

PII: S0038–1098(98)00035-0

 A SIMPLE ANALYSIS OF THE H_A CENTRE DESTRUCTION TEMPERATURES FOR DOPED ALKALI HALIDES

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(Received 25 August 1997; accepted 26 December 1997 by B. Lundqvist)

A simple relation for the destruction temperatures T_d of the H_A centres (H centres trapped by an impurity cation) as a function of the difference in the radii for a host cation and impurity in alkali halide crystals is presented and theoretically justified. This relation allows to predict T_d for H centres trapped by other monovalent cation impurities.
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The structure and properties of the fundamental halogen defects in the alkali halides are now well established [1–5]. The interstitial halogen atom known as the H center and the interstitial halogen negative ion known as the I centre have been studied in great detail.

At temperatures $T_0 \geq 30$ –60 K the ‘‘jump’’ diffusion of the H centres takes place, thus enabling them to interact with various defects. The recombination of H centres with F and F' centres was studied experimentally more than once (see [1, 6, 7] and references therein), whereas F , H recombination has been theoretically analyzed in [6, 7]. The stabilization of H centres by ‘‘foreign’’ ions of alkali metals with the formation of the so-called H_A centres has been abundantly studied by optical absorption and EPR and reviewed previously [1–5]. In this case, the H centre is stabilised next to the alkali ion which does not become involved to any extent in a molecular bond with the trapped H centre. Indeed, as it was shown by Schoemaker *et al.* [1, 4], H_A centres manifest themselves all as $[ha \log en]_2^-$ molecular ions, just as the basic H centre, but with geometries and properties dependent upon the particular alkali impurity and the host lattice. In fact, four distinct H_A centre structures have been observed in various alkali halides [4]. For example, the structure of $H_A(\text{Li})$ in KCl is quite different from $H_A(\text{Na})$ centre. H_A centres trapped by cation impurities with radius exceeding that of the host

cation were identified in KCl–Rb by Lushchik [8] and in KBr–Rb by Tanimura [9].

A second class of cation impurities which can trap interstitials are s^2 ions. Although their structure has not been studied yet by EPR technique, some luminescence data as well as TSL peaks ascribed to $H_A(s^2)$ centre destruction have been reported for KCl and KBr crystals with monovalent s^2 ions such as In^+ and Ga^+ [10, 11]. It should be mentioned that EPR study has been made for trapped interstitials in KCl doped with divalent s^2 cations– Pb^{2+} and Sn^{2+} [12].

Available literature data on the H_A centre destruction (i.e. the temperature of H centre delocalization from monovalent and s^2 impurities) are plotted in Table 1. As one can see, there exist a clear correlation between impurity cation radius R_{A^+} and the delocalization temperature, T_d : the larger R_{A^+} , the lower T_d . Let us analyse this relation theoretically.

As is well-known, the energy of an elastic interaction of close point defects (H centre with impurity cation in our case) arises due to the overlap of the lattice deformation fields of the two defects. It has the following general form [17, 18]

$$E_{\text{int}}(\mathbf{r}) = -\frac{A\Omega(\theta, \varphi)}{r^3} \Delta V_H \Delta V_A, \quad (1)$$

where ΔV_A is the crystal volume change around the defect $A(=H, A^+)$, r the distance between defects (the nearest-neighbour (NN) distance in our case), A constant dependent on the elastic constants c_{ij} of a material, $\Omega(\theta, \varphi)$ factor describing anisotropy. Assuming that H and A^+ defects are isotropic, $\Omega(\theta, \varphi) = \text{const}$, their elastic

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Table 1. The destruction temperatures for different H_A centres in KCl and KBr

Impurity	Ionic radius \AA	KCl T_d (K)	KBr T_d (K)
Li ⁺	0.68	240 (a)	205 (b)
Ga ⁺	0.81	170 (c)	—
Na ⁺	0.98	120 (a)	100 (d)
In ⁺	1.04	110 (e)	90 (e)
Rb ⁺	1.48	65 (f)	55 (g)
host K ⁺	1.33	T_0 (K)	T_0 (K)
H centre		40–50 (h)	35–45 (i)

(a) Schoemaker, D. and Kolopus, J.L. [13].

(b) Giuliani, G. [14].

(c) Zazubovich, S.G. and Osminin, V.S. [10].

(d) Tanimura, K. and Okada, T. [15].

(e) Ashimova, S. and Usarov, A.S. [11].

(f) Lushchik, Ch.B. and Lushchik, A.Ch. [8].

(g) Tanimura, K. [10].

(h) see discussion in Kotomin, E. *et al.* [6].(i) Akilbekov, A. *et al.* [16].

interaction energy is

$$E_{\text{int}} = \text{const} \cdot \Delta V_{A^+} = \text{const} \cdot 4\pi R_{K^+}^2 \Delta R, \quad (2)$$

where $\Delta R = |R_{K^+} - R_{A^+}|$, R_{K^+} is the K^+ -ionic radius and R_{A^+} impurity cation radius. Destruction of the H_A centre takes place at the temperature T_d when the H centre due to thermal motion is able to make several ($N > 1$) jumps per second outwards the impurity cation. In other words, the jump frequency reads

$$\nu = \nu_0 \exp(-[E_{\text{int}} + E_a]/kT_d) = N, \quad (3)$$

where E_a is the H centre diffusion activation energy in a perfect lattice and ν_0 the frequency (attempt) factor. The typical magnitude of $\nu_0 \approx 10^{13} \text{ s}^{-1}$ is known from the optical dichroism measurement for H centres [2].

The uncertain parameter N could be excluded using the analogous relation for a free H centre diffusion

$$\nu_0 \exp(-E_a/kT_0) = N, \quad (4)$$

where T_0 is the delocalization temperature for a free H centre. Combining equations (3) and (4), one gets easily that

$$\frac{E_a + \text{const} \Delta R}{kT_d} = \frac{E_a}{kT_0}, \quad (5)$$

That is, the delocalization temperature is a linear function of the difference in cation radii:

$$T_d = T_0 + B\Delta R \quad (6)$$

where B is a constant depending on the particular crystal.

In Fig. 1 we have plotted experimental data for KCl and KBr crystals. As one can see, a linear dependence in both cases is valid until $\Delta R \approx 0.5 \text{ \AA}$. Deviation at

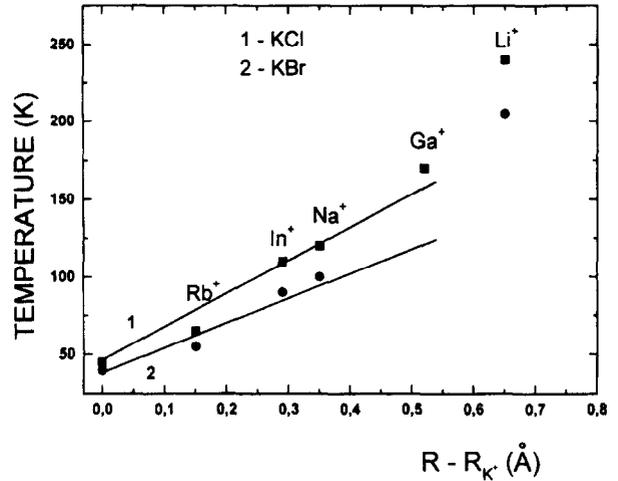


Fig. 1. The destruction temperatures of H_A centres in KCl and KBr as a function of the difference in cation radii (in \AA).

larger ΔR from the linear dependence is caused by the second-neighbour relaxation neglected in our simple estimate.

In conclusion, we have presented in this paper a simple linear relation equation (6) between the H_A centre destruction temperature and the radius of the relevant impurity cation A^+ . Using Fig. 1, one can easily predict the T_d for other cation impurities. In particular, for Cu^+ (0.98 \AA) impurity in KCl and KBr $T_d = 115\text{--}125 \text{ K}$ and $95\text{--}105 \text{ K}$, respectively.

Similar behaviour of alkali and s^2 impurities demonstrated in this paper contradicts the hypothesis [19] that H centres can ionize s^2 ($A^+ = \text{In}^+, \text{Ti}^+$ etc) impurities when approach them. Very likely, this is in fact a two-step process: $H + \alpha \rightarrow V_k$ and then $V_k + A^+ \rightarrow A^{2+}$.

Acknowledgements—Authors are indebted to Prof. Noriaki Itoh for stimulating discussion. This work was partly supported by the Latvian Council for Science (grant #96.0666).

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