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DISSOLUTION KINETICS OF PRECIPITATES OF DIVALENT CADMIUM IN SODIUM CHLORIDE STUDIED BY MEANS OF IONIC THERMOCONDUCTIVITY *

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ABSTRACT

In OH^- "free" NaCl: Cd system the isothermal time evolution of the solution process of I.V. (impurity-vacancy) dipoles to achieve the thermodynamical equilibrium was studied by means of the I.T.C. (ionic thermoconductivity) method in the annealing temperature range from 323° to 423° K. Two stages were found, both described by a monomolecular first order kinetics. The early fast stage and the subsequent slow one are characterized by activation energies of $\epsilon_1 \sim 1$ eV and $\epsilon_2 \sim 0.8$ eV, comparable with the activation energy for impurity diffusion, and pre-exponential frequency factors $\nu_{01} \sim 6 \times 10^{11}$ and $\nu_{02} \sim 3 \times 10^6 \text{ sec}^{-1}$. The sources of I.V. dipoles in the two stages were tentatively identified with dipolar precipitates responsible for the additional peaks in I.T.C. spectrum. The energy required to decompose one kind of the above microprecipitates $\epsilon_B^s \sim 0.24$ eV is close to the solution energy of I.V. dipoles.

The role of preannealing on thermodynamical equilibrium value n_s and on the solution kinetics was also analyzed.

Recent precipitation and solubility measurements⁽¹⁻⁸⁾ show that the knowledge of the aggregation state of divalent cation impurities in alkali halides is preliminary to both optical and electrical studies. Information about precipitation phenomena is still restricted and sometimes contradictory⁽¹⁻⁶⁾, chiefly with regard to the nature of the first precipitation products. The occurrence of an initial stage of dimerization⁽⁴⁾ of I.V. (impurity-cation vacancy) dipoles was recently discussed by Crawford^(9, 10) and Wintle⁽¹¹⁾: the latter has shown that a diffusion-controlled dimerization reaction can simulate the third order kinetics, experimentally detected by many authors by means of various techniques in different alkali halide systems^(1-6, 10). Precipitation of divalent impurities out of the solid solution is accompanied by the growth, in addition to microprecipitates, of larger aggregates of metastable phases and stable segregated ones, which were detected by means of x-ray diffraction⁽¹²⁾, electron microscopy⁽¹³⁾, and Mössbauer spectroscopy⁽¹⁴⁾.

On the other hand the solution of the impurities can supply a complementary view on the nature of the precipitates. The study of the thermodynamical equilibrium^(8, 15) concentration of I.V. dipoles vs. temperature gave considerably lower solution activation energies for I.V. dipoles of the order of 0.1-0.2 eV in various systems. Moreover it was shown that the thermodynamical equilibrium value is reached quite slowly even at rather high annealing temperatures.

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In our opinion a detailed analysis of the isothermal time evolution of I.V. dipole concentration in the solution process can throw light both on the dynamics of the solution reaction and on the nature of I.V. dipole sources. Moreover additional information can be gathered from the solution kinetics by affecting the nature and distribution of the early precipitates by submitting the sample to suitable preannealing.

To monitor the I.V. dipole concentration we employed the ionic thermoconductivity method⁽¹⁶⁾ which, due to its high sensitivity, allows the detection of relaxation peaks associated with even low concentration of dipolar microprecipitates. Moreover I.T.C. runs are performed at temperatures below 273°K so that the point defects situation determined by annealing at higher temperatures can be frozen in. We chose NaCl : Cd system because precipitation measurements⁽⁴⁾ suggested that defect mobility is high, so the thermodynamical equilibrium concentration can be achieved in a reasonably short time.

Experimental Procedures

The samples were grown in our laboratory by means of the Kyropoulos method in controlled atmosphere (dry nitrogen) in order to minimize contamination by OH⁻, H₂O, and oxygen⁽¹⁷⁾, which are present in air and affect solubility and precipitation phenomena⁽¹⁸⁾. Cadmium dichloride salt was added to the molten NaCl in percentages ranging from 10⁻⁴ to 10⁻² by weight.

In order to get samples with very low OH⁻ concentration (< 10¹⁴/cm³), the starting powders were submitted to a suitable procedure. An alternative treatment with Cl₂ followed by HCl (at the pressure of ~ 250 mm Hg) is very efficient in eliminating OH⁻, O²⁻, Br⁻, and I⁻ if the gases react in the powdered salt at about 700°C, *i.e.*, about 100° below the melting point of NaCl^(19, 20).

The I.T.C. measurements were performed by the usual technique⁽¹⁶⁾. The crystal slab (area: 2.3 cm², thickness: 0.5-1 mm) was polarized in a static electric field (ranging from 10⁴ to 3 x 10⁴ V/cm) for 3 min at the temperature T_p and then cooled down to the temperature T_f , generally 120°K; after which the field was switched off. During these steps the dipoles become polarized at saturation and remain orientated in the same configuration obtained at the polarization temperature, because at low temperature the relaxation time is practically infinite. The crystal was then warmed up at the nearly constant rate of 0.1°K/sec: the dipole relaxation time for orientation gets shorter and the dipoles lose their preferred orientation giving rise to a depolarization current. This was detected at linearly increasing temperature by a vibrating reed electrometer (Cary 31V) and recorded by Speedomax. The apparatus can measure currents as low as 10⁻¹⁶ A.

The procedure followed in order to obtain solubility and precipitation curves is described in detail in a previous paper⁽⁸⁾.

The aging of samples at temperatures below 530°K was performed directly in the measuring cryostat; in order to "quench" the sample the cryostat was filled with dry N₂ and cooled down to 273°K in a time shorter than 4 min.

Two cryostats with different performances were employed: the former, with vertical

Identical shaped aluminum electrodes assured the minimum temperature gradient through the sample; in the latter, with horizontal gold electrodes, the top one can be put in contact with liquid nitrogen in order to get a very fast quenching of the sample. The electrical contact between sample and electrodes was improved with colloidal graphite. The reproducibility of measurements was within 2%.

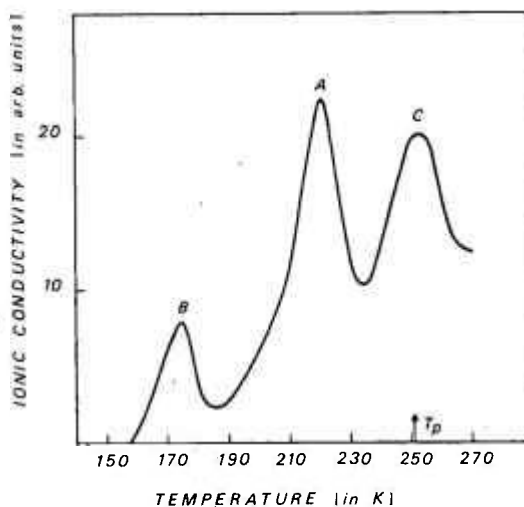


Fig. 1. Ionic thermocurrent of NaCl:Cd (OH^- free): the polarization temperature is indicated by an arrow.

Results

The ionic thermoconductivity curve for a sample of NaCl:Cd "chlorinated" as described above, and polarized at $T_p = 252^\circ\text{K}$ shows three principal peaks at 174° , 220° , and 250°K . The activation energies for orientation of the dipole responsible for the three peaks are 0.4; 0.67⁽¹⁶⁾, and 0.62 eV. The peak at 220°K (peak A) is due to I.V. dipole relaxation, the peak at 174° (peak B) is related to microprecipitates, and that at 250°K (peak C) was usually detected in samples with very high Cd concentration⁽⁸⁾. The curve in Fig. 1 corresponds to the I.T.C. of a sample "as received", i.e., after aging for a long time at room temperature. The isothermal time evolution of I.V. dipole concentration to achieve the thermodynamical equilibrium value was studied by measuring the I.V. dipole concentration* as a function of the aging time at a given temperature, until a saturation is reached.

The isothermal time evolutions of I.V. dipoles were studied for annealing temperatures T_a : 323° , 331° , 340° , 346° , 353° , 364° , 374° , 390° , 405° , and 423°K . In Fig. 2 are shown the

* The concentration can be evaluated from the area under dipole peak or from the height if the warming rate during I.T.C. measurements is held constant⁽⁸⁾.

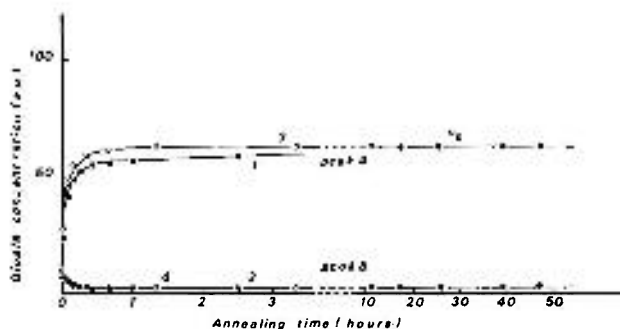


Fig. 2. Solubility curves at $T_a = 353^\circ\text{K}$. Intensity of peak A (curve 1) and peak B (curve 2) vs. annealing time in a sample aged only at temperatures lower than 346°K (first run). Curve 3 and 4, the same as above, but related to same sample annealed at R.T. after getting curves 1 and 2 (second run).

solubility curves at $T_a = 353^\circ\text{K}$ for peak A (curve 1) and for peak B (curve 2) in a sample aged only at temperatures lower than 346°K . Solubility curves always at $T_a = 353^\circ\text{K}$ for peak A (curve 3) and peak B (curve 4) are related to the same sample but annealed at room temperature after obtaining curves 1 and 2. Figure 2 exemplifies the behavior of solubility curves in the annealing temperature range between 323° and 374°K both for first and second run. It must be pointed out that the higher the annealing temperature T_a , the faster the saturation value was achieved. A change in the solubility curve behavior occurred between 374°

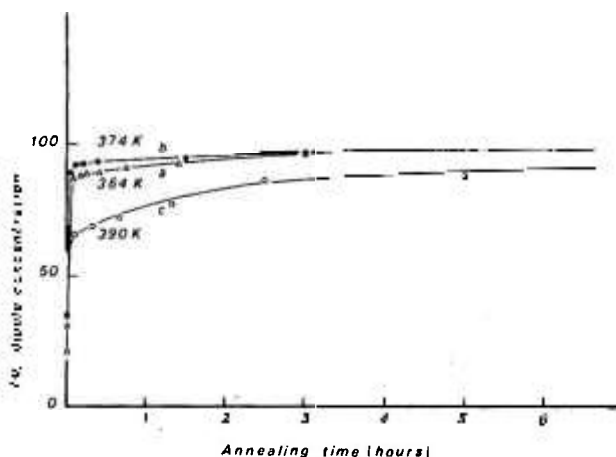


Fig. 3. Solubility curves (first run) at different annealing temperatures T_a for I.V. dipoles (peak A). The dipole concentration was normalized to the saturation value at each annealing temperature. Curve a: $T_a = 364^\circ\text{K}$, curve b: $T_a = 374^\circ\text{K}$, and curve c: $T_a = 390^\circ\text{K}$.

and 390°K , as can be observed in Fig. 3, where the I.V. dipole concentration normalized to the saturation value at each T_a vs. annealing time are compared for $T_a = 364^\circ, 374^\circ$, and 390°K , respectively curves a, b, and c. On going from 374° to 390°K the solubility process was slowed down and the saturation value was attained in a longer time. Starting from $T_a = 390^\circ\text{K}$ the rate of solution became again faster by increasing the annealing temperature.

The isothermal time evolution of the solution process was strongly affected by the "thermal history" of the sample. In Fig. 4 are shown the precipitation and solubility curves at $T_a = 331^\circ\text{K}$. Curve a shows the precipitation of I.V. dipoles after quenching from $T_q = 470^\circ\text{K}$; curve b, the solubility after quenching from $T_q = 470^\circ\text{K}$ followed by a precipitation at room temperature; curve c (open circles), the solubility of a sample annealed at room temperature after obtaining curve a; curve c (full circles), the solubility of a sample annealed previously at the same T_a and left at room temperature. Both curves a and c show a monotonic decrease and increase, respectively, to the saturation value n_s , while curve b shows an initial overshoot followed by a smooth decrease to n_s .

From Fig. 2 and 4 it turns out that the same saturation value n_s at a given T_a is obtained independently of the previous "thermal history" of the sample.

The results reported above were checked on different samples.

Discussion

Influence of preannealing on the solution reaction. — The experimental results show that the solution process at a given T_a is a complex one depending on the thermal history of the sample, even if the saturation value n_s is the same, as one would expect for thermodynamical

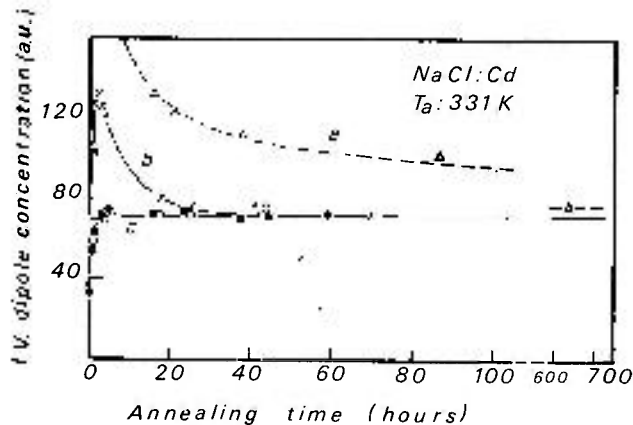


Fig. 4. Precipitation and solubility curves for I.V. dipoles at $T_p = 331^\circ\text{K}$. Curve a: precipitation, after quenching from $T_q = 470^\circ\text{K}$ (only a part of curve is drawn for the sake of convenience; the ordinate at $t = 0$ is 1200; curve b: solubility after quenching from $T_q = 470^\circ\text{K}$ followed by precipitation at R.T.; and curve c: (open circles) solubility of the sample annealed at R.T. after getting curve a; (full circles) solubility of the sample annealed at R.T. after getting curve c (open circles).

equilibrium situation. As shown in Fig. 2 the I.V. dipole concentration grows monotonically with the annealing time while dipoles responsible for the small peak B decrease to a saturation value in both runs. This behavior supports that peak B must be related to precipitates, whose dissolution contributes to the I.V. dipole growth. The saturation value of I.V. dipole concentration is reached more quickly in the second annealing, for instance, at $T_a = 353^\circ\text{K}$ the saturation is obtained after ~ 15 hr and after $1\frac{1}{2}$ hr in the first and second runs, respectively, further runs show practically the same features as the second one. The disparity between the first and second run in the early stage of the solution reaction can be explained by different kinds and distribution of the precipitates in the sample, due to different preannealing. In fact at the beginning of the second run (also at higher T_a) the concentration of B dipoles is always higher than that at the beginning of the first run.

The role of preannealing is still more evident in Fig. 4, where the overshoot which appears in curve b can be interpreted as follows: during the annealing at room temperature after quenching from T_q , the thermodynamical equilibrium among I.V. dipoles and microprecipitates is not yet achieved, due to the low mobility of defects. The latter ones are in excess with respect to the thermodynamical equilibrium, so the subsequent annealing at $T_a >$ room temperature breaks readily the microprecipitates to give I.V. dipoles concentration higher than n_s at T_a ; n_s is then reached by precipitation of I.V. dipole excess. Moreover it is noteworthy that n_s is reached more quickly by solution process than by precipitation from supersaturated solution (curves a and c) even if the early stage of precipitation is extremely fast.

Analysis of solubility curves. — As reported in a previous work⁽¹⁸⁾ dissolution of I.V. dipoles to reach thermodynamical equilibrium value n_s in KBr:Sr at relatively high temperature (334°K) takes long annealing times (~ 100 hr) and can be described by the simple law

$$n = n_0 + (n_s - n_0) [1 - \exp(-t/\tau)] \quad [1]$$

where n , n_0 are the actual and initial I.V. dipole concentration, t is the time, and τ the time constant. A logarithmic plot vs. annealing time t of $n_s - n$ obtained from our solubility data at T_a ranging from 346° to 423°K does not show a behavior as simple as that predicted by [1]. Curve a of Fig. 5 exemplifies the solution reaction (first run) in our NaCl:Cd at $T_a = 353^\circ\text{K}$. Two straight lines instead of one alone fit the experimental data well enough. The solution reaction appears more complex, with a "fast" early stage followed by a slower one. Hence the experimental results suggest that solubility reaction is better described by introducing two time constants τ_1 and τ_2 for the "fast" and "slow" stages, respectively. The second run data always at 353°K , reported for comparison in Fig. 5 (curve b) show surprisingly that the early "fast" stage predominates and now the reaction appears to follow closely the simple equation [1]. The inset in Fig. 5 shows the logarithmic plot at various T_a for second run solubility data. The occurrence mainly of a "fast" stage in the second run can be explained by the presence of small microprecipitates. These, grown during the former annealing at T_a and subsequent precipitation at room temperature, are easily and rapidly broken during the latter annealing at T_a . The "slow" stage can be attributed to the slow dissolution of "hard" and larger microprecipitates. Hence the whole isothermal time evolution of I.V. dipoles is assumed to be governed by the following monomolecular kinetics combination

$$n_s - n = A_1 (n_s - n_0) \exp(-t/\tau_1) + A_2 (n_s - n_0) \exp(-t/\tau_2) \quad [2]$$

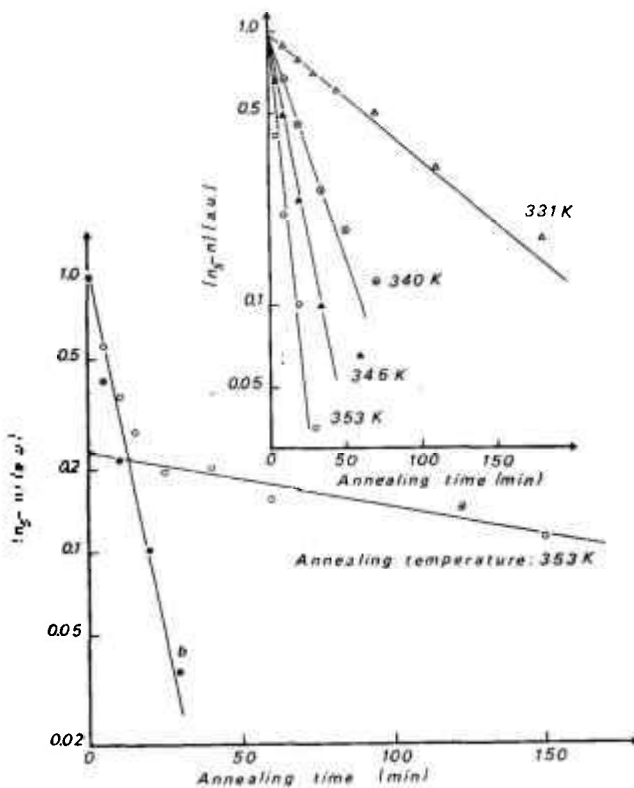


Fig. 5. Logarithmic plot vs. annealing time of $n_s - n$ at $T_a = 353^\circ\text{K}$: open circles, first run; full circles, second run. The inset gives the logarithmic plot vs. annealing time at various T_a (second run).

where $A_1 + A_2 = 1$, A_1 and A_2 are the statistical weights of the "fast" and "slow" stages, respectively. Moreover A_1 and A_2 can be related to the concentration of different kinds of microprecipitates: the easily and the hardly soluble ones. It is worthwhile noticing that the drastic change in the solubility curves between 374°K and 390°K in Fig. 3, can be interpreted as follows: at 390°K the fast stage contributes at comparatively lower extent to the solution reaction, while the slow stage fractional contribution increases. This effect will be better understood in the light of different kinds of precipitates, discussed in the section on Microprecipitates and thermodynamical equilibrium.

τ_1 and τ_2 characteristics. — From Fig. 5 it turns out that the information about τ_1 and τ_2 can be more conveniently obtained utilizing data from second and first runs, respectively. The values of $1/\tau_1$ and $1/\tau_2$ are then reported in the Arrhenius plot shown in Fig. 6: activation energy $\epsilon_1 \sim 1$ eV and $\epsilon_2 \sim 0.8$ eV and pre-exponential factor $\nu_{01} \equiv (\tau_{01})^{-1} \sim 6 \times 10^4 \text{ sec}^{-1}$ and $\nu_{02} \equiv (\tau_{02})^{-1} \sim 3 \times 10^6 \text{ sec}^{-1}$ are evaluated for the first and second stage,

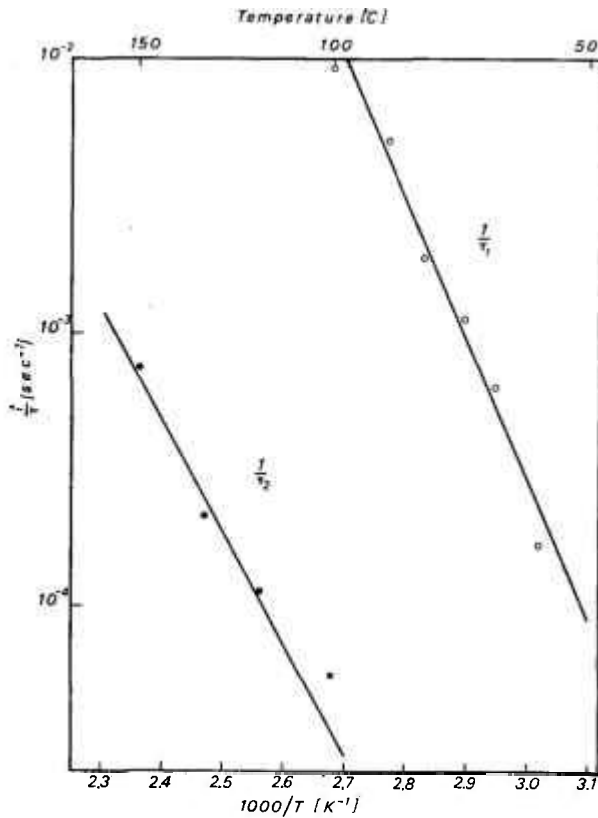


Fig. 6 Arrhenius plot of the reciprocal of time constants τ_1 and τ_2 vs. $1000/T$.

respectively. The activation energy values are comparable with $\epsilon_d = 0.92$ eV, the activation energy for diffusion, *i.e.*, the exchange energy⁽²¹⁾ chiefly if one takes into account that the data for the ϵ_2 calculation are not precise enough.* Therefore one can assume that the solution process is ruled by diffusion of impurity-vacancy dipole far from the precipitates in a similar way as that proposed by Wintle⁽¹¹⁾ for the precipitation reaction in a supersaturated solid solution. An appreciable insight on the nature of precipitates is pursued by comparing ν_{01} and ν_{02} . The rather high value of ν_{01} permits the assumption that only a few atomic jumps are required to release the I.V. dipole from the parent microprecipitate, and to give it the reorientability necessary to be monitored by I.T.C. technique. On the other hand ν_{02} is at least five orders of magnitude lower than ν_{01} , indicating that a convenient sequence of events able to liberate the I.V. dipole occurs with a very low probability and requires a very large number of atomic jumps. These results are consistent with the assumption that the solution stage

* It must be outlined that in the temperature range $346^\circ - 364^\circ$ K the values obtained for τ_2 do not show a definite temperature dependence, possibly due to a mixing of different processes.

characterized by τ_1 involves the break-up of simple I.V. clusters, so the free dipoles can escape easily enough. The extremely long sequence of atomic jumps which precedes the solution of a I.V. dipole in the stage described by τ_2 can be accounted for if large and "hard" precipitates are the only I.V. dipole sources still present. Geometrical and correlation factors can play a very important role in determining the most favorable jump sequence.

Microprecipitates and thermodynamical equilibrium. — The study of thermodynamical equilibrium concentration of dipoles responsible for peak A, B, and C vs. annealing temperature can throw light on the nature of microprecipitates involved in the solution process. In Fig. 7 the logarithmic plot of the saturation value of peak B is reported vs. $1000/T_a$ as obtained from the present work; for comparison the similar plot for peak A (I.V. dipoles) and peak C are drawn from Ref. (8). The behavior of peak A was also checked by using the present data. Moreover the temperature ranges where τ_1 and τ_2 were more conveniently measured, are indicated. In thermodynamical equilibrium, the dipoles responsible for peak B decrease with increasing

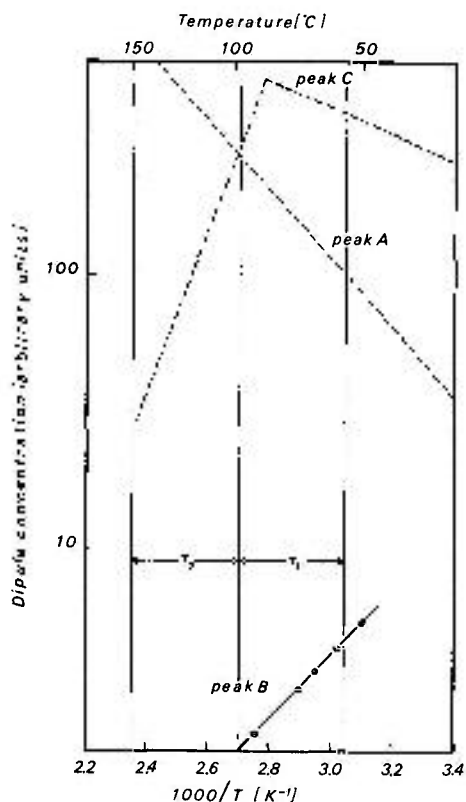


Fig. 7 Arrhenius plot of the thermodynamical equilibrium concentration of A (I.V.), B, and C dipoles vs. $1000/T$. The dotted lines are taken from Ref. (8). The temperature ranges, where the time constants τ_1 and τ_2 were measured more conveniently, are indicated.

temperature, further supporting the assumption that they are microprecipitates and I.V. dipole contributors. At annealing temperatures higher than 375°K the B dipole contribution becomes negligible. Peak C after a moderate growth till 365°K shows a sharp decrease in temperature range between 365° and 415°K . It is worthwhile noticing that in the temperature ranges where τ_1 and τ_2 were more conveniently studied, there occurs the decrease of peak B and C, respectively. This coincidence strongly supports that B and C dipoles are the principal sources of I.V. dipoles during the fast and slow stages, respectively. In the section on Results it was pointed out that on raising the annealing temperature from 374° to 390°K the solution process is slowed down: this can be understood by considering that decomposition of B dipoles contributes to I.V. dipole solution for a smaller fraction, and the thermodynamical equilibrium concentration n_s can be achieved only by the slow dissolution of the hard microprecipitates. From the straight line of Fig. 7 an activation energy of 0.24 eV is obtained for the B dipoles dissolution, which is quite close to the I.V. dipole solution energy $\epsilon_s^{\text{I.V.}} = 0.235 \text{ eV}^{(8)}$.

Conclusions

The accurate analysis of the time evolution of I.V. dipole concentration to achieve the thermodynamical equilibrium value has shown that:

1. The saturation value does not depend on the previous thermal history of the sample, as thermodynamical equilibrium requires.
2. The saturation value is reached more readily if the solution process is preceded by a proper preannealing which breaks the hard precipitates and allows the growth of the simpler ones.
3. At least two stages can be distinguished in the solution process: the early one is much faster than the subsequent one. Both can be separately described by first order monomolecular kinetics, in which the time constants τ_1 and τ_2 are temperature dependent. The difference in activation energy for diffusion⁽²¹⁾ is within 8 and 13% of the activation energies of our fast and slow stages, so the time evolution of the solution process is assumed to occur through a diffusion of I.V. dipoles from precipitates, in fact the energy to release an I.V. dipole from precipitates, i.e., $\epsilon_s^{\text{I.V.}}$ turns out to be considerably less (0.235 eV)⁽⁸⁾. Both the relatively high diffusion energy and the pre-exponential factors of τ_1 and chiefly of τ_2 explain why the solution reaction is so slow even at moderately high temperatures.

Moreover the study of thermodynamical equilibrium values vs. annealing temperature of dipoles responsible for peak B and C suggests that:

1. The growth of I.V. dipoles in the fast and in the slow stage can be related mainly to the decay of B and C dipolar precipitates.

2. The activation energy for the thermal decomposition of B dipoles is the same as the solution energy of I.V. dipoles⁽⁸⁾ as expected if a single I.V. dipole is released from the dipolar microprecipitate B.

From the above results one has the general impression that the precipitation and dissolution of impurities in solids is a rather intricate phenomenon. In order to understand it, a

careful and detailed study of its behavior is necessary avoiding schematic and oversimplified descriptions.

Acknowledgments

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Any discussion of this paper will appear in a Discussion Section to be published in the December 1973 Journal.

RESUMO

No sistema NaCl : Cd com OH⁻ "livre", a evolução temporal isotérmica do processo de solução de dipolos I-V (impureza - vacância), para atingir equilíbrio termodinâmico, foi estudado usando o método de I.T.C., no intervalo de 323 a 423 K de temperatura de recozimento. Foram encontrados dois estágios, ambos descritos pela cinética monomolecular de primeira ordem. O estágio inicial rápido e o seguinte mais lento, são caracterizados pelas energias de ativação de ~ 1 eV e ~ 0,8 eV, respectivamente, valores da ordem de energia de difusão, e fatores de frequência respectivos de 6×10^{11} e $3 \times 10^6 \text{ s}^{-1}$. As fontes de dipolos I - V nos dois estágios foram tentativamente identificados com precipitados dipolares, responsáveis pelos picos adicionais no espectro de I.T.C. A energia de ativação necessária para decompor um tipo de microprecipitados acima, da ~ 0,24 eV, foi calculada e foi encontrado em valor muito próximo da energia de dissolução de dipolos I - V. O efeito de pré-recozimento sobre n_0 e sobre a cinética de solução foi também analisado.

RÉSUMÉ

Dans le système NaCl: Cd avec des radicaux OH⁻ "libres" l'évolution temporelle isothermique du procédé de solution des dipôles I - V (impureté-lacune) pour arriver à l'équilibre thermodynamique, a été étudié par la méthode de I.T.C. dans l'intervalle de température de recuit de 323 à 423 °C. Deux étages ont été trouvés, décrit par la cinétique monomoléculaire de première ordre: L'étage initiale rapide et le suivant plus lent sont caractérisés par les énergies d'activation respectivement d'environ 1 eV et 0,8 eV, valeurs comparables à l'énergie de diffusion et par les facteurs de fréquence respectivement de $6 \times 10^{11} \text{ s}^{-1}$ et $3 \times 10^6 \text{ s}^{-1}$.

Nous avons tenté d'identifier les sources de dipôles I - V aux précipités dipolaires, responsables des pics additionnels dans le spectre de I.T.C.

L'énergie d'activation exigée par la décomposition d'un type de précipités microscopiques au-dessus de l'ordre de 0,24 eV a été calculée et nous avons trouvé une valeur très proche de celle de l'énergie de dissolution des dipôles I - V.

L'effet du pré-recuit sur n_0 et sur la cinétique de solution a été aussi analysé.

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