

Negative activation volumes of defects in solids

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A macroscopic model has been recently proposed which permits the calculation of the formation and activation volumes of defects. It is shown that this model can adequately explain the unusual negative activation volume v^{act} observed recently in *B-4* AgI (and earlier in cerium). Furthermore, it can quantitatively explain the large ($\sim 300\%$) temperature variation of v^{act} from room temperature up to 400°K. The latter justifies an earlier proposal of the authors that the thermal-expansion coefficient of the formation (or activation) volume of a defect can exceed the bulk coefficient by an order (or orders) of magnitude.

The ionic conductivity or the self-diffusion coefficient usually decreases on compression. This decrease implies a positive activation volume v^{act} which, in the case of thermally created defects, is the sum of the formation volume v^f and the corresponding migration volume (whereas in the case of Schottky or Frenkel disorder $v^{\text{act}} = \frac{1}{2}v^f + v^m$).

Allen and Lazarus¹ have recently studied the pressure variation of the ionic conductivity of β -AgI (*B-4* phase).

They found that v^{act} is about $-3 \text{ cm}^3/\text{mole}$ at room temperature but, as the temperature increases, becomes more negative so that at 400°K it is about $-9.5 \text{ cm}^3/\text{mole}$. This result is very unusual in two respects: (a) the value of v^{act} is negative in contrast to the usual behavior of most solids, and (b) it clearly shows that the thermal variation of the activation volume can be quite large even if the host lattice does not show a macroscopic expansion (remember that in the case of *B-4* AgI the thermal-volume-expansion coefficient has a small negative value which, in view of the high-temperature dependence of v^{act} , can be considered to be practically zero). This is a very interesting result because, in the usual theoretical calculations, the thermal-expansion coefficient β^{act} of the volume v^{act} is arbitrarily assumed to be zero or equal to the bulk coefficient β .

Simultaneously with the above experiment a macroscopic model has been proposed² which emphasized the dominant role of anharmonicity in the calculation of formation or activation volumes of defects in solids. This model not only permits the direct calculation of v^{act} from well-known macroscopic properties of the solid, but also indicates that $\beta^{\text{act}} \gg \beta$. The application of this model to the other silver halides (i.e., AgCl and AgBr) (Ref. 3) and to a variety of other solids² led to v^f values that were in excellent agreement with the experimental data. It is therefore of interest to examine here whether this model could explain the unusual

behavior observed in *B-4* AgI.

The activation volume v^{act} is given by the relation

$$v^{\text{act}} = \frac{h^{\text{act}}}{B_0^{\text{SL}}} (dB/dP - 1) \exp\left(\int_0^T \beta dT\right), \quad (1)$$

where h^{act} is the activation enthalpy, B is the isothermal bulk modulus, and B_0^{SL} the bulk modulus of the harmonic crystal, i.e., the intercept of the straight line extension of the linear part $B=f(T)$ with the vertical axis.

The elastic behavior of the *B-4* phase of AgI has been recently studied by Shaw^{4,5} who found that it exhibits an unusual behavior. The room temperature measurements showed that dB/dP has a very small positive value but it becomes distinctly negative when the temperature increases; for 122°C the measurements showed that $dB/dP \approx -2$.

We apply now Eq. (1) at 122°C. By using the values^{1,4-6} $dB/dP = -2$, $h^{\text{act}} = 0.8 \text{ eV}$, $B_0^{\text{SL}} \approx B$ (at room temperature) = 240 kbar, and $\exp(\int_0^T \beta dT) \approx 1$, Eq. (1) gives $v^{\text{act}} = -9.6 \text{ cm}^3/\text{mole}$; this value is in excellent agreement with the experimental value¹ of about $-9.3 \text{ cm}^3/\text{mole}$ if one takes into account the experimental errors in the quantities used.

A similar application of Eq. (1) at room temperature (RT) (where dB/dP is practically zero) immediately gives that v^{act} must be close to $-3 \text{ cm}^3/\text{mole}$. This value is again in excellent agreement with the experimental value of $-3 \text{ cm}^3/\text{mole}$ obtained by Allen and Lazarus.

We see therefore that Eq. (1) gives the correct value of v^{act} for each temperature, i.e., predicts the large temperature variation of v^{act} .

The large temperature variation of v^{act} can be also explained from the same model² in a different way. The expansion coefficient β^{act} of the volume v^{act} is given by

$$\beta^{\text{act}} = \beta + \frac{d/dT (dB/dP)}{(dB/dP) - 1};$$

by using the values $(dB/dP)_{RT} \approx 0$ and $(dB/dP)_{T=122^\circ\text{C}} = -2$ we get

$$\frac{d}{dT} \left(\frac{dB}{dP} \right) \approx -\frac{2}{100} \text{ grad}^{-1}.$$

Therefore the value of β^{act} at 122°C is ($\beta \approx 0$):

$$\beta^{\text{act}} = -\frac{2}{100} / (-3) = 6.7 \times 10^{-3} \text{ grad}^{-1}.$$

This result is in agreement with the value $\beta^{\text{act}} \approx 6.5 \times 10^{-3} \text{ grad}^{-1}$ obtained from Fig. 11 of Allen and Lazarus. We see therefore that the large *positive* value of the expansion coefficient of the *negative* activation volume is adequately explained within the framework of the macroscopic model.

At temperatures higher than $\sim 400^\circ\text{K}$ silver iodide transforms into the *B-23* phase (or α phase, in which it shows superionic behavior). In this phase the activation volume v^{act} has a small positive value. This behavior can be also explained from Eq. (1) if one takes into account that (in this phase): (1) the activation enthalpy is 0.1 eV, i.e., by one order of magnitude smaller than the corresponding value at the *B-4* phase, and (2) according to the measurements of Shaw⁶ the derivative dB/dP is definitely positive ($dB/dP > 1$) with a low but not unreasonable value. On the other hand, in this phase the shear modulus (μ) pressure derivative has a definite negative value⁴; this latter result indicates that when we use in Eq. (1) the derivative $d\mu/dP$ instead of dB/dP then we get a negative activation volume which contradicts the experimental data. The use of μ instead of B has been proposed many times in the past; however, the experiment of Allen and Lazarus in conjunction with the success of Eq. (1) to describe the activation (formation and migration) volumes in a

large variety of solids confirms that B and not μ is the appropriate elastic modulus. This conclusion is further strengthened when one examines the situation in KCl. Lazarus⁷ and later Bartel and Schuele⁸ found that although dB/dP has a positive value (~ 5.34), the derivative dC_{44}/dP is negative. If one uses Eq. (1) as it stands, one actually obtains a large positive formation volume v^f per Schottky defect in close agreement with the experimental value of Yoon and Lazarus⁹; on the other hand the use of dC_{44}/dP (instead of dB/dP) in Eq. (1), leads to a negative v^f value which contradicts again the experimental data.

A last remark should be added. The strange behavior of *B-4* AgI in becoming more compressible with increasing pressure is similar to that observed in fcc cerium^{4, 10} (in cerium the value of dB/dP is around¹⁰ -5). But also in this case the diffusion coefficient rises with pressure¹¹ (thus implying a negative activation volume) in agreement with the predictions of Eq. (1).

The unusual negative activation volume of *B-4* AgI can be adequately explained within the framework of a recent macroscopic model. Furthermore, it explains quantitatively the "strange" fact that v^{act} becomes more negative as the temperature increases. This result strengthens our recent proposal that β^{act} can exceed β by a considerable amount. The negative activation volume observed in fcc cerium is also in accord with the model.

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