

to decrease with increasing V concentration, very likely due to the large atomic size difference between Fe and V atoms, allowing for greater openness at large V concentration. In FeCo, however, where the atoms are very nearly the same size, the activation volume for self-diffusion in the disordered bcc phase is equal to approximately what one would expect for a monatomic metal. Measurements in the fcc alloy Au-34 at. % Ag, where the atoms are also the same size, show a similar effect.<sup>15</sup>

Gupta and Jeffery have made measurements of the effect of pressure on diffusion in ordered AuZn alloys of near-equiatomic composition.<sup>16</sup> In that system the activation volume for 50:50 composition was found to be approximately 1.1 times the molar volume, indicating that outward relaxation of the atoms around a vacancy actually takes place. The reason for this large activation volume is thought to be closely related to the nature of the ordering energy in these CsCl-type alloys. Other measurements of outward relaxation have been reported in alkali halides<sup>17</sup> and certain close-packed polyvalent metals (Al and Be).<sup>18,19</sup> The former shows the strong influence of Coulombic repulsion of next nearest neighbors around vacancies in an ionic crystal and the latter presumably reflects oscillations in the screening potential surrounding vacancies in metals. The low value of  $\Delta V/V_M$  for disordered FeCo compared to ordered AuZn illustrates quite dramatically what an important role the ordering energy plays in determining crystal properties.

Measurements of the isotope-effect parameter  $\Delta K$  for FeCo alloys<sup>1</sup> likewise points up the similarity of disordered FeCo and simple monatomic metals. Several correlations have been suggested between  $\Delta K$  and  $\Delta V$ . Barr and Mundy observed that for several metals  $\Delta K \sim \Delta V/V_M$ , with large values of  $\Delta K$  going with large values of  $\Delta V/V_M$ , and vice versa.<sup>20</sup> In Zn, however,  $\Delta K$  is 0.88–0.93,<sup>21,22</sup> whereas  $\Delta V/V_M$  is only 0.44.<sup>23</sup> Hence this relationship is not generally valid.

Another correlation between  $\Delta V$  and  $\Delta K$  was

suggested by LeClaire,<sup>24</sup> and is expressed by the relation

$$\Delta K \approx \frac{1}{1 + \frac{1}{3}n(1 - \Delta V_f/V_M)}, \quad (3)$$

where  $n$  is the approximate number of atoms which relax in the unstable mode of vibration which leads to the jump and  $\Delta V_f$  is the activation volume of formation. A value of  $n$  of approximately 2–3 is deduced from Eq. (3) for FeCo using the estimated value of  $\Delta K$  (0.73) and  $\Delta V_f \approx 0.5V_M$ .

Although the exact form of the correlation between  $\Delta K$  and  $\Delta V$  is not apparent at the present time, it seems clear that they are closely related in some way. It is to be hoped that future measurements of the two parameters in a larger number of systems may lead to a more complete picture of the defect structure in crystals.

It would clearly be of interest to measure the activation volume in FeCo in the ordered as well as the disordered phase. However, since the magnitude of  $D$  in the ordered phase is  $10^{-13}$  cm<sup>2</sup>/sec or smaller,<sup>1</sup> the anneal times required would be prohibitively long for high-pressure diffusion experiments (of the order of 30 days). An alloy system in which high-pressure measurements in both ordered and disordered phases would be possible is  $\beta$  CuZn. In such a system, the ratio  $\Delta V/V_M$  would be expected to become larger as the degree of long-range order increases.

In conclusion, we have found that the activation volume for diffusion of Fe<sup>59</sup> in near-equiatomic FeCo alloys is equal to  $4.38 \pm 0.89$  cm<sup>3</sup>/mole or  $0.60 \pm 0.12$  times the molar volume at 944.5 °C and over the pressure range 0–5 kbar. This value of  $\Delta V$ , coupled with the previously reported value of the isotope-effect parameter  $\Delta K$ , indicates that diffusion in disordered bcc FeCo is quite similar to that expected for a simple monatomic metal.

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