J. Phys. C: Solid State Phys., Vol. 6, 1973. Printed in Great Britain. © 1973

The self trapped hole in alkaline earth fluorides: II. Hopping motion

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MS received 25 September 1972

Abstract. The activation energies for the hopping motion of a self trapped hole (V_k centre) have been calculated for CaF_2, SrF_2 and BaF_2. The estimates use the well known small polaron model, together with the microscopic model used successfully for the static properties in the previous paper. The results are in reasonable agreement with observation. Unfortunately, the only data available refer to temperatures so low that simple thermal activation is not expected, and the most serious approximation appears to be the relation of the calculated and observed parameters. In CaF_2 90° jumps are not observed, in contrast to all simple theories. Possible explanations are discussed; chemical bonding between the V_k ions and the nearest axial anions is not adequate, but a modification of the corresponding repulsive interaction has the correct properties. Experiments under uniaxial stress to alter the relative rates of 90° and 180° transitions, or measurements at higher temperatures, could clarify some of the remaining uncertainties.

1. Introduction

The self trapped hole moves through the crystal lattice by a hopping motion which is qualitatively different from the propagative motion of electrons in metals. Its motion can be regarded as a succession of random independent jumps between equivalent sites in the lattice. This view of the V_k centre and its motion corresponds to the 'small polaron' models of Yamashita and Kurosawa (1958) and of Holstein (1959). Appel (1968) has reviewed these approaches. Similar models have been proposed for a variety of hopping processes (eg Flynn 1971). The strong coupling of the hole to the lattice phonons is an essential element in the theory. In the present paper we discuss the V_k motion in alkaline earth fluorides quantitatively in terms of small polaron theory.

Observations of V_k motion in the alkaline earth fluorides have been made by Beaumont *et al* (1970). Two types of jump are possible: those in which the V_k orientation is not altered (180° jump†) and those in which the initial and final configurations are at right angles (90° jump). These are shown in figure 1. In suitable cases the two processes can be distinguished. Thus if the V_k centres are optically aligned, the time dependence of their dichroism comes solely from the 90° jumps. On the other hand, both 90° and 180° jumps contribute to the annealing of the V_k centres, where any motion through the lattice leads ultimately to the appropriate defect sites. We shall be concerned with the relative

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† Beaumont *et al* call these jumps '0° jumps'. We prefer 180°, since the activation energy increases with jump distance in the simplest theories (eg Flynn 1971); with our choice the jump distance also increases monotonically with the angle.

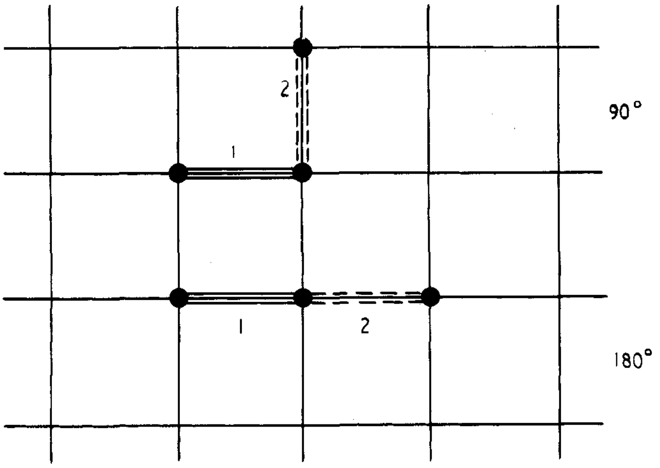

Figure 1. The 100 plane of the F^- sublattice, showing the two distinct V_k jumps.

magnitudes of the activation energies for the two types of jump, as well as with absolute values.

Song (1970, 1971) and Flynn (1971) have given previous estimates of activation energies for V_k motion. These authors concentrated on the alkali halides, where the data of Murray and his colleagues are available (Keller and Murray 1965, 1966, Murray and Keller 1965, Keller *et al* 1967, Popp and Murray 1972). In the alkali halides, four jumps are possible: 60°, 90°, 120° and 180°. We shall be concerned with the alkaline earth fluorides, where the simple cubic anion lattice makes analysis more straightforward. Previous calculations also simplify the calculation of the lattice energies very greatly. Thus Flynn† uses a continuum model with dispersionless longitudinal optic phonons and no elastic contribution to the energy. Song (1970) allowed only the two V_k ions to move, and in his later work (Song 1971) used just the displacements calculated by Jette *et al* (1969) for their inner relaxed region. Our treatment differs from these earlier ones in the improvements made in calculating the lattice energies, the improvements in the interatomic potentials used, and in some aspects of the analysis of the temperature dependence of the hopping rate.

2. Theory of hopping

2.1. Basic assumptions

The jump probability of a small polaron hopping through a lattice can be calculated using the standard approach to nonradiative transitions. Thus the transitions occur between the sensibly-exact eigenstates $|i\rangle$ and $|f\rangle$ in which the V_k centre is located on the initial and final sites i and f respectively. The states $|i\rangle$ and $|f\rangle$ describe both the electronic and vibrational states of the whole system. They are exact eigenstates of a hamiltonian which differs only slightly from the full hamiltonian, and it is this difference which induces the transitions. Since it is the motion of the hole which is of interest, and not the

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† Equation 6 of Flynn (1971) is dimensionally incorrect. The correct form is given on p 365 of Flynn (1972).

occupancies of the various lattice modes, the transition probabilities $w(\mathrm{i} \rightarrow \mathrm{f})$ must be thermally averaged over the initial lattice states and summed over final lattice states. Thus the desired hopping rate is

$$W_{\mathrm{if}} = \sum_{\substack{\mathrm{f} \\ \text{lattice} \\ \text{states}}} \langle w(\mathrm{i} \rightarrow \mathrm{f}) \rangle_{\substack{\mathrm{i} \\ \text{lattice} \\ \text{states}}}. \tag{2.1}$$

The expressions are simplified by a number of assumptions. The first is the Born–Oppenheimer approximation, used to separate the electronic and nuclear motion. This means that there is a unique potential energy for each configuration of the nuclei. The second is the Condon approximation, namely that the electronic matrix element $J_{\mathrm{if}}(\boldsymbol{R})$ for the transition is independent of the lattice configuration given by $\boldsymbol{R}$. It is very difficult to improve on this assumption, except in special circumstances (eg Flynn and Stoneham 1970). These two approximations factorize the transition probability. If the lattice states are $\Phi_{\mathrm{i}\alpha}$ when the hole is at site i, then

$$w_{\alpha\beta}(\mathrm{i} \rightarrow \mathrm{f}) = \frac{2\pi}{\hbar^2} |J_{\mathrm{if}}|^2 \left| \int \mathrm{d}^{3n}\boldsymbol{R}\, \Phi^*_{\mathrm{i}\alpha}(\boldsymbol{R}) \Phi_{\mathrm{f}\beta}(\boldsymbol{R}) \right|^2 D(E_{\alpha\beta}) \tag{2.2}$$

where the factor $D(E_{\alpha\beta})$ is present to ensure energy conservation. The importance of the self trapping distortion becomes clear here. The lattice overlap depends on the phonon mode occupancies specified by α and β, but has also a strong dependence on the *difference* in the self trapping distortions for $\mathrm{V_k}$ sites i and f.

Two other simplifications are also customary. The first is the harmonic approximation, and the second is that we need only consider linear hole–lattice coupling. The distortions near a $\mathrm{V_k}$ centre are large, and we shall later discuss corrections to these two approximations. However, we first consider the simpler results appropriate at high temperatures (to be defined in detail in § 2.3) if all the approximations are valid. The main result is that, in this limit, the hopping is given by:

$$W_{\mathrm{if}} = \left(\frac{\pi}{4\hbar^2 E_{\mathrm{a}} kT} \right)^{1/2} |J_{\mathrm{if}}|^2 \exp(-E_{\mathrm{a}}/kT). \tag{2.3}$$

We now consider the evaluation of E_{a} and the hopping rate at the lower temperatures relevant here.

2.2. *Expressions for E_{a}*

The activation energies observed are related to E_{a}, but not equal to it because the experiments are done at low temperatures where this expression does not hold. However, E_{a} is the important parameter calculated in § 3. It is a lattice activation energy. Thus if the lattice modes have effective masses M_α and frequencies ω_α, then

$$E_{\mathrm{a}} = \tfrac{1}{2} \sum_{\alpha} M_\alpha \omega_\alpha^2 |\tfrac{1}{2}\Delta Q_\alpha|^2 \tag{2.4}$$

where ΔQ_α is the change in the mean (self trapping) displacement of mode α during the jump.

This energy can be expressed in a better form for calculation by rewriting it as a relaxation energy. For a perfect distorted harmonic lattice, the energy can be written as a constant term plus $\frac{1}{2}\boldsymbol{Q} \cdot \mathbf{A} \cdot \boldsymbol{Q}$, where $\mathbf{A}$ is the force constant matrix. Linear hole–lattice coupling gives an extra term $-\boldsymbol{F}_{\mathrm{i}} \cdot \boldsymbol{Q}$ for the hole on site i. The static equilibrium configuration has distortions Q_i given by:

$$Q_i = \mathbf{A}^{-1} \cdot \boldsymbol{F}_i \tag{2.5}$$

and a relaxation energy

$$E_i = -\tfrac{1}{2}\boldsymbol{F}_i \cdot \mathbf{A}^{-1} \cdot \boldsymbol{F}_i. \tag{2.6}$$

The change in displacement which appears in E_a is just

$$\Delta Q = Q_f - Q_i = \mathbf{A}^{-1} \cdot (\boldsymbol{F}_f - \boldsymbol{F}_i). \tag{2.7}$$

Two expressions can now be written down for E_a. They are equivalent only for a harmonic lattice with linear coupling. One is expressed in terms of the relaxation energy under half the difference in forces from the V_k centre on the initial and final sites:

$$E_a = \tfrac{1}{2}\{\tfrac{1}{2}(\bar{\boldsymbol{F}}_i - \boldsymbol{F}_f)\} \cdot \mathbf{A}^{-1} \cdot \{\tfrac{1}{2}(\boldsymbol{F}_i - \boldsymbol{F}_f)\}. \tag{2.8}$$

The second form resembles the more usual activation energy expressions, since it is the difference between the relaxation energy in the initial configuration and the relaxation energy under the average of the initial and final forces:

$$E_a = \tfrac{1}{2}\bar{\boldsymbol{F}} \cdot \mathbf{A}^{-1} \cdot \bar{\boldsymbol{F}} - \tfrac{1}{2}\boldsymbol{F}_i \cdot \mathbf{A}^{-1} \cdot \boldsymbol{F}_i \tag{2.9}$$

where $\bar{\boldsymbol{F}}$ is $\frac{1}{2}(\boldsymbol{F}_i + \boldsymbol{F}_f)$. When it becomes hard to justify the linear coupling and harmonic approximations, we have preferred to use this second expression just because of its resemblance to commoner ways of writing activation energies.

2.3. Temperature dependence of the hopping

The expression (2.3) for W_{if} is only valid asymptotically at high temperatures. We need to know the range of validity of (2.3), and also we need to estimate an 'effective activation energy', U. The observed temperature dependence of the hopping rate is always fitted to an expression

$$W_{obs} = W_0 \exp(-U_{obs}/kT). \tag{2.10}$$

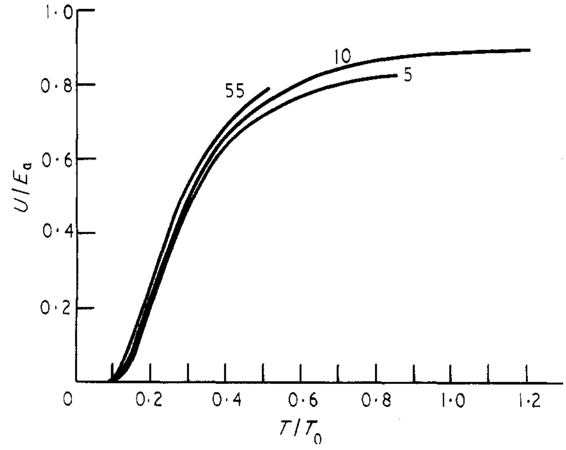

Figure 2. The ratio of the apparent activation energy, U, to the calculated hopping energy, E_a, as a function of temperature according to (2.12). Here kT_0 is equal to $\hbar\omega$, the phonon energy, and $E_a/\hbar\omega$ is marked on each curve.

Our effective activation energy is defined by fitting the predicted W_{if} to this form at any appropriate temperature using:

$$U = kT^2 \frac{\mathrm{d}}{\mathrm{d}T} \ln \{W_{\mathrm{if}}(T)\}. \tag{2.11}$$

Note that the slight temperature dependence of the pre-exponential factor in (2.3) means that U is always less than E_{a}.

The simplest prediction of the temperature dependence is that of Yamashita and Kurosawa†, which Song used in his analysis. It assumes coupling to phonons of one frequency, ω, alone. If we write $y \equiv \hbar\omega/2kT$ and $X \equiv 4E_{\mathrm{a}}/\hbar\omega$, then

$$U = E_{\mathrm{a}}\, 2\, \mathrm{cosech}^2(y) \left(\frac{I_1(X\, \mathrm{cosech}\, y)}{I_0(X\, \mathrm{cosech}\, y)} \cosh y - 1 \right) \tag{2.12}$$

where I_0 and I_1 are modified Bessel functions. The dependence of U/E_{a} on X is rather slight in the ranges of interest, and is shown in figure 2. Most of the experiments on fluorites have been done at lower temperatures, where U is sensitive to y. We shall usually use (2.12) to relate our data to experiment, although more appropriate expressions are available with extra effort.

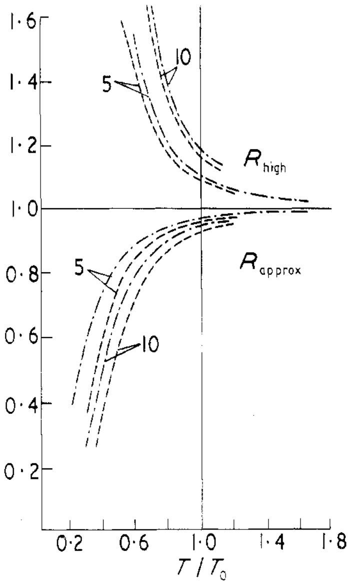

Figure 3. Ratios of the 'true' rate to the high temperature asymptote (2.3) and to the approximation corresponding to (2.12), R_{high} and R_{approx} respectively. The 'true' rate assumes uniform coupling to a band of phonons from energy $(1 - L)\hbar\omega$ to $\hbar\omega$. As in figure 2, $T_0 \equiv \hbar\omega/k$ and $E_{\mathrm{a}}/\hbar\omega$ is shown. Note the scales are *not* logarithmic. – – – – $L = 0{\cdot}5$; –·–·–· $L = 0{\cdot}7$.

An example of a more general treatment is one which allows coupling to a range of frequencies, with the coupling and phonon density of states chosen to be constant in this range. Numerical integration is necessary, and the methods developed by Stoneham (1972) for a related diffusion problem were used. In figure 3 we see the effects of varying

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† As Holstein observes, this result is derived incorrectly in the original paper; a term is omitted and a divergent infinite integral replaced arbitrarily by a finite one. However, the correct result is achieved.

the width of the band of phonons and of varying X. It is clear that the asymptotic form (2.3) holds to temperatures below $\hbar\omega_{\mathrm{max}}/k$, but that there are deviations in the regimes where experiments are carried out.

There is a problem in deciding which frequency or range of frequencies should be used in these calculations. It is an important problem, for E_a may be three times larger than U. We have usually taken the longitudinal optic frequency, although results will be given for other choices later. In all cases we find that if $E_a(180°)$ is larger than $E_a(90°)$, then $U(180°)$ exceeds $U(90°)$; relative sizes are not changed.

3. Calculation of E_a

We have calculated E_a using equation (2.9), but going beyond the harmonic approximation. Thus the second term is just the V_k centre defect energy calculated in the previous paper. In the same way, we estimate the first term by minimizing the explicit potential energy of the hydrid defect configuration formed by averaging the initial and final defect states.

The preceding paper on the single V_k centre describes the method of such calculations. We have also described the potentials used for the lattice and the F_2^- molecule. In that paper, we gave results calculated with three potentials which differ only in the interaction of the lattice and defect.

The first two models (I and II*a*) were designed to show that the polarization of the V_k centre by lattice electric fields has no significant effect on the calculated results. We have used both models to calculate the energy of the hybrid 'transition state' corresponding to 90° and 180° jumps. The results collected in table 1 show that the two models make similar predictions as to the value of E_a.

Table 1. Energies of transition states and activation energies E_a (in eV)

90° transition	Energy of transition state			Activation energy, E_a		
	Model I	Model II*a*	Model II *b*	Model I	Model II*a*	Model II*b*
CaF	6·09	6·06	5·93	1·05	1·07 (Flynn 0·63)	1·04
SrF_2	5·89	5·85	5·79	1·14	1·15 (Flynn 0·58)	1·14
BaF_2	5·57	5·52	5·51	1·22	1·26 (Flynn 0·57)	1·26

180° transition	Energy of transition state			Activation energy, E_a		
	Model I	Model II*a*	Model II*b*	Model I	Model II*a*	Model II*b*
CaF_2	6·27	6·27	5·39	1·23	1·28 (Flynn 1·26)	0·5
SrF_2	6·11	6·11	5·40	1·36	1·41 (Flynn 1·16)	0·75
BaF_2	5·88	5·87	5·24	1·53	1·61 (Flynn 1·13)	0·99

Unfortunately, the 90° jump has a lower value of E_a than the 180° jump for all three substances. This contradicts the experimental observation that 180° jumps are observed in CaF_2 at low temperatures before 90° motion begins. This observation led us to consider a third model (II*b*) which was mentioned briefly in the previous paper.

According to equations (2.6) and (2.7), E_a depends on the product of the displacements of ions during the transition with the difference in forces due to the initial and final defect configurations. The ions that undergo the largest displacement are the fluoride ions where the hole is localized in either the initial or final configurations. The energy E_a is thus very sensitive to the form of the potential of the F_2^- molecule but equally to the interaction of the molecule with the lattice fluoride ion to which the hole moves during the diffusion process. More especially, the relative energies of 90° and 180° jumps are sensitive to any difference in the interaction of the F_2^- molecule with neighbouring F^- ions along the defect axis and at right angles to it. It is possible to account for the lower activation energy for 180° jumps only if there is some attraction between the molecule and the nearest fluoride ions along the defect axis, or equally, if there is a reduced overlap repulsion.

One obvious possibility is chemical binding of the V_k ions with the neighbouring axial fluorines. This would have the correct trend with crystal, since the binding should be largest for smaller lattice parameters. However, this explanation must be ruled out. The spin resonance data suggest that the amplitude of the hole wavefunction on these neighbours is so small that enhanced binding is probably negligible. This has been confirmed by a series of semi-empirical molecular orbital calculations using the CNDO approximation, which show that there is no significant extra binding.

The alternative possibility is that the bonding of the molecule contracts the charge clouds of the V_k ions more along the defect axis than perpendicular to it. This need not to be a large effect in terms of a reduction in ionic radius to have a significant effect on the calculated difference in E_a for 90° and 180° jumps. We include this effect in model II*b* in which the axial interaction between the ions of the F_2^- molecule and the nearest lattice F^- ion is reduced arbitrarily by a half. This corresponds to a reduction of only ~10% in the ionic radius. This anisotropy in the overlap interaction then gives the desired result that the 180° jumps have lower values of E_a. As expected, the effect is much greater for CaF_2 than SrF_2 and BaF_2.

4. Discussion

We now compare our various calculations with each other and with experiment. The predictions will be related to experiment using (2.12), so that the effects of different choices of $\hbar\omega$ must be assessed. Various values of $\hbar\omega$ have been tried in the range of optic phonon energies.

The predicted energies E_a are insensitive to the differences in model, with the special exception of model II*b* results for 180° jumps. In other cases, the largest differences are about 5%. Three trends are apparent. First, the values of E_a are all appreciably larger than the effective activation energies observed. Second, the E_a increase along the sequence CaF_2, SrF_2, BaF_2. This is not trivial, since there are no simple trends in the separation of the two V_k ions. Third, the 180° jumps have higher activation energies than the 90° jumps for both models I and II*a*. The ratios $E_a(180°)/E_a(90°)$are 1·18(CaF_2), 1·21(SrF_2) and 1·27(BaF_2). All are considerably less than in Flynn's simple model, which gives a ratio of 2 in all cases. However, there is conflict with experiment, and it was for this reason that model II*b* was proposed. This shows that the modification of the repulsive forces can reduce $E_a(180°)$ substantially, without any comparable change in $E_a(90°)$. Further, the reduction decreases rapidly along the sequence CaF_2, SrF_2, BaF_2.

Values of U derived from E_a using (2.12) are given in table 2. Two choices of ω have been used: the transverse and longitudinal optic frequencies. In principle, the lattice relaxation program contains information sufficient to work out $\hbar\omega$, at least in the harmonic approximation. In practice, this is too difficult to extract. The comparison of predicted values U with observed activation energies suggests that the best single frequency to use is close to the longitudinal optic frequency, ω_{LO}.

Table 2. Effective activation energies

System	Observed value (eV)	Predicted values (eV)† 90° Model II*a*	180° Model II*a*	180° Model II*b*
CaF_2 (90 K)	0·19	0·08	0·09	0·03
[180° jump]		0·25	0·30	0·11
CaF_2 (120 K)	0·31	0·21	0·25	0·09
[180° jump]		0·43	0·53	0·20
SrF_2 (110 K)	0·21	0·43	0·54	0·28
[180° jump]		0·63	0·78	0·41
SrF_2 (120 K)	0·30	0·50	0·61	0·32
[90°, 180°?]		0·69	0·85	0·45
BaF_2 (95 K)	0·30	0·50	0·64	0·39
[90°, 180°?]		0·77	0·99	0·61
BaF_2 (115 K)	0·38	0·65	0·84	0·51
[90°, 180°?]		0·89	1·15	0·70

† The lower figure uses the transverse optical frequency, the upper the longitudinal optic frequency, in conversion from E_a to U.

Agreement of predicted and observed activation energies is satisfactory. In fact, the agreement is better than the table suggests, since the discrepancies are greatly enhanced by the very nonlinear form of (2.12). This can be seen by using (2.12) in reverse to derive an 'experimental' E_a. The ratio of the experimental to the theoretical value for the 90° BaF_2 jumps proves to be 0·92 ± 0·06, using $\omega = \omega_{LO}$; the errors quoted here are experimental. A very modest change in parameters can remove the inconsistency. One of the problems of the fluorite system is that the experiments have been performed at temperatures where the relation of U and E_a is the weakest link in the calculation. It is for this reason that we do not quote values of the hopping integrals J; their variation with small changes in model is so large as to make them meaningless.

The trend from crystal to crystal appears to be correctly given. Thus the activation energies get higher along the sequence CaF_2, SrF_2, BaF_2, and the 90° jump becomes progressively more favoured in comparison with the 180° jump. Both these features show improvements over Flynn's attractive and very simple treatment, where a slight opposite trend in activation energies along the sequence is indicated.

5. Conclusions

We have seen that the small polaron model gives a reasonable general picture of the hopping motion of V_k centres in the alkaline earth fluorides. There are two cases where experiments would help our understanding of the theory. First, it would be useful to have results at higher temperatures. In analysing the data available, we have found the major inaccuracy lies in relating U to E_a; at higher temperatures the relation is much less sensitive to the parameters we use. Further, the hopping integral J can be most easily derived from high temperature data. It is also our lack of such data which has prevented us from deciding if the anharmonicity and nonlinear hole–lattice coupling have significant effects (cf § 2). A second experiment would be to attempt to detect 90° jumps in CaF_2 by observing motion under uniaxial stress. If the relative magnitudes of the 90° and 180° jump activation energies could be sorted out, it would be possible to say more about the mechanisms which favour 180° jumps in this special case.

Acknowledgments

The authors wish to thank Dr M Hayns for his assistance with the CNDO calculations.

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