuit (220 °C) aux dépens des dipôles impuretés-lacune (I.L.). Des mesures parallèles de thermocourants ioniques sont faites pour déterminer indépendamment la concentration des dipôles I.L. soit après les recuits, soit dans des échantillons trempés avec différentes concentrations de plomb (1,2-144 ppm).
On utilise différents modèles pour analyser les courbes expérimentales $K(T)$, d'où l'on déduit les dimensions et la forme des agglomérés de la phase de Suzuki. Un nouveau modèle phénoménologique est proposé pour l'interaction phonon-dipôles (I.L.).

Abstract. — Thermal conductivity (K) measurements in the range 5×10^{-2}-100 K are exploited to analyze the Suzuki-like phase (S.L.P.) occlusions growing for increasing annealing times at 220 °C at the expenses of impurity vacancy (I.V.) dipoles. Parallel ionic thermocurrents I.T.C. are used to monitor independently the concentration of I.V. dipoles both along the I.V. → S.L.P. conversion and in quenched samples containing different Pb amounts (1.2-144 ppm).
Different models are used to fit the experimental K *vs.* T curves and to obtain the size and the shape of the growing S.L.P. occlusions. A new phenomenological model is proposed for the phonon-resonance, induced by I.V. dipoles, which fits nicely the K curves for different Pb concentrations.

1. **Introduction.** — Thermal conductivity (K) measurements in alkali halides in the low temperature range are very sensitive to the presence of lattice defects such as point defects, clusters and microprecipitates of increasing sizes [1], which escape the detection by electron microscope and X-ray diffraction.

The *dip* occurring on the high temperature side ($20 \div 30$ K) of the K *vs.* temperature plot (see for instance figure 1, full circles) has been attributed to a resonant phonon scattering induced by impurities, regardless they are monovalent cations or anions or divalent cations [2]. For the last ones the compensating cation vacancy (to give the impurity-vacancy, I.V. dipole) can also interact in a determinant way with the phonons.

The theoretical models proposed up to now can be schematized according to two lines. The former considers the mass defect as responsible for one-phonon scattering process [3] with a further refinement, which takes into account two-phonons interactions as well [4]. According to the latter, the one-phonon scattering process is caused by the force constant changes related to the presence of the cation vacancy [5]. For instance the experimental results by Schwartz *et al.* [3] have been interpreted along this line; the impurity playing a role only if its size differs from that of the substituted cation. However the fitting of the experimental data on the basis of the proposed models is not satisfactory, overall when samples of increasing impurity concentrations are systematically studied.

The former part of this work is devoted to search a phenomenological model to fit our experimental data related to KCl doped with increasing Pb^{++} concentrations. By means of parallel I.T.C. [6] and optical absorption measurements the concentration either : 1) of simple defects, such as I.V. dipoles (the fraction of free impurities and vacancies being negligible, due to the high association degree in KCl:Pb [7]) and 2) of the overall Pb are monitored in samples quenched in order to minimize the presence of clusters [7].

The latter part of the work exploits the sensitivity of the low temperature side of the K *vs.* T (see figure 1, open circles) plot to analyze again in KCl:Pb the growth and the shape of extended defects, namely of the metastable Suzuki-like phase (S.L.P.) [8] occlusions, which are formed upon long annealing at 220 °C at the expenses of I.V. dipoles [7, 9, 10]. The

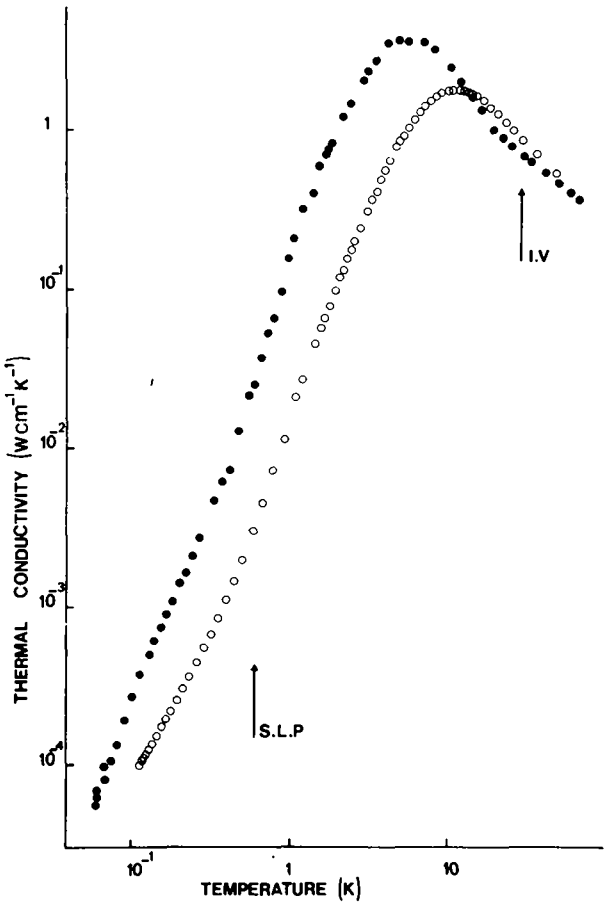

Fig. 1. — Thermal conductivity *vs.* temperature plot for KCl:Pb (32 ppm); full circles : sample quenched from 500 °C ; open circles : 300^{h} annealing.

kinetics of this process are followed by parallel I.T.C. measurements which monitor the growing S.L.P. occlusions through a interfacial relaxation process [7] in addition to the I.V. dipole loss. Different models of the S.L.P. occlusions shape are used to fit the experimental K curves and to obtain the size of the occlusions as a function of the annealing times.

2. **Experimental details.** — The samples were single crystals grown by means of the Kyropoulos method [7]. The overall lead contents were determined from the optical absorption coefficient of the A-band [11], by using a Cary 15 Recording spectrophotometer. The thermal conductivity measurements were performed in the range $5 \times 10^{-2} \div 10^{2}$ K using the technique described in details elsewhere [9]. Special cares were taken [12] for preparing the thermal conductivity samples in order : 1) to obtain a fast quenching (in principle difficult due to their massive shape) and 2) to avoid breakage occurring whenever brittle samples (such as those containing S.L.P.) are assembled.

The I.T.C. measurements were performed according ref. [6, 7].

3. **Experimental results.** — 3.1 PHONON RESONANCES INDUCED BY I.V. DIPOLES. — Samples of different overall Pb concentrations n_t (as measured by optical means, see 2) were quenched from 500 °C in order to put the lead in solid solution as simple defects mainly I.V. dipoles. Their concentration $n_{I.V.}$ was determined by means of I.T.C. technique. At high lead contents, $n_{I.V.}$ and n_t are significantly different because the quenching is never fast enough to avoid the growth of small clusters [7].

The thermal conductivity plots in the range 1.3-200 K for various $n_{I.V.}$ and n_t are shown in figure 2 : the dip appearing in the region $20 \div 35$ K becomes deeper and deeper by increasing both n_t and $n_{I.V.}$. Also the K maximum is affected being lowered and shifted towards lower T.

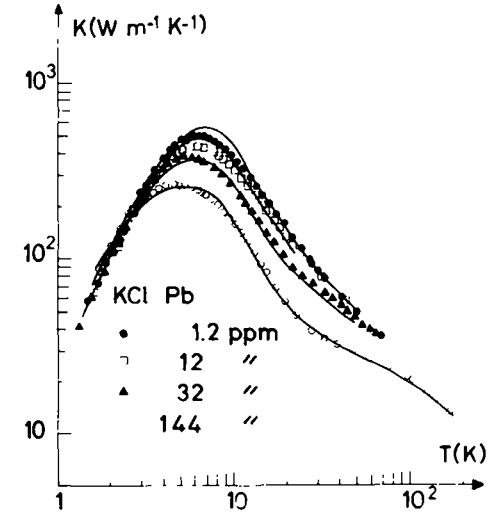

Fig. 2. – Thermal conductivity *vs.* temperature plot for KCl samples containing different Pb concentrations (n_t), quenched from 500 °C. Circles, squares and triangles give the experimental points ; the lines give the fitting.

3.2 I.V. S.L.P. CONVERSION. — The samples quenched from 500 °C were subsequently annealed at 220 °C for increasing times. The relative I.T.C. spectra show the I.V. dipole peak at 236 K which decrease along the annealing and a huge band (B-band or S.L.P. band) at 272 K which grows (see for instance figure 1 of ref. [10]). Figure 3 shows the time evolution of I.V. dipole concentration and of S.L.P. band, for a sample with n_t 32 ppm. It is worthwhile noticing that at 700^{h} there is (not shown in figure 3) a remarkable decrease of S.L.P. band and an increase of I.V. dipole concentration, probably consistent with the metastable nature of Suzuki phase. Thermal conductivity measurements were performed on the same 32 ppm Pb doped KCl, submitted to the same sequence of quenchings and annealings at 220 °C : figure 1 displays for the sake of example the curve after the quenching (full circles) and after a subsequent 300 hours annealing (open circles). The high

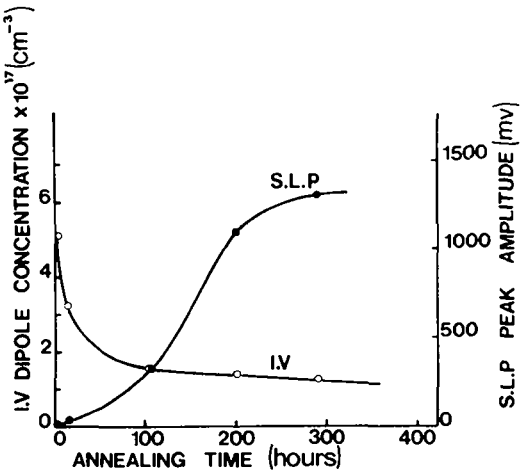

Fig. 3. — I.V. dipole → S.L.P. conversion *vs.* annealing time at 220 °C as detected by means of I.T.C. technique in KCl : Pb (32 ppm).

temperature *dip*, attributed to I.V. dipoles, is evident in the quenched sample, while disappears in the annealed one, in agreement with the I.T.C. results (Fig. 3). The low temperature side of the latter curve is heavily lowered if compared with the former, supporting the hypothesis that large obstacles to the phonon transport are formed. Some of the K results for the same sample and for different annealing times are plotted as K/T^3 *vs.* T to stress furtherly the low temperature side effect (Fig. 4). Similar results were obtained for higher Pb concentration (90 ppm).

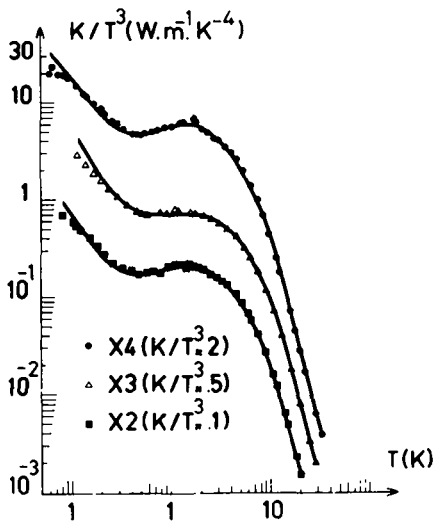

Fig. 4. — K/T^3 *vs.* T plot for KCl : Pb (32 ppm) for different annealing times t_a at 220 °C : full circles : t_a = 103^h ; open triangles : t_a = 300^h ; full squares : t_a = 700^h.

4. Discussion and conclusions. — 4.1 PHONON SCATTERING. — The thermal conductivity results for both the problems fronted were analysed by using the Debye model for phonon conduction, as explained in details in [9]. The total mean free path $l(\omega)$ as a function of the phonon frequency ω is given by

$$l^{-1}(\omega) = \Sigma_i\, l_i^{-1}\,,$$

where the l_i are the mean free paths related to different scattering mechanisms (i.e. scattering at boundaries, dislocations other phonons, point defects (isotopes, impurities), I.V. dipoles and aggregates). The first four contributions were considered by using the expressions derived in [9].

4.2 PHONON RESONANCE INDUCED BY I.V. DIPOLES. — Of the last two terms only the one due to point defects is considered, assuming that all impurities are dispersed in the lattice, thanks to the fast quenching. The attempts to fit the experimental data of figure 2 by using the available models [2, 3, 4] failed, overall for the high Pb concentration (144 ppm). Hence we propose a model which starts from the well known Pohl [13] expression for the relaxation time τ_E related to elastic scattering processes

$$\tau_E^{-1} = D\omega^4/(\omega^2 - \omega_0^2)^2 \qquad (1)$$

where D is a coefficient proportional to the concentration of resonant impurity defects and ω_0 the resonance frequency. The (1) was modified by introducing an explicit temperature dependence, which accounts for the phonon-phonon interactions [4] which are no longer negligible in the temperature range where the *dip* occurs. The experimental results (symbols in figure 2) are nicely fitted (see the continuous lines) for the following expression :

$$\tau_{Pb}^{-1}{}_{+\,+} = \exp(-\,6.76\; T/T_D)\; T^2\; \tau_E^{-1} \qquad (2)$$

where T_D is the Debye temperature.

Figure 5 gives the plots of D and A (the so called point defect coefficient [2]) as obtained from the above fittings, *vs.* either the I.V. dipole concentration $n_{I.V.}$ and the *total* Pb concentration (see §§ 2 and 3.1). Rather good linear relationships are found

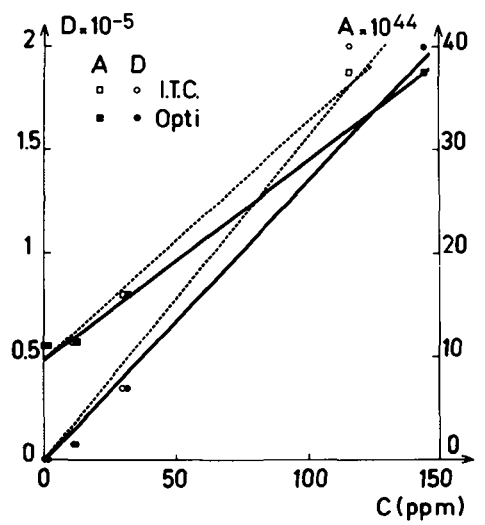

Fig. 5. — Plot of A (squares, scale on the right) and D (circles, scale on the left) coefficients *vs.* impurity concentration for KCl : Pb samples of figure 2. Open symbols : their abscissa is the concentration determined by I.T.C. measurements, i.e. $n_{I.V.}$; Full symbols : their abscissa is concentration determined by optical absorption measurements, i.e. n_t.

for both D and A *vs.* concentration over two orders of magnitude of this last.

The fitting *vs.* n_t looks better than those *vs.* $n_{I.V.}$. The linearity between A and n_t suggests that in well quenched samples, where simple I.V. dipoles are present and at maximum very small clusters are allowed to grow (in highly doped samples $n_t = 144$ ppm), the lead can be regarded as point defects. The key role played by the cation vacancy on the dip is supported by the resonance frequency ω_0 which turned out to correspond to 29 K [3]. This can be justified in KCl:Pb by the fact that 1) the impurity is n.n.n. of the vacancy [7] and also in very small clusters there is not strong interaction between impurity and vacancy, as supported by optical absorption measurements [7, 10]. However it must be remarked that not all lead related cation vacancies contribute to the 29 K dip : for instance, when Suzuki phase, i.e. an ordered arrangement of I.V. dipoles in n.n.n. coordination, is formed, the dip disappears progressively.

4.3 S.L.P. NUCLEATION. — The last contribution mentioned in 4.1 can be properly studied in samples containing the S.L.P. occlusions (see § 3.2). On the basis of previous I.T.C. [7] and K [9] results, a phonon scattering model for cylindrical occlusions is considered (of height H and diameter d). At low frequencies, we expect Rayleigh-type scattering and the scattering cross-section σ_H is taken to be proportional to the square of the scattering volume $V = \pi H d^2/4$ and proportional to $(\omega/v)^4$. If the occlusion is cylindrical, it has been shown (see for instance [14]) that this must be modified to $(\omega/v)^n$ where $n \leqslant 3$ so that

$$\sigma_H = gV^2(\omega/v)^3 \quad \text{for} \quad \frac{H\omega}{v} < b\,.$$

The cross-over condition is given by $b = 1.5$ and g is a dimensional constant to take into account the ω^3 dependence of σ_H.

For higher frequencies, we assume that σ_H decreases and describe this by a gaussian multiplier

$$\sigma'_H = \sigma_H \exp\left(-\left(\frac{\omega - (bv/H)}{c}\right)^2\right) \quad \text{for} \quad \frac{\omega H}{v} > b\,.$$

At still higher frequencies, we define a scattering cross-section σ_d associated with the diameter d and a cross-over condition $a = 1.5$.

For $\omega d/v \geqslant a$, we assume a geometrical cross-section $\sigma_d = dH$.

For $\omega d/v < a$, we assume $\sigma_d = dH(d\omega/av)^4$.

The combined cross-section $\sigma_c = \sigma_d + \sigma_H$ gives the usual expression for the mean free path by

$$l^{-1} = N_c\,\sigma_c$$

where N_c is the number of cylindrical objects per cm^3.

The model is used to fit the data of figure 4.

The overall agreement with experimental results is quite good. Some residual disagreement at the lowest temperatures is taken as an indication that there, the frequency dependence should be perhaps $(\omega/v)^n$ with $n < 3$ in agreement with [14].

From the above analysis it turns out that cylinders (with H ranging between 200 and 400 Å and $d \sim 20$ Å) are formed for rather long annealing times also in moderately doped samples (35 ppm) in agreement with the previous suggestions. Moreover the rather high H/b ratio further supports the hugeness of the I.T.C.-B band [7].

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DISCUSSION

Question. — L. SLIFKIN.

It's interesting that the particles found by you and Dr. Capelletti have shapes so different from those photographed by Guerrero, Butler and Pratt (previous paper).

Reply. — M. LOCATELLI.

We have a different system, i.e. KCl:Pb instead of NaCl:Cd, Mg, Mn. The cylindrical (or rod-like) occlusions are supported by light scattering measurements made by Marculescu and by the analysis (1) according to Maxwell-Wagner approach of the ITC B-band and, (2) according to Wert-Zener of the time evolution of it along the conversion process.

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