DIFFUSION D’ESPÈCES ATOMIQUES ET IONIQUES RARE GAS ATOMS IN IONIC CRYSTALS: METHODS, RESULTS AND APPLICATION TO THE STUDY OF LATTICE DEFECTS

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RARE GAS ATOMS IN IONIC CRYSTALS: METHODS, RESULTS AND APPLICATION TO THE STUDY OF LATTICE DEFECTS

F. W. FELIX

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Abstract. — Ever since the preparation of the first terrestrial helium by degassing uranium minerals in the year 1895 rare gas/solid systems have been of interest in science and technology (e.g. the Hahn emanation method, the determination of the geological age of potassium minerals, the behaviour of fission gases in reactor fuels).

In the last ten years a fundamental aspect, namely the atomic transport of Ar, Kr and Xe in simple cubic ionic crystals (alkali halides of NaCl- and CsCl-structure, and alkaline earth fluorides of CaF2-structure) has been studied thoroughly. This paper gives a survey of the hitherto published literature, however, with emphasis on the work based on the introduction of rare gas atoms by transformation of lattice components with nuclear reactions.

The two main features of these investigations are that the gas atoms are mobile in most cases as interstitials and that they react with lattice defects. Such defects may be e.g. thermally or chemically introduced cation vacancies and radiation induced defects.

The experimental technique to determine the gas mobility with the help of radioactive tracers is briefly described. The main experimental results are summarized and compared with the calculations of Norgett and Lidiard.

0. Introduction. — This paper gives a survey on the literature published on transport measurements of gas atoms in simple cubic ionic crystals. The emphasis is on the work based on introduction of radioactive gas atoms by nuclear reactions with reactor neutrons.

Section 1 gives an historical account of the development of this field and its connections to technological and cosmological investigations. Section 2 describes the fundamental experimental techniques for gas production and measurement of gas release together with a comparison with other gas introducing methods, as ion bombardment, recoil injection, etc. Section 3 outlines the evaluation of gas release measurements. Section 4 summarizes the results of gas transport in alkali halides and alkaline earth fluorides both after low irradiation doses in pure crystals and in crystals with high defect concentrations. In section 5 conclusions are drawn by comparing the experimental results with the model and the calculated values of Norgett and Lidiard.

1. Historical development and motivation. — The fundamental studies on gas transport in ionic crystals described in this paper are part of a large complex of investigations on gas containing solids (Table I). The historical starting point may be set to the year 1895 when Ramsay and Rutherford observed that Ra samples continuously emit a radioactive gas namely Rn. Later, Hahn and Müller could establish a relationship between the so-called emanation power of a solid and its specific surface. This Hahn emanation method could be and still is used to characterize solids after a theoretical base had been given by Flügge and Zimen [1]. These authors showed, that the Rn-release is partly due to recoil of freshly formed gas atoms and partly to diffusion to the surface. With the beginning of the nuclear age, reactors became the instruments, which not only made a variety of new gas nuclides easily available, but also brought up severe technological problems due to...
formation of large amounts of the fission gases Kr and Xe in solid reactor fuels and He production in structural materials. Without going into detail, topics like atomic transport, interaction of gas atoms with radiation induced defects, formation of gas bubbles at high gas concentrations have had to be studied. The motivation to study the same phenomena with ionic crystals lies in the fact that these systems are experimentally much easier to handle and also theoretically easier to characterize than the technological materials are up to date.

Also another method, the determination of the geological age of minerals can be traced back to the classical times of nuclear science: Already Rutherford explained that the He content in natural U and Th minerals is of radiogenic origin and thus a measure for the time of existence that the mineral spent in solid state. Since 1927 many other systems have been investigated, also with non-gaseous radiogenic partners. But obviously have radiogenic gases the great advantage to be most easily separable from the solid material. This advantage, however, turns into the most important drawback, as any release before the age determination may pervert the result. This is another motivation to study the transport behaviour of gases.

2. Experimental techniques. — 2.1 Nuclear chemistry of the investigated systems. — 2.1.1 Gas producing reactions. — Figure 1 summarizes the possibilities for gas producing neutron reactions in the relevant part of the periodic system of the elements. He, Ne and Rn are not available for the method of radioactive gas release measurements, being non-radioactive, of too short a half-live or product of an artificial element resp. As only some general remarks are given here, the reader is referred for details to [2] :

— (n, p)- and (n, α)-reactions on alkali and alkaline earth elements need fast neutron irradiation.

— The (n, γ)-reaction on halogen elements works with thermal neutrons. Every activated halogen is transformed by β^-decay into a stable rare gas nuclide and it is this reaction which determines in any halogen containing material the gas concentration. During irradiation this concentration increases continuously, often to such amounts that a second neutron activation produces detectable amounts of a radioactive gas nuclide.

— By the fission reaction several Kr and Xe isotopes are formed amongst a large variety of other nuclides. However, any fissile material does not contain after a decay period of about five days after neutron-irradiation any radioactive gas but Xe-133. An unambiguous assay of fission Kr is possible with Kr-88, the only Kr-isotope with a radioactive daughter product.

2.1.2 Gas mixtures. — Different combinations of the gas producing reactions are possible and offer an important opportunity to gain information on gas transport mechanism :

— pure alkali halides: reaction (1) and (3) always occur simultaneously, however, KI and RbI are most suited to form Ar/Xe and Kr/Xe mixtures ;

<table>
<thead>
<tr>
<th>Year</th>
<th>Event</th>
</tr>
</thead>
<tbody>
<tr>
<td>1895</td>
<td>Ramsey and Raleigh</td>
</tr>
<tr>
<td>1900</td>
<td>Rutherford</td>
</tr>
<tr>
<td>1927</td>
<td>Rutherford</td>
</tr>
<tr>
<td>1932</td>
<td>Hahn and Müller</td>
</tr>
<tr>
<td>1939</td>
<td>Flügge and Zimen</td>
</tr>
<tr>
<td>1942</td>
<td>Zimen</td>
</tr>
<tr>
<td>&gt; 1942</td>
<td>Nuclear age</td>
</tr>
<tr>
<td>1969</td>
<td>Space age</td>
</tr>
</tbody>
</table>

Table I

Classical and modern aspects of rare gas/solid systems

<table>
<thead>
<tr>
<th>Event</th>
<th>Isolation of He from Cleveite</th>
</tr>
</thead>
<tbody>
<tr>
<td>1900</td>
<td>Solid Ra compounds emit Rn</td>
</tr>
<tr>
<td>1927</td>
<td>Radiogenic He as geological clock</td>
</tr>
<tr>
<td>1932</td>
<td>Hahn emanation method</td>
</tr>
<tr>
<td>1939</td>
<td>Theory of Hahn's emanation method</td>
</tr>
<tr>
<td>1942</td>
<td>Artificial nuclides in emanation studies</td>
</tr>
<tr>
<td>&gt; 1942</td>
<td>Xe-135 as reactor poison</td>
</tr>
<tr>
<td>&gt; 1969</td>
<td>Solar wind experiments in the Apollo program</td>
</tr>
</tbody>
</table>
— mixed alkali halides: usually any gas mixture from reactions (1) in mixed halides is easily separated by analysing the radioactive decay curve of a gas sample. Only in the case of a mixture of the long-living Ar-39 and Kr-85 a chromatographic separation becomes necessary:

— U-doped alkaline earth fluorides: these crystals take sufficiently enough U⁴⁺ into the lattice, so that fission Kr and Xe can be introduced besides the (n, α)-gases.

2.1.3 Nuclear doping with alienvalent elements. — Up to date no effect of the formation of non-gaseous impurities on the defect structure of irradiated ionic crystals has been studied. This is certainly due to the fact that the concentration is usually much smaller than the natural concentration of impurities (e.g. transformation of K after neutron-activation into Sr by β-decay).

2.2 Other gas introducing methods. —

2.2.1 Homogeneous gas distribution. — Besides the already mentioned production of fission gases in situ of U-containing materials, one also may isolate fission iodine from the bulk of fission products, add it in a suitable form to an iodine containing material and let it decay to Xe. This method has an important advantage, as the gas production is accompanied by a negligible radiation damage. This method has been used already in 1942 by Zimen to investigate AgI after precipitation from a fission iodine containing solution [3]. Recently, Mears and Elleman [4] made an extensive study of Xe-133 mobility in crystals of the alkali-iodides, which were grown from a melt containing the fission product I-133.

2.2.2 Emanation method and in-pile experiments. — These methods belong in a way to the homogeneous distribution case, they are, however, characterized by a continuous gas production in the solid.

The measured gas release rate is in this case the result of an equilibration of production rate vs radioactive decay and diffusion to the surface. Very few experiments have been performed by the emanation technique on ionic crystals e.g. the study of sintering and melting behaviour of KBr by Zaborensko et al. [5]. Any attempt to transfer the emanation technique to an in-pile experiment with ionic crystals has not yet been made. Such an experiment should be planned as valuable information is to be expected.

2.2.3 Superficial labelling. — A large amount of results have been published dealing with gas release from superficially labelled ionic crystals. This labelling may be performed either by injection of suitable recoil atoms from a nuclear reaction or by exposing the solid to a beam of accelerated radioactive gas ions.

— Recoil doping: in this technique, the to be labelled solid is in intimate contact with a nuclear source. For Rn-labels this is done by impregnating the solid with e.g. a Th-228 solution, cf. [6]. [7]. For Xe-133 the solid is wrapped in a U-foil enriched in U-235 and reactor irradiated, cf. [8].

— Ion bombardment: the great methodical variability of ion bombardment technique has been demonstrated by numerous papers of Jech, Kelly and Matzke, cf. their summarizing paper [9] and [10] by Matzke. Obviously, these techniques have an unlimited application to any solid material. However, when compared with the nuclear chemical gas doping, certain disadvantages have to be mentioned: Depending on the kinetic energy the injected gas ions penetrate from some atomic layers up to 10⁻⁶ cm into the solid. In order to be above the limit of detection in the following gas release experiment, this rather small surface layer has to be loaded with very high gas concentrations (10¹⁵-10¹⁸ cm⁻³ which compares to about 10¹⁰ cm⁻³ for nuclear doping at its limit of detection) which is unavoidably combined with high damaging of the lattice. To exclude disturbance of any surface effects, Pronko and Kelly [11] refined the ion bombardment technique considerably by stripping the damaged surface layer and then by measuring but the release of those gas atoms which penetrated by channeling deeply into the undisturbed lattice.

2.3 Apparatus for measuring gas release kinetics. — The equipment for studying gas release mea-

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**Fig. 2.** — Measurement of gas release after neutron irradiation. A Discontinuous method with direct sample taking; B Discontinuous method with gas collection by adsorption; C Continuous method; F Furnace, LS Lead shield, PC Proportional counter, CT Charcoal trap in liquid air.
measurements is rather simple, minor complications arise only if rather high temperatures have to be reached (alkaline earth fluorides) or if a controlled atmosphere (e. g. the hygroscopic alkali fluorides) becomes necessary. Figures 2 and 3 give some principal features of the technique, for more details see [2]. As already mentioned in section 2.1 the assay of the radioactive gases does not pose problems and may be performed with standard equipment.

![Fig. 3. Heating arrangement for alkali halide crystals (above), CS Czacko type stopcock; PVC Rubber seal; A Asbestos thermal insulation; Q Quartz rod to reduce free gas volume; M Metal block; C Crystal probe; TC Thermocouple. Container for gas sampling and radiometric assay (below), G glass; P picein seal; M brass chamber; H organic foil; E epoxy resin seal.](image)

**Fig. 3.** Heating arrangement for alkali halide crystals (above), CS Czacko type stopcock; PVC Rubber seal; A Asbestos thermal insulation; Q Quartz rod to reduce free gas volume; M Metal block; C Crystal probe; TC Thermocouple. Container for gas sampling and radiometric assay (below), G glass; P picein seal; M brass chamber; H organic foil; E epoxy resin seal.

3. Evaluation of gas release experiments. —

3.1 INTERPRETATION OF RELEASE KINETICS. — As rare gases are practically insoluble in solid materials, one expects a gas concentration gradient between the bulk and the surface of the sample as long as the sample is not completely exhausted. The decrease of this gradient has been described by Intohoff and Zimen [12] by solving Fick's 2nd law for the appropriate boundary conditions, shown in figure 4. For many different shapes similar solutions are tabulated as $F$ vs. const. $\times$ Dt, cf. Lagerwall and Zimen [13].

A large number of gas release experiments did in fact follow this ideal diffusion pattern. However, perhaps the larger part of the experimental work did show deviations, which were very early ascribed to trapping of gas atoms by lattice defects, cf. Schmeling [14].

Mathematically such a trapping effect has been introduced in Fick's law by adding absorption and desorption terms on the basis of a quasichemical reaction between mobile gas atoms and a stable distribution of traps (Fig. 5).

Solutions of this problem have been published by Hurst [15] in numerical and by Gaus [16] in analytical form. The number of parameters ($D$, the reaction rates, $\mu$ and $b$ and the initial fraction of mobile and trapped gas, $p_0$ and $q_0$ resp.) is sufficiently large now to describe almost any shape of a release curve. Caution is therefore recommended, when the physical significance of this mathematical model has to be checked.

A detailed discussion of non-ideal kinetic behaviour of gases in highly irradiated ionic crystals will be given in reference [17].

An important special case of the Hurst-Gaus model is given when the trapping reaction has reached its thermal equilibrium: the differential equation reduces to the simple Fick type, but with $D_{app}$, which is smaller than $D$ for undisturbed diffusion. So whatever the initial conditions are, if the equilibrium is reached during the experiment, reliable diffusion coefficients can be evaluated.

This is illustrated in figure 6 with three examples for diffusion with trapping behaviour. The curve $\text{KCl: Sr}$ represents trapping into cation vacancies with rapid equilibration, thus a curve of apparent ideal behaviour results. The other two curves start from an initial non-equilibrium, due to radiation induced traps. In one case all atoms are trapped initially, $p_0 = 0$, in the other freely mobile, $p_0 = 1$. However, both curves reach asymptotically the ideal one.

![Fig. 4. Boundary conditions for gas release from a homogeneously doped sphere (above) and theoretical gas release curve with approximative solutions (below) according to Lagerwall, Zimen [13].](image)
Ideal diffusion: Fick's 2nd law

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \]

Trapping reaction:

\[ E + T \xrightarrow{\mu} ET \]
\[ [E] = c, \text{ at } t = 0 \quad c = p_0 \]
\[ [ET] = m, \text{ at } t = 0 \quad m = q_0 \]

with \( p_0 + q_0 = 1 \).

\[ \frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} - \mu c + bm \]

\[ \frac{\partial m}{\partial t} = \mu c - bm \]

... with rapid equilibration

\[ \frac{\partial c}{\partial t} = D_{app} \frac{\partial^2 c}{\partial x^2} \]

with

\[ D_{app} = \frac{D}{1 + \frac{\mu}{b}} \]

D. G. Hurst H. Gaus

Fig. 5. — Differential equations for gas release with interaction of traps, according to Hurst [15], and Gaus [16].

3.2 Other initial profiles. — For the superficially labelled solid similar solutions have been published for both ideal diffusion and for trapping behaviour: for a linearly decreasing profile cf. DiCola, Matzke [18], and Mears, Elleman [19] and for an exponentially decreasing profile cf. Kelly, Matzke [20].

4. Results. — The aim of this section is to demonstrate by a selection of Arrhenius-diagrams the most typical facts of gas mobility and trapping behaviour.

4.1 Gas diffusion in nominal pure crystals after low dose neutron irradiation. — Figure 7 summarizes all results on diffusion of gases produced by \( n, p \) reaction on the alkali in all alkali halides available to the method of nuclear doping. The \( 1/T \)-scale is normalized with respect to the absolute melting point. Three groups are to distinguish:

— Non-fluorides of NaCl-structure: The very high \( D \)-value at the melting point (comparable to diffusion in liquid state) and the low activation energy at high temperatures indicate an interstitial diffusion mechanism. The increased activation enthalpy below about \( \frac{2}{3} \) of the absolute melting point means, that the trapping equilibrium, mentioned in section 3.1, is moved in favour of the formation of gas/trap associates.

— The alkali fluorides do not show but a single and very high activation enthalpy. The diffusion coefficients differ much for KF, RbF and CsF. A trapping mechanism is assumed for the whole temperature region by analogy to the low-temperature branch of the other alkali halides.

— The CsCl-type alkali halides again show a single activation energy with very similar \( D \)-values for the different halides.

Very similar \( D \)-values were also observed for different rare gases, when crystals slightly doped with K.
and Rb could be investigated. By this interesting observation the assumption of an interstitial mechanism for the CsCl-structure became doubtful.

The difference of gas diffusion with respect to the NaCl- and CsCl-lattice is very instructively shown in figure 8 for CsCl with its phase transformation at 469 °C [21]. In the low-temperature CsCl-phase all gases have practically the same mobility, but in the NaCl-phase a tremendous separation of Ar, Kr and Xe takes place, for the former e. g. by a 200 fold higher $D$. As the interstitial space is extremely small in the CsCl-structure, the gas has to move by another mechanism. The calculations of Müller and Norgett [22], [23] showed that mobile gas-divacancy associates quantitatively fit the experimental results.

![Figure 8](image)

**Figure 8.** Rare gas release from CsCl, from Felix, Meier [21]

Figure 9 finally shows the results with alkaline earth fluorides. In principle the behaviour is the same as in the nonfluorides of NaCl-structure, i. e. again very high $D$-values at the melting point, however, with greater activation enthalpies. The diffusion mechanism should therefore be an interstitial one again, as first discussed by Lagerwall [25] and later theoretically supported by Norgett [26]. The higher enthalpies with respect to the NaCl-structure reflect the much denser structure of the CaF₂-lattice.

4.2 EFFECT OF HIGHER DEFECT CONCENTRATIONS.
— Until now no specification has been given on the nature of the traps. The first step in this direction is to investigate in the traditional way the influence of doping with divalent cations.

The resulting increase in the concentration of cation vacancies was determined by measuring the ionic conductivity. (These values are transformed in figures 10 and 11 by the Nernst-Einstein relation into $D$-values to enable direct comparison with the gas-diffusion.)

![Figure 9](image)

**Figure 9.** Rare gas release from alkaline earth fluorides, from Felix, Lagerwall [24].

Figure 10 clearly shows the double nature of cation vacancies, acting as diffusion carriers for self diffusion and as traps to decrease the gas mobility in KBr.

Figure 11 gives the interesting case of KI, where the gas atoms are obviously unaffected by an increase of cation vacancies. The trapping behaviour is in this case due to other defects, as pre-existing or radiation-induced ones.

Figure 12 shows then, that in the NaCl-lattice, here K$_{0.3}$Rb$_{0.7}$Cl, a reduction of the gas mobility is achieved.

![Figure 10](image)

**Figure 10.** Influence of Sr$^{2+}$-doping in KBr on Ar-release from KBr, from Felix, Müller [27].
through introduction of defects as well chemically as by high irradiation doses. Second, in accordance with the interstitial mechanism, different gases diffuse and also react independently with the dominating defects.

The fact that at a given temperature, the same decrease in gas mobility can be produced either chemically or by irradiation resolved earlier contradictions about the influence of divalent dopants, see Felix, Müller [27].

Figure 13 gives the similar behaviour for Xe-diffusion in both CsCl-modifications. It is interesting that also in the CsCl-phase a distinct trapping effect exists. This means that in both phases the immobile gas defect-associates are the same, but not the mobile gas species. In this respect a very important result is, that the radiation induced defects are stable not only against thermal annealing (even in the vicinity of the melting point) but also against the phase transformation itself.

4.3 Comparison with the theoretical calculations. — The information about transport mechanism and trapping behaviour was confirmed and refined by the theoretical calculations of Lidiard and Norgett [30]. Starting from the same trapping equation from section 3.1 interpreted in terms of the mass action law the authors gave a complete description of the temperature dependence of gas diffusion with interaction of point defects in the extrinsic and intrinsic region and radiation induced defects. As an example shows figure 14 two typical equations which describe diffusion with trapping into point defects, corresponding to the experimental case of trapping into cation vacancies. In the extrinsic region (constant trap concentration) \( D_{app} \) is in fact inversely proportional to the trap concentration. In the intrinsic region (traps in thermal equilibrium) a simple Arrhenius type equation is valid, however, with activation enthalpy slightly larger than the value for pure undisturbed mobility, namely corrected by the difference between the binding energy of the gas atom into the trap and the formation energy of the trap itself.

The important of this work is, that every contribution to the apparent activation enthalpy could be quantitatively calculated on the basis of a Born-model. Table II gives a summary of the results, from [22], [23] and [31].

4.4 Comparison with results by other experimental techniques. — One would expect, that different gas introducing methods should nevertheless come to the same conclusions. This is up to date not the case to a very large extent. There are still controversial results and it would be of great value, if one could plan now some cross-experiments.
Temperature dependence...

\[ D = D_0 \exp - \left( \frac{\Delta H_m}{kT} \right) \]

... with trapping equilibrium

\[ E + T = ET \]

\[ \frac{[E]}{[ET]} = \exp - \left( \frac{\Delta H^*}{kT} \right) \]

\[ p = \frac{[E]}{[E] + [ET]} = \frac{1}{1 + c_T \exp(\Delta H_u/kT)} \]

\[ D_{app} = pD \]

and constant trap concentration

\[ D_{app} = D_0 \exp \left( - \frac{\Delta H_m + \Delta H_b}{kT} \right) \]

or traps in thermal equilibrium

\[ c_T = \exp - \left( \frac{\Delta H_f}{kT} \right) \]

\[ D_{app} = D_0 \{ \exp - (\Delta H_m + \Delta H_b - \Delta H_f)/kT \} \]

A. B. Lidiard and M. J. Norgett

**FIG. 14.** — Equations for temperature dependence of the gas diffusion-coefficient with interaction of point defect traps, according to Lidiard and Norgett [30].

The best confirmed observation is that higher doses in the ion-bombardment and the recoil-doping technique result in lower \( D_{app} \) values, in accordance with the assumption that more traps are produced. One has to bear in mind, however, that a higher dose also means a higher gas concentration, that is to say the reduction in gas-mobility might also be due to e. g. formation of less mobile gas-bubbles. Such a gas-gas-interaction has not yet been found in any neutron irradiated system where the gas is assumed to move interstitially (e. g. in any multi-gas diffusion experiment Ar, Kr and Xe always diffused independently, regardless of the relative gas concentrations). A useful attempt to clearly separate gas- and trap-concentration contributions was made by Mears and Elleman [4] by using the \( I-133 \) doping method (see section 2.2.1). Unfortunately are the given results not sufficient to decide for or against a gas-concentration effect.

In many ion-bombardment experiments, the degassing was performed by a linear or an isochronal temperature program [9]. This technique revealed that the gas release can occur by different more or less defined steps. The cause may be that some gas atoms are situated in less efficient traps than others, or, that different traps anneal with different activation energies. Complimentary experiments are lacking, by which such different mechanisms could be studied in isolated form. Also the diffusion of channelled ions, see section 2.2.3, [11] should be investigated further: the published \( D \) values for this technique are surprising lower than the corresponding values after the

<table>
<thead>
<tr>
<th>Table II</th>
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</thead>
</table>

Comparison of theoretical and experimental values of the apparent enthalpies (eV) for gas mobility in nominal pure crystals at higher temperatures, Lidiard, Norgett [31], Müller, Norgett [22], Felix [2]

<table>
<thead>
<tr>
<th>Lattice</th>
<th>System</th>
<th>( \Delta H_m )</th>
<th>( \Delta H^* )</th>
<th>( \Delta H_{corr} )</th>
<th>( \Delta H_{app}^{\text{th}} )</th>
<th>( \Delta H_{app}^{\exp} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>A) Mobile gas interstitials.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>KF Ar</td>
<td>0.2</td>
<td>([V_e V_a] )</td>
<td>1.0</td>
<td>1.2</td>
<td>1.8</td>
</tr>
<tr>
<td>KCl</td>
<td>0.2</td>
<td>( V_e )</td>
<td>0.2</td>
<td>0.4</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>KBr</td>
<td>0.2</td>
<td>( - )</td>
<td>0</td>
<td>(0.2)</td>
<td>0.4</td>
<td></td>
</tr>
<tr>
<td>KI</td>
<td>0.3</td>
<td>0</td>
<td>0.3</td>
<td>0.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>RbF Kr</td>
<td>0.2</td>
<td>([V_e V_a] )</td>
<td>1.9</td>
<td>2.1</td>
<td>1.4</td>
<td></td>
</tr>
<tr>
<td>RbCl</td>
<td>0.2</td>
<td>( V_e )</td>
<td>0.5</td>
<td>0.7</td>
<td>0.6</td>
<td></td>
</tr>
<tr>
<td>RbBr</td>
<td>0.2</td>
<td>( V_e )</td>
<td>0.4</td>
<td>0.6</td>
<td>0.5</td>
<td></td>
</tr>
<tr>
<td>Rbl</td>
<td>0.3</td>
<td>( (V_a) )</td>
<td>0.2</td>
<td>(0.5)</td>
<td>0.3</td>
<td></td>
</tr>
<tr>
<td>CsF Xe</td>
<td>0.9</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta )-CsCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CaF&lt;sub&gt;2&lt;/sub&gt;</td>
<td>CaF&lt;sub&gt;2&lt;/sub&gt; Ar</td>
<td>2.2</td>
<td>( V_e )</td>
<td>0.3</td>
<td>2.5</td>
<td>3.0</td>
</tr>
<tr>
<td>SrF&lt;sub&gt;2&lt;/sub&gt; Kr</td>
<td>2.2</td>
<td>( V_e )</td>
<td>0.8</td>
<td>3.0</td>
<td>(1.2)</td>
<td></td>
</tr>
<tr>
<td>BaF&lt;sub&gt;2&lt;/sub&gt; Xe</td>
<td>2.8</td>
<td>( V_e )</td>
<td>0.7</td>
<td>3.5</td>
<td>3.5</td>
<td></td>
</tr>
<tr>
<td>B) Mobile gas/([V_e V_a]) associates.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CsCl</td>
<td>( \alpha )-CsCl Xe</td>
<td>0.66</td>
<td>( V_a )</td>
<td>0.43</td>
<td>1.09</td>
<td>1.0</td>
</tr>
<tr>
<td>CsBr</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
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highest investigated neutron-dose. From the neutron-irradiation experiments one should expect for diffusion in the undisturbed lattice $D$-values larger by several orders of magnitude.

5. Conclusions. — The behaviour of rare gas atoms in simple cubic ionic crystals can today be regarded as satisfyingly well understood on the basis of a systematic experimental and theoretical investigation. The determination of gas mobility in a crystal lattice is not only a very simple and non-destructive experimental method, but also a powerful instrument to study the defect structure of the host lattice. For the study of radiation induced defects it has to be emphasized, that this method has an unlimited range of application concerning the irradiation dose, starting from the conditions of a practically undisturbed lattice up to any value.

Acknowledgments. — A sincere thank is first of all expressed to Prof. Dr. K. E. Zimen, who after his pioneering work introduced the author in this scientific field. Many thanks are also due to the numerous members of the Hahn-Meitner Institute who took and still take part in this research.

References


[29] Felix, F. W., Meiер, M. to be published.

DISCUSSION

A. L. Laskar. — 1) Why is there hysteresis type behavior in the Arrhenius plot of conductivity in CsCl in the region of phase change?

The reader is referred to the original paper of Weijsa and Westra, Phys. Stat. Sol. (a) 11 (1972) 729.

2) Since at higher temperature, the NaCl structure is more open compared to fcc structure at low temperature, is it not natural to expect larger change in activation energy?

In CsCl there is not only the phase transformation, but also a change in the diffusion mechanism. Therefore, the activation energies cannot be directly compared, as e. g. in the case of KCl/Ar and CaF$_2$/Ar where in fact a large change in the activation energy for interstitial mobility is observed.