Formation Energies of a Vacancy and an Interstitial in Solid Xenon†

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The formation energies of a vacancy and an interstitial in solid xenon were calculated to be 0.164 and 0.582 eV, respectively. The only stable form of interstitial was found to be the split-100 type.

IMPROVEMENTS in the experimental techniques for studying solid rare gases have recently led to increased activity in the determination of defect properties in these materials. The vacancy formation energy, for instance, is now known to within fairly fine limits for krypton.[1] It is therefore appropriate that detailed atomistic calculations of these energies be attempted. Similar calculations for metals have so far produced poor results because the effects of electron redistribution cannot adequately be allowed for. This trouble is not encountered in molecular solids, and for these solids the interactions between atoms are found to be well approximated by sums of two-body interactions.[2] One might hope that this would lead to good agreement between theory and experiment. Reasonably good agreement in the case of the vacancy formation energy was found recently for krypton[3] and for solid argon.[4]

The present calculations involved the central force approximation and the interatomic interactions were represented by a Morse function

$$V(r)=D[e^{-2\alpha(r-r_0)}-2e^{-\alpha(r-r_0)}],$$

where D, α, and r_0 are constants. The constants were determined by the method of Girifalco and Weizer,[5] using the sublimation energy E_s at 0°K (0.166 eV),[6] the compressibility at 0°K (2.8×10^{-11} cm²/dyn),[7] the lattice constant at 0°K (6.131 Å),[8] and the stability criteria derived by Born.[9] The constants were determined as a function of the number of atoms falling within the sphere of influence of a given atom (i.e., as a function of the truncation of the interatomic potential). Table I shows the constants for truncations up to 320 neighbors. The potential parameters remained constant for all larger truncations. For a truncation of 176 neighbors no atoms which make a significant energy contribution are excluded.

The final equilibrium configuration of both the vacancy and the interstitial were determined by an iterative procedure in which each of the 250 atoms in the central region of a model crystal containing 4000 discrete atoms (surrounded by an elastic continuum) were permitted to move independently. For the vacancy the nearest-neighbor atoms were found to relax radially inwards through a distance $0.005d_0$, where d_0 is the nearest-neighbor distance. The vacancy formation volume was found to be 0.95 atomic volumes. The corresponding vacancy formation energy E_F was 0.164 eV. The only stable interstitial to emerge from the calculation was the split-100 configuration, in which the two atoms of the "dumbbell" were separated by a distance $0.86d_0$. This compares with $0.85d_0$ for the corresponding

TABLE I. Constants of the Morse potential as a function of truncation N.

N	D (in eV)	α (Å^{-1})	r_0 (Å)
12	0.027675	1.36174	4.3353
18	0.025494	1.35269	4.3759
42	0.024212	1.34862	4.4085
54	0.024086	1.34859	4.4124
78	0.024026	1.34885	4.4145
86	0.024021	1.34890	4.4147
134	0.024011	1.34909	4.4151
140	0.024011	1.34910	4.4151
176	0.024010	1.34913	4.4151
200	0.024010	1.34914	4.4152
248	0.024010	1.34915	4.4152
320	0.024010	1.34916	4.4152

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distance in solid krypton.[3] The formation energy was found to be 0.582 eV, and the formation volume was 0.89 atomic volumes (compared with 0.75 atomic volumes in krypton).

Because electron redistribution effects are not appreciable in the molecular solids, one would expect the vacancy and sublimation energies to be about equal. The ratio E_F/E_S for these calculations is 0.99. For krypton the ratio was 0.98 by calculation[3] and 0.67 by experiment.[1] Losee and Simmons interpret this discrepancy as being probably due to many-body interactions.

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Luminescence of RbI:Tl†

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Emission spectra of RbI:Tl for excitation in A, B, C, and D absorption bands were measured at 4.2, 77, and 300°K. At 4.2°K, four prominent bands are observed at 3.42, 4.24, 2.82, and 2.58 eV. The 3.42- and 4.24-eV emission bands appear most prominently for A and B excitations. They are thus assigned T_{1u} and $T_{2u} \rightarrow A_{1g}$ transitions, respectively. The 2.82- and 2.58-eV bands appear for both C and D excitations. These are also stimulated with high efficiency in the first exciton region of RbI. Both these bands are attributed to the decay of self-trapped excitons adjacent to thallium ions.

INTRODUCTION

SINGLE crystals of alkali halides doped with thallium halides show absorption bands in regions where crystals are normally transparent. Irradiation in these absorption bands normally labeled A, B, C, and D gives rise to emissions characteristic of the thallium ion. Several workers have studied this luminescence.[1–10] Edgerton and Teegarden[6] made detailed measurements of emission spectra in potassium halides. They gave an energy level scheme based on a model proposed by Seitz[11] for interpreting the absorption spectra and assigned specific electronic transitions to various emission bands. Illingworth[7] studied lifetimes and variation of intensity with temperature of some of the emission bands, and gave a quantitative description of the decay of emission for A-band excitation. He also found that four of the emission bands had lifetimes consistent with the model proposed by Edgerton and Teegarden but the decay of the low-energy emission band did not agree with this model. In the case of KI:Tl the two emission bands at 3.69 and 2.88 eV have been assigned to transitions from the Jahn-Teller split components of the T_{1u} level to the ground level by Trinkler and Plyavin.[8] Their measurements were performed at 80°K for irradiation in A band only. Donahue and Teegarden[10] have studied the emission of thallium in potassium halides with emphasis on A and D excitations and have proposed that the lowest-energy emission band is due to self-trapped excitons perturbed by neighboring thallium ions.

Since the thallium ion which enters the lattice substitutionally gives rise to the emission, it should be similar if the host lattice is changed. Sodium iodide doped with thallium has absorption bands similar to potassium halides,[12] but the emission spectra are slightly different. With this in view, the emission spectra of thallium-doped rubidium halides have been investigated. In this paper the results on RbI:Tl are reported. Excitation spectra of some of the emission bands of thallium ion for energies extending into the fundamental absorption region up to 7.5 eV are presented.

EXPERIMENTAL

Single crystals of RbI:Tl were grown by the Kryropolous method in air. Emission spectra were

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