



Analysis of self-trapped hole mobility in alkali halides and metal halides



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ABSTRACT

The small radius hole polarons (self-trapped holes (STH) known also as the V_k centers) are very common color centers observed in numerous alkali halides and alkaline-earth halides. Their mobility controls the rate of secondary reactions between electron and hole defects and thus radiation stability/sensitivity of materials. We have analysed here the correlation between the temperatures at which hole polarons start migration in a series of alkali halides (fluorites, chlorides, bromides, iodides) and the lattice displacement around quasi-molecule. These results are especially important for identification of the self-trapped holes, for example, in novel scintillating materials such as SrI_2 , as well as in a large family of perovskite halides and more complex halide materials.

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1. Introduction

The mobilities of small radius polarons affect properties of many insulating materials and thus attract considerable attention [1–3]. The self-trapped hole (STH) polarons (called V_k centers), in which a hole is shared by two nearest halogen ions, X_2^- , are very common color centers created in alkali halides, alkaline-earth halides and some other halides under various kinds of irradiation (UV light, electrons, gamma rays, neutrons, heavy swift ions) [4–28]. Their mobility controls the rate of secondary reactions between electron and hole defects and thus radiation stability/sensitivity of materials.

The hole polarons start to migrate and recombine above certain onset temperatures (in the range 50–200 K). Their diffusion-controlled decay has been observed by different experimental techniques in almost all alkali halides, as well as in some other binary halides, but also in complex halides, such as perovskite halides, ammonium halides, halide sodalites etc. [8,11,12,15,23,25,26,28–30].

In this paper, we review and analyse the STH migration temperatures for a series of alkali halides as a function of halogen-halogen (X–X) distance in a regular crystalline lattice as well as the bond length in isolated X_2^- molecular ions.

2. Analysis of the STH migration

Due to formation of chemical bond, the equilibrium distance of a X_2^- hole polaron is smaller than the distance between two nearest host halogens in perfect crystals and very close to that in a gas-phase molecule

[31] (Fig. 1). Above certain temperatures the STH migration occurs via a quasi-molecule reorientation by 60° or 90° (dependent on the f.c.c. or b.c.c. lattice), during which one of the two halogens becomes a common partner in the old and new quasi-molecule (*bond switching*). Application of the small radius polaron theory to the V_k centers [32] has shown that its hopping probability W is expected to be an exponential function of the migration energy E_a

$$W = \nu_0 \exp(-E_a/kT) \quad (1)$$

$$E_a = S \hbar \omega / 4, S = A M \omega \Delta^2 \quad (2)$$

where ν_0 is a pre-factor, S the so-called Huang-Rhys factor, dependent on the displacement Δ of the halogen from the regular lattice site after formation of the chemical bond (Fig. 1), ω is the LO optical phonon frequency, M the halogen mass, and A pre-factor depending on the reorientation angle ($A = 0.9$ for 60°). The hole delocalization/reorientation occurs when during thermal fluctuations one of halogens in the STH approaches the regular lattice site. Eqs. (1) and (2) show that a decrease of displacement Δ lowers the migration energy and hence the onset temperature T_{migr} at which hole migration begins. The latter may be defined by the temperature at which STH performs one jump per second, $W = 1 \text{ s}^{-1}$

$$T_{\text{migr}} = A M \omega \Delta^2 / 4 k \ln \nu_0 \sim \Delta^2 \quad (3)$$

i.e. is a quadratic function of the ionic displacement.

Tables 1–4 summarize the experimental migration temperatures and inter-halogen distances for different types of crystalline structures – f.c.c., b.c.c., fluorite, and some more complicated structures (wurtzite, layered matlockite etc.) corresponding to four classes of halides –

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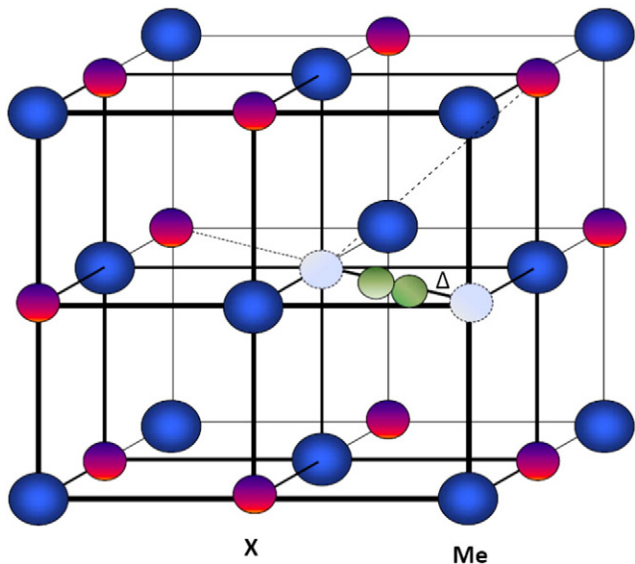


Fig. 1. Schematic view of the STH in f.c.c. structure, Δ is halogen displacement from the perfect lattice site as a result of the STH formation.

fluorites, chlorides, bromides, and iodides. These literature data are used for analysing the dependence of the migration temperatures on the halogen-halogen distances in the above-mentioned four classes of halogen-containing solids (Figs. 2–5).

As one can see, the migration temperatures show a *linear* dependence on the displacement Δ , rather than the theoretically predicted quadratic one. (The first point at 0 K corresponds to the equilibrium distances in free X_2^- molecules.) The reason for this is not clear at the moment. What is more striking is that this linear dependence holds for each class, e.g. fluorides, *irrespective* on the specific lattice structure, e.g. f.c.c. LiF, fluorite CaF_2 , perovskite $KMgF_3$. This observation clearly demonstrates that the main factor determining the migration temperature is the lattice displacement.

These results may be useful in the following cases:

1. Very often thermoluminescence peaks or optical absorption annealing stages are attributed to the self-trapped holes, but it remains

Table 1

Compilation of migration temperature of V_k centers in some metal halides, obtained via thermal annealing of optical absorption, electron paramagnetic resonance (EPR) as well as thermally stimulated luminescence (TSL) measurements. Alkali halides with NaCl-type lattice Cl–Cl distance = $a/\sqrt{2} = 0.707a$, a is the lattice constant.

Material	Type	Lattice constant	Halogen-halogen distance	$T_{migr}(V_k)$, °K
LiF	NaCl	4.028	2.8482	125; 132; 150 [9,33–36]
NaF	NaCl	4.634	3.2767	160; 175; 180 [9,33,37]
KF	NaCl	5.348	3.7816	175; 210 [9,33]
RbF	NaCl	5.63	3.9810	216 [33]
F_2^-			1.90 [31]	
LiCl	NaCl	5.14	3.6345	115, 120, 123 [9,33,38]
NaCl	NaCl	5.64	3.9881	150; 160; 165; 168 [9,33,39,40]
KCl	NaCl	6.294	4.4505	205; 208; 210 [9,33,41,42]
RbCl	NaCl	6.582	4.6542	220; 240 [9,33]
Cl_2^-			2.71 [31]	
LiBr	NaCl	5.502	3.8905	122 [33]
NaBr	NaCl	5.978	4.2271	115; 134 [9,33]
KBr	NaCl	6.596	4.6641	160; 170; 175 [9,33,43,44]
RbBr	NaCl	6.89	4.8720	170; 206 [9,33]
Br_2^-			2.90 [31]	
LiI	NaCl	6.00	4.2426	
NaI	NaCl	6.474	4.5778	58; 60 [9,33]
KI	NaCl	7.066	4.9964	105; 110 [9,33]
RbI	NaCl	7.342	5.192	125 [9,33]
I_2^-			3.28 [31]	

Table 2

The same as Table 1 for alkali halides with CsCl-type lattice, Cl–Cl distance = a .

Material	Type	Lattice constant	Halogen-halogen distance	$T_{migr}(V_k)$, °K
CsCl	CsCl	4.123	4.123	202 [33,45,46]
CsBr	CsCl	4.286	4.286	122; 130 [33,47]
CsI	CsCl	4.5667	4.5667	60 (linear); 85 (jump) [48]
NH_4Cl	CsCl	3.8756	3.8756	180 [33]
NH_4Br	CsCl	4.0594	4.0594	120 [33]
TlCl	CsCl	3.8340	3.8340	Not found
TlBr	CsCl	3.97	3.97	Not found
TlI	CsCl	4.108	4.108	Not found

unclear, whether it is captured by impurities or self-trapped in a regular lattice. This linear relationship certainly helps to make a more specific conclusion.

2. For STH in complex structures with several halogen-halogen distances, the linear law allows us to estimate the range of lattice sites where the STH could exist. For example, there are 12 symmetrically distinct I–I ion pairs in a novel efficient scintillator SrI_2 [55–57], with a broad range of the distances, 3.9–5.0 Å [56]. From our analysis for the iodides (Fig. 5), we expect that migration temperatures of V_k centers in SrI_2 fall into range 50–100 K, respectively. Indeed, Yang et al. [57] have recently reported thermoluminescence of X-rayed $SrI_2:Eu$ consisting of 9 peaks, between liquid helium temperature (LHeT) and room temperature, including three peaks below 100 K. It is important, however, that the peak at 50 K dominates the thermoluminescence glow curve, which is more than an order of magnitude stronger than any other peak, which is typical for V_k centers in ionic solids. The position of this peak corresponds to the lowest distance among all I–I pairs where the V_k center could be localized.

This analysis indicates how to interpret the thermoluminescence peaks in this and similar complex materials, but also allows conclusions about stable local atomic configurations, in terms of the carrier self-trapping. Moreover, it allows us to understand how to use impurity doping of the material for controlling the channels of the electronic excitation relaxation.

Another example of complex materials is the family of metal fluorohalides, which are important media for X-ray and neutron imaging [54,58–62]. In $BaFCl$ layered matlockite crystals, only Cl_2^- in-plane configuration was found (see Table 4). Simple analysis of Fig. 3 allows

Table 3

The same as Table 1 for metal halides with fluorite lattice, F–F distance = $a/2 = 0.5a$.

Material	Type	Lattice constant	Halogen-halogen distance	$T_{migr}(V_k)$
CaF_2	CaF_2	5.4626	2.7313	126 K [49,50]
SrF_2	CaF_2	5.800	2.900	110; 120 [49,50]
$SrCl_2$	CaF_2	6.9767	3.488	105 [51]
CdF_2	CaF_2	5.3895	2.695	95 [52]

Table 4

The same as Table 1 for several other halides with crystalline structures different from those in Tables 1–3.

Material	Type	Lattice constant	Halogen-halogen distance	$T_{migr}(V_k)$
AgI	Wurtzite	$a = 4.580$; $c = 7.494$	$a = 4.580$	Not found
NH_4F	Wurtzite	$a = 4.390$; $c = 7.02$	$a = 4.390$	Not found
$KMgF_3$	Perovskite	$a = 3.93$	$a/\sqrt{2} = 0.707a = 2.78$	110 [53]
$BaFCl$ (only Cl_2^-)	Layered matlockite	$a = 4.394$; $c = 7.225$	4.11 (in-plane) 2.72 (out-of-plane)	130 [54]

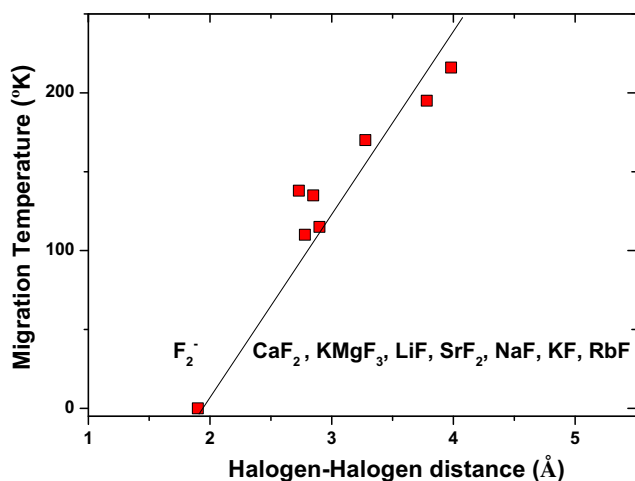


Fig. 2. Dependence of the STH delocalization and migration temperature for a series of fluorides as a function of halogen-halogen distances in the perfect crystal (see Table 1).

one to conclude that V_k in-plane configuration with $T_{\text{mig}} \sim 130 \text{ K}$ [54] fits well the proposed linear relation, and to predict that the V_k migration for out-of-plane configuration (with the distance of 2.72 \AA close to 2.71 \AA in free molecule) could begin only at very low temperatures. This is why such V_k centers have not been observed in commonly used experiments performed above LHeT. We suggest that only experiments at temperatures below LHeT could help to observe this type of defects.

From the viewpoint of scintillator engineering, materials are required with fast hole diffusion (and thus recombination) at room temperatures, which holds for STH with small lattice displacements and thus low delocalization temperatures, e.g. NaI.

- It is established that V_k centers are produced and well studied in all fluoroperovskites (KMgF_3 (Fig. 2), BaLiF_3 , KZnF_3). We have demonstrated here that their thermal stability/migration follow the same pattern as simple binary halides. This makes it possible to straightforwardly assess the thermal stability of the STH for a wide range of AMX_3 materials.

Note that in some metal halides, such as AgI or AgCl , V_k centers were not observed. Polaron stability and polaronic motion of self-trapped holes in silver halides were recently discussed in details in [63] on the basis of first principle calculation of self-trapped holes in AgCl and AgBr for which extensive experimental data exist.

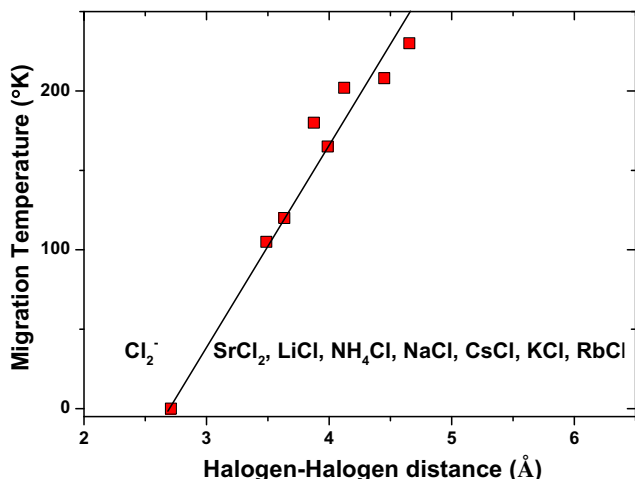


Fig. 3. The same as Fig.2 for chlorides,

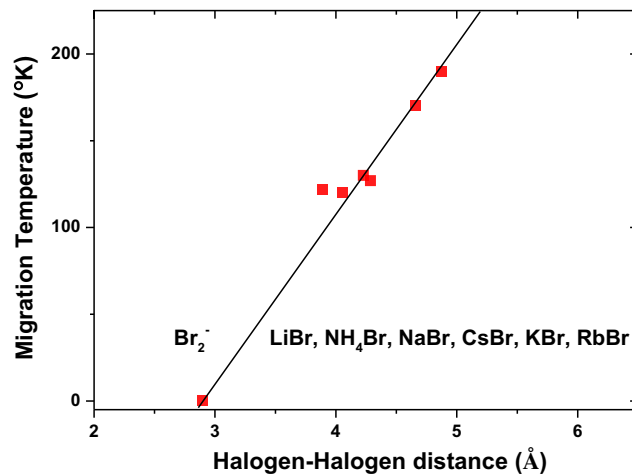


Fig. 4. The same as Fig. 2 for bromides.

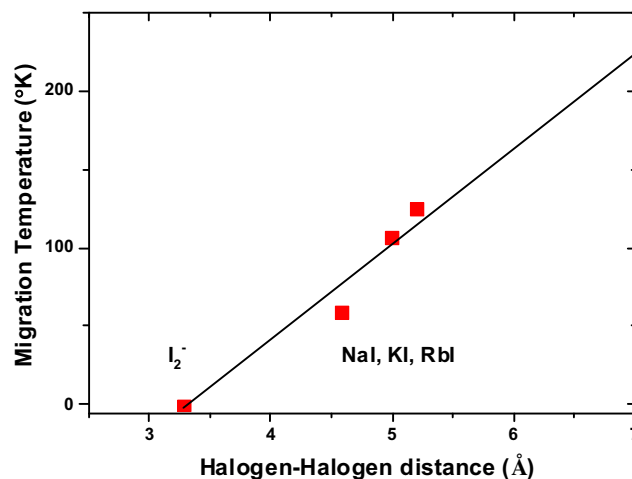


Fig. 5. The same as Fig. 2 for iodides.

In forthcoming paper we plan to discuss the behavior of V_k centers in more details.

3. Conclusions

A simple linear dependence of the migration temperatures of self-trapped holes in several classes of ionic solids was established as a function of the two halogen atom displacement constituting the X_2^- quasi-molecule from the regular lattice sites. As demonstrated in the paper, this correlation allows us to identify the STH and their structural configuration in various cases, including the promising scintillating material SrI_2 .

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