Isotope Effects in Close-Packed Metals and in Alkali Halides *

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An expression was obtained earlier by the authors, on the basis of Vineyard's rate theory, for the sharing of the kinetic energy of a diffusing isotope at the saddlepoint with other host atoms. The theory is expressed in terms of the (imaginary) frequency of the localised vibration in which the diffusing atom at the saddlepoint is coupled to its neighbours.

Numerical results are presented for the case of a Cu isotope diffusing by the vacancy mechanism in a pure Cu lattice. The pair potential determined by Englert, Tompé and Bullough, which fits the phonon spectra and the stacking fault energy, has been employed in the calculation.

The effects of coupling between the diffusing atom and its immediate neighbours are very small with this potential. The main coupling is found to be to the eight third-nearest neighbours. Treating the vibrations of these nine atoms, a sharing of kinetic energy is found, which is in quantitative agreement with the experimentally observed isotope effect, assuming a vacancy mechanism for self-diffusion. This situation for Cu is in marked contrast to Na, where it was shown in earlier work that the present theory could not explain the observed mass effect, assuming a vacancy mechanism for diffusion.

The diffusion of Cs in the CsCl lattice is also discussed using the same theory. Following our earlier work on NaCl, the localized normal mode considered is that in which the Cs isotope at the saddlepoint is at the centre of a square with four Cl near-neighbour ions at the vertices. A formula for the sharing of kinetic energy is derived, and it is pointed out that, as for NaCl, the force constants can be obtained from the classical approach of Mott and Littleton. An argument is proposed which suggests that, as with NaCl, the sharing of kinetic energy will be small. No experimental data appear as yet to be avaialable for the CsCl structure.

1. Introduction

In previous work, the present authors (BROWN et al. [1,2]) have shown how the rate theory of VINEYARD [3] can be used to discuss the sharing of kinetic energy which occurs between the diffusing atom at its saddlepoint and its near-neighbours.

Essentially, this sharing of kinetic energy is given by the diffusion coefficients D_1 and D_2 for isotopes of mass M_1 and M_2 diffusing in the crystal, according to

$$[D_2/D_1 - 1]/[\sqrt{M_1/M_2} - 1] = f\,g \qquad (1.1)$$

where f is the usual correlation factor and g represents the sharing of kinetic energy referred to above.

In the present paper, we shall briefly report the results of calculations we have carried out on

(i) Cu metal,
(ii) Alkali halides with the CsCl structure.

These calculations complement our earlier work [1,2] on Na metal and NaCl.

2. Localised Vibration in Cu with Diffusing Atom at its Saddlepoint

It is universally accepted that in Cu self-diffusion occurs via vacancies. The problem then is to evaluate the theory we gave earlier, which expresses g in terms of the frequency ν of the normal mode in which the diffusing atom at its saddlepoint is coupled to surrounding atoms. The result for g is

$$g = -\frac{\delta\nu^2}{\nu^2}\,\frac{M}{\delta M} \qquad (2.1)$$

where the difference δM in the masses of the isotopes is assumed small. Hence we must determine $\delta\nu^2/\delta M$, from a dynamical treatment of the localised mode.

Two problems immediately arise. It is first ne-

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[1] R. C. BROWN, J. WORSTER, N. H. MARCH, R. C. PERRIN, and R. BULLOUGH, 1970, Proceedings of the Thomas Graham Memorial Symposium, University of Strathclyde, 22nd—24th September 1969.

[2] R. C. BROWN, J. WORSTER, N. H. MARCH, R. C. PERRIN, and R. BULLOUGH, 1971, Phil. Mag. (in the press).

[3] G. H. VINEYARD, J. Phys. Chem. Solids **3**, 121 [1957].

cessary to choose a potential, from which the force constants required to calculate the normal mode can be determined, and it is then necessary to decide, with this form of potential, which atoms to regard as involved in the normal mode. Clearly it is impractical to include more than a very limited number of atoms.

The potential we shall use is that of ENGLERT, TOMPÉ and BULLOUGH[4] which has been constructed so that

(i) It fits the phonon spectrum.
(ii) The stacking fault energy is correctly given.
(iii) The vacancy formation energy is in agreement with experiment.

We shall say a little more about this potential which is shown in Fig. 1 below. We made preliminary calculations with this potential, and concluded that the immediate neighbours to the diffusing atom at its saddlepoint, because of the nature of the pair potential, are only coupled rather weakly to it.

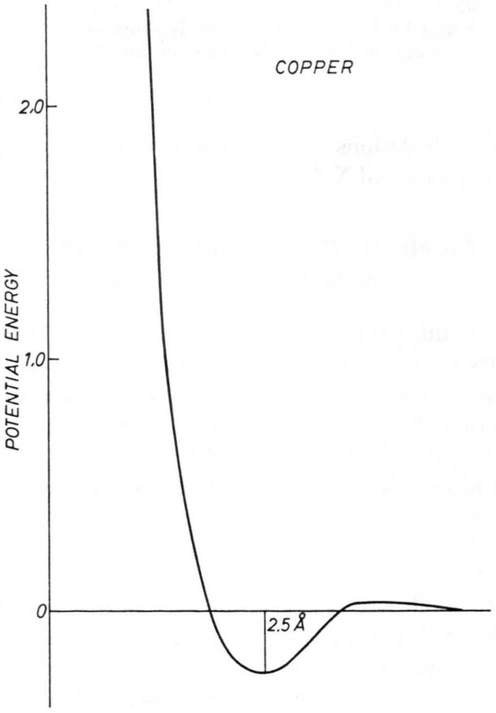

Fig. 1. The pair potential for copper constructed by ENGLERT, TOMPÉ, and BULLOUGH[4].

Because it is not practicable, as yet, to include coupling simultaneously to the first 3 sets of neighbours, the results we present are obtained from a model in which we assume, following the above preliminary calculations, that the diffusing atom is coupled only to its eight, third nearest neighbours. These eight atoms lie on the vertices of a rectangular block. The symmetry is sufficiently low for three independent displacements y, z and w, of the eight atoms, to be required in the analysis of the normal mode, as shown in Figure 2.

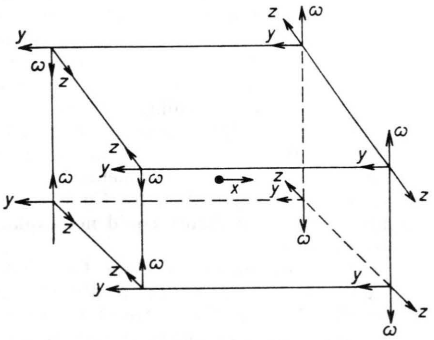

Fig. 2. The independent displacements associated with the third neighbour normal mode at the saddle point in the face centred cubic lattice.

The equations of motion are then readily shown to take the form:

$$\begin{aligned} M_1 \ddot{x} &= a x + c y + d z + e w \\ 8 M_2 \ddot{y} &= c x - b y + f z + g w \\ 8 M_2 \ddot{z} &= d x + f y - h z + k w \\ 8 M_2 \ddot{w} &= e x + g y + k z - p w \end{aligned} \tag{2.2}$$

where M_1 is the mass of the isotope at the saddlepoint, and M_2 the mass of the lattice atoms. The force constants a, c, d, etc. will eventually be calculated from the pair potential of Figure 1.

The determinant from which the frequency of the localised normal mode is to be found is given by

$$\begin{bmatrix} a - M_1 \nu^2 & c & d & e \\ c & -(b + 8 M_2 \nu^2) & f & g \\ d & f & -(h + 8 M_2 \nu^2) & k \\ e & g & k & -(p + 8 M_2 \nu^2) \end{bmatrix} = 0 . \tag{2.3}$$

This yields a quartic in ν^2, which is explicitly

$$\begin{aligned} & A M_1 M_2^3 \nu^8 + (B M_1 M_2^2 + C M_2^3) \nu^6 \\ & + (D M_1 M_2 + E M_2^2) \nu^4 + (F M_1 + G M_2) \nu^2 + H = 0, \end{aligned} \tag{2.4}$$

where A, B, etc. are expressions involving simply the force constants a, c, etc.

This equation can now be solved for ν^2 using Newton's method. The equation is differentiated

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[4] A. ENGLERT, H. TOMPÉ, and R. BULLOUGH, 1970, Proceedings of Conference on Fundamental Aspects of Dislocation Theory, April 21st—25th, 1969, Washington, N.B.S.

with M_1 as an implicit function of ν^2 and the resultant value of g is given by

$$g=\frac{A\,\nu^6+B\,\nu^4+D\,\nu^2+F}{4\,A\,\nu^6+3\,(B+C)\,\nu^4+2\,(D+E)\,\nu^2+F+G}\,. \qquad (2.5)$$

In (2.5), ν^2 is now to be inserted for $M_1=M_2$, in view of Eq. (2.1).

The rest of the calculation is now standard and we need only report the results. Calculating the force constants a, c, etc. from the pair potential of Fig. 1, the constants A, B, etc. in (2.4) were evaluated numerically. The value found for g was 0.92, to be compared with the result 0.89 found experimentally by ROTHMAN and PETERSON (see this Conference).

We conclude then that there is semi-quantitative agreement between theory and experiment, and, provided we accept that refinements of the pair potential used here, and the inclusion of more atoms in the normal mode (which will lower the calculated value of g) will eventually be necessary, there is no basic difficulty in reconciling the measured isotope effect with the rate theory based on a vacancy mechanism.

This is quite different from the situation we found earlier for Na, where it was impossible to understand the measured isotope effect from the rate theory with a vacancy mechanism.

3. Isotope Effect in Alkali Halides

For the case of Na isotopes diffusing in the Na sublattice of NaCl, the localised vibration can be represented by a much simpler model than that described above for Cu. The Na ion is, in the simplest model, coupled to its two near neighbour Cl ions, and we have a problem analogous to the vibrations of a linear triatomic molecule (see, for example, HERZBERG[5]).

When this is solved for the frequency of the localised mode, and this is inserted in (2.1), we obtain (BROWN et al.[2])

$$g=\left[1+\left(1+\frac{8\,m\,M\,c^2}{\{2\,M\,a+m\,b\}^2}\right)^{-1/2}\right] \qquad (3.1)$$

where m and M are the masses of the positive and negative ions respectively, a and b are the "restoring force" constants and c represents the coupling between Na and Cl ions. Since this has been discussed in some detail elsewhere, we shall describe a calculation for CsCl, where we obtain a result analogous to (3.1).

We (BROWN et al.[2]) have calculated the force constants a, b and c in (3.1) by means of the classical approach of MOTT and LITTLETON[6]. The results show that the force constant c is very small due to a striking cancellation between Born-Mayer repulsive terms and electrostatic terms. The Born-Mayer contribution to the force constant is in fact more than ten times as large as the resultant value of c.

It is the force constant c which describes the coupling between the Na and Cl ions, and with $c=0$ in (3.1) we see that the Einstein result $g=1$ is regained. With the results found from the Mott-Littleton approach, we obtain

$$c/a=0.23\,,\qquad c/b=0.031 \qquad (3.2)$$

and hence from (3.1), $g=0.998$. Thus we find a very small isotope effect, which seems in general accord with experiment. In principle, from (3.1), we could have $1 \leqq g \leqq \tfrac{1}{2}$.

For the case of CsCl, the localised normal mode, in its simplest form, is one in which the Cs isotope at its saddlepoint is at the centre of a square, four Cl near-neighbour ions being at the vertices. There are again two independent displacements, x for Cs and y for the Cl ions. The equations of motion are then simply

$$M_1\,\ddot{x}=a\,x-c\,y\,,\quad 4\,M_2\,\ddot{y}=c\,x+b\,y\,. \qquad (3.3)$$

The solution for the normal mode frequency is straightforward, the result being

$$g=\left\{1+\left(1+\frac{16\,M_1\,M_2\,c^2}{(4\,M_2\,a+M_1\,b)^2}\right)^{-1/2}\right\}. \qquad (3.4)$$

Once again, the bounds of g are seen to be given by $\tfrac{1}{2} \leqq g \leqq 1$, the upper bound of course corresponding again to an Einstein model of independent vibrations.

When experiments become available on alkali halides, it will be a straightforward matter to apply the method we used for calculating the force constants for NaCl, based on the approach of Mott and Littleton, to the CsCl structure. In the absence of experimental data, we have not, at this stage, proceeded to numerical evaluation of the force constants in this case.

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[5] G. HERZBERG, Infrared and Raman Spectra of Polyatomic Molecules, Van Nostrand, New York 1945.

[6] N. F. MOTT and M. J. LITTLETON, Trans. Faraday Soc. **34**, 485 [1938].

4. Conclusion

For Cu metal, a model for the localised normal mode has been set up, and the appropriate force constants calculated from the pair potential of Englert et al. The calculated factor g representing the sharing of kinetic energy between the diffusing atom and, in our model, its third nearest neighbours is found to be $g = 0.92$, which is clearly an upper bound for our chosen pair potential. This is in semi-quantitative agreement with the measured value of 0.89, which assumes a vacancy mechanism.

There is therefore no basic difficulty in reconciling the measured isotope effect in Cu with the rate theory based on a vacancy mechanism. This is in marked contrast with Na, where the measured isotope effect cannot be interpreted in terms of diffusion via vacant sites.

Finally, an expression is obtained for g for the CsCl structure, for Cs ions diffusing by a vacancy mechanism in the Cs sub-lattice. Numerical evaluation of g is now a routine matter, once measurements begin to appear on alkali halides with this structure.