

and 1.22, respectively. When these values are compared with 9.17 and 1.5 for vanadium<sup>5</sup> and tin,<sup>6</sup> and 7.6 and 1.32 for aluminum,<sup>3</sup> all at the same reduced temperatures, it is evident that the law of corresponding states of the Bardeen, Cooper, and Schrieffer theory is not obeyed. The values of  $a$  and  $b$  predicted by the theory are 8.6 and 1.44.<sup>7</sup>

The lowest-temperature points must be interpreted with some caution because of the uncertainty in the temperature scale, but the deviations from Eq. (3) are outside the estimated experimental error. Any error in the thermometer calibration will change the normal and superconducting state heat capacities by the same factor, and while the lowest temperature normal state points are 5% higher than expected, the corresponding superconducting state points are greater than  $5.8\gamma T_c \exp(-1.22T_c/T)$  by 85%. A recalculation of the superconducting-state points using  $\Delta = 0.028^\circ$  as discussed above for the normal state does not appreciably alter their fit to an exponential.

The difference in heat capacity between the normal and superconducting states has been integrated to obtain the critical field  $H_C$  as a function of temperature. The value of  $H_0$ , the critical field at absolute zero, is 51.8 gauss, in good agreement with the value 52.5 gauss obtained by an extrapolation of direct magnetic measurements.<sup>8</sup> At  $T_c/2$  the critical field is about 5% less than that calculated from the parabolic temperature dependence.

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## CORRELATION CORRECTION TO THE ACTIVATION ENERGY FOR DIFFUSION IN CRYSTALLINE SOLIDS

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Experimentally, many investigators have found that for tracer diffusion in homogeneous single crystals, the variation of the diffusion coefficient with temperature may be represented by a simple Arrhenius equation,

$$D = D_0 \exp(-Q/RT), \quad (1)$$

where  $D$  is the diffusion coefficient,  $D_0$  and  $Q$  are experimentally determined constants,  $R$  is the gas constant, and  $T$  is the absolute temperature. The form of Eq. (1) is consistent with the concept of an elementary diffusion jump process, with the jump frequency,  $\nu$ , satisfying the equation

$$\nu = C \exp(-H/RT), \quad (2)$$

where  $H$  is an activation energy and  $C$  is a constant.

In the comparison of theory and experiment,  $Q$  has often been assumed to be equal to  $H$ , the relation between the diffusion coefficient and the jump frequency being taken as

$$D = \gamma a^2 \nu, \quad (3)$$

where  $a$  is the jump distance and  $\gamma$  is a constant depending on geometry. Actually, there should be an additional factor  $f$ , called the correlation factor,<sup>1-4</sup> on the right-hand side of Eq. (3).

This factor is equal to unity only if the directions of successive jumps are not related. If the correlation factor is a function of temperature,  $Q$  will no longer equal  $H$ , but instead,

$$Q = H - R [d \ln f / d(1/T)]. \quad (4)$$

The additional term in Eq. (4) may be quite important. To demonstrate this, the correction required for diffusion of Cd, In, Sn, and Sb in pure silver has been calculated.

Lidiard and LeClaire<sup>2,3</sup> have shown that for diffusion of an impurity  $B$  by a vacancy mechanism in a fcc lattice of  $A$  atoms,

$$f \cong \frac{2w_1 + 7k_1}{2w_2 + 2w_1 + 7k_1}, \quad (5)$$

where  $w_2$ ,  $w_1$ , and  $k_1$  are the probabilities per

second that a vacancy that is a nearest neighbor of a  $B$  atom will exchange with the  $B$  atom, with any particular one of the four  $A$  atoms that are nearest neighbors of both  $B$  and the vacancy, and with any particular one of the other seven atoms adjacent to the vacancy, respectively.

Because of the electrostatic and elastic effects from the presence of the impurity  $B$ , neither  $w_1$  nor  $w_2$  will equal  $w_0$ , the value in an environment of pure  $A$ . Thus,

$$w_1 = w_0 \exp(\Delta E_m/RT), \quad (6)$$

and

$$w_2 = w_0 S \exp(\Delta Q_m/RT), \quad (7)$$

where  $\Delta E_m$  is the difference between the energy for motion for a  $w_0$ -jump and that for a  $w_1$ -jump,  $\Delta Q_m$  is the corresponding difference for  $w_0$ - and  $w_2$ -jumps, and  $S$  is the ratio of the pre-exponential factor for  $w_2$  to that for  $w_0$ . The corresponding ratio for  $w_1$  and  $w_0$  will be assumed to be unity since an  $A$  atom is diffusing in both of these cases.

If there is a binding energy,  $\Delta E_f$ , between the impurity and the vacancy, the probability of a  $k_1$ -jump, in which the vacancy and the impurity dissociate, will be decreased. Thus, in a simplified model with next nearest neighbor effects assumed to be negligible,

$$k_1 = w_0 \exp(-\Delta E_f/RT). \quad (8)$$

The variation of the correlation factor with temperature changes the apparent activation energy. Also, the correlation factor enters into  $D_0$  but not into the  $w$ 's. Thus, assuming that the temperature variation of the binding energy is negligible,

$$S = \frac{D_{0B}}{D_{0A}} \frac{f_A}{f_B} \exp(-\Delta H/RT), \quad (9)$$

where  $D_{0A}$  and  $D_{0B}$  are the values of  $D_0$  for  $A$  and  $B$  diffusing in pure  $A$ ,  $f_A$  and  $f_B$  are the corresponding correlation factors, and  $\Delta H$  is the correction term in Eq. (4), equal to  $Q-H$ , for  $B$  diffusing in pure  $A$ . The correction term is zero for  $A$  diffusing in pure  $A$  since, in this case,  $w_1 = w_2 = k_1$  at all temperatures, and  $f_A$  is a constant.

If  $Q_B$  is the activation energy determined from Eq. (1) for  $B$  diffusing in pure  $A$  and  $Q_A$  is that for  $A$  diffusing in pure  $A$ , with  $\Delta Q = Q_A - Q_B$ ,

$$\Delta Q + \Delta H = \Delta Q_m + \Delta E_f. \quad (10)$$

From Eqs. (4) to (10), the activation energy  $H$  and the pre-exponential factor  $A = \gamma a^2 C$ , as defined in Eqs. (2) and (3), can be calculated numerically. Tomizuka, Sonder, and Slifkin<sup>5-7</sup> have measured  $Q_A$ ,  $Q_B$ ,  $D_{0A}$ , and  $D_{0B}$  for diffusion of Cd, In, Sn, and Sb in pure silver in a temperature range centered at approximately 1000°K. Binding energies,  $\Delta E_f$ , have been calculated by Alfred and March,<sup>8</sup> using an extension of Lazarus' screening theory.<sup>9</sup> The value of  $K = \Delta E_m/\Delta Q_m$  is not known; however, it is reasonable to assume  $0 \leq K \leq 1$ . Calculations were done for  $K = 0, \frac{1}{4}, \frac{1}{2},$  and  $1$  using  $T = 1000^\circ\text{K}$  and the values are listed in Table I.

The resulting values of  $H$  and  $A$  are given in Table II. If  $K = 1$ , the effect of correlation on the activation energy is almost within experimental error. However, if  $K = \frac{1}{2}$  or  $\frac{1}{4}$ , the effect is quite pronounced, and, if  $K = 0$ , the effect is so large that it gives negative activation energies, which are physically impossible. The effect on the pre-exponential factor also is quite large. The analysis given here is only approximate; however, with any reasonable set of assumptions, there should be a non-negligible correlation correction if  $K = 0, \frac{1}{4},$  or  $\frac{1}{2}$ . The

Table I. Values used in calculation of correction correction for diffusion in pure silver.

Tracer	Activation energy $Q$ (kcal/mole)	Frequency factor $D_0$ ( $\text{cm}^2/\text{sec}$ )	Binding energy $E_f$ (kcal/mole)
Ag	44.09	0.395	0.00
Cd	41.7	0.44	0.81
In	40.6	0.41	1.31
Sn	39.3	0.25	1.75
Sb	38.32	0.169	2.07

Table II. Calculated values, with correction for correlation, of activation energy  $H$  and pre-exponential factor  $A$  for tracer diffusion in pure silver for various values of the parameter  $K$ .

Tracer	$K = 1$	$K = \frac{1}{2}$	$K = \frac{1}{4}$	$K = 0$
Activation energy $H$ (kcal/mole)				
Ag	44.09	44.09	44.09	44.09
Cd	41.2	40.5	39.8	38.4
In	40.1	38.8	37.0	16.6
Sn	38.9	37.5	35.2	a
Sb	38.1	36.6	34.2	a
Pre-exponential factor $A$ ( $\text{cm}^2/\text{sec}$ )				
Ag	0.48	0.48	0.48	0.48
Cd	0.57	0.45	0.35	0.21
In	0.55	0.37	0.19	$2.2 \times 10^{-5}$
Sn	0.32	0.20	0.084	a
Sb	0.23	0.13	0.050	a

<sup>a</sup>Negative activation energy.

deviation of the correlation factor from a simple exponential dependence on the temperature will cause very little curvature in the  $\log D$  vs  $1/T$  plot unless  $\Delta H$  is very large.

Whenever more than one energy for motion enters into the determination of the correlation factor, there will be a nonzero correction to the activation energy. This can occur when diffusion in alloys, diffusion in noncubic lattices, or diffusion of impurities in otherwise pure crystals takes place by means of a vacancy or interstitial mechanism.

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## DETERMINATION OF THE HYPERFINE STRUCTURE OF ATOMIC NITROGEN BY OPTICAL ORIENTATION\*

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The problems of producing a high degree of dissociation of molecular nitrogen and of detecting nitrogen atoms have prevented, so far, the determination of the hyperfine structure of atomic nitrogen by the method of atomic beams. In the method of optical orientation with spin exchange<sup>1</sup> these problems are simply and effectively solved: fractional dissociation of only about one part in  $10^7$  is required, and detection is effected with a photocell. In this note we report new precise values for the hyperfine intervals of the ground state of atomic nitrogen. The precision obtained in the present results (about 25 ppm) does not represent the limit of the optical method and it is expected that the  $N^{14} - N^{15}$  hyperfine structure anomaly can be determined with good precision. The only previous radio-frequency spectroscopy reported on atomic nitrogen is the work of Heald and Beringer<sup>2</sup> who used the method of paramagnetic resonance absorption. These workers obtained a value for the hyperfine interaction energy with an estimated uncertainty of two parts in one thousand.

The method of atomic orientation by optical pumping with spin exchange has been described previously in connection with the orientation of alkali and hydrogen atoms.<sup>1,3-5</sup> The present experiment is performed in a 500-cc flask filled with  $N_2$  at a pressure of 3.0 cm Hg, He at 0.5 cm Hg, and Rb vapor at a temperature of  $50^\circ\text{C}$ . The rubidium atoms are optically oriented with circularly polarized and filtered rubidium resonance radiation. The orientation of the rubidium is monitored by the transmission method.<sup>1</sup> Nitrogen atoms are produced by a pulsed discharge between aluminum electrodes mounted along a diameter of the bulb. The electrodes have a diameter of 0.5 in. and are separated by 2.0 inches. Both rf and dc discharges have been used; the best signals are obtained with a 5-msec rf pulse. Zeeman modulation is used to facilitate observation of the resonances and the resonances in atomic nitrogen are observed by their effect on the optical transmission of the bulb.

The ground state of  $N^{14}$  consists of three hyper-