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Comments on Diffusion of Kr Isotopes in Solid Ar

J. J. Burton

Henry Krumb School of Mines, Columbia University, New York, New York 10027

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Recently, the isotope effect for Kr diffusion in Ar was found to be $f\Delta K\sim 0.48$. The results are consistent with a divacancy diffusion mechanism with $\Delta K\sim 1$.

Parker, Smith, and Glyde[1] have recently studied the diffusion of krypton isotopes in solid argon. They found an activation energy of

$$Q=3500-3900 \text{ cal/mole} \quad .$$

They also measured the isotope effect for Kr^{78} and Kr^{86} and found

$$f\Delta K=0.48\pm 0.25 \quad .$$

Parker *et al.* interpreted their results as due to krypton atoms diffusing via a single-vacancy mechanism. This assumption of a single-vacancy mechanism is based on the belief that self-diffusion in argon occurs via a single-vacancy mechanism.[2,3] This view is also supported by the agreement between the experimental Q and that calculated for Kr diffusion via single vacancies in Ar,[4] assuming that the atomic interactions may be described by an additive pair potential. Assuming a single-vacancy mechanism, Parker *et al.* concluded that $\Delta K\sim 0.6$ (f is known to be 0.78 for single-vacancy self-diffusion,[5] and was estimated by Parker *et al.* to be only slightly larger than 0.78 for krypton diffusion via single vacancies). This value of ΔK is rather low for single vacancies in fcc solids,[5] for which ΔK is often ~ 1.

This author has pointed out that the agreement between experimental values of Q for diffusion in solid argon and the values calculated from pair potentials may be accidental.[6] Losee and Simmons[7,8] measured the vacancy formation energy in solid krypton and concluded that the many-body effects are large. The pair-potential calculations neglect many-body effects and fail to give a vacancy-formation energy in rare-gas solids in agreement with the experimental result.[6] The vacancy-formation energy and the activation energy for self-diffusion in argon have been estimated assuming that the many-body interactions are large, as is indicated by the Losee-Simmons experimental result. Both triple-dipole interactions[9] and Jansen superexchange interactions[10] were included in the calculations. There has been some controversy[11] about the validity of the Jansen interaction. The calculated value of Q is in good agreement with experiment for a divacancy mechanism; a satisfactory vacancy-formation energy was also obtained. As inclusion of many-body effects gave good values of both the vacancy-formation energy and the diffusion activation energy, the author suggested that self-diffusion in rare-gas solids may occur via a divacancy mechanism.[6] This suggestion is compatible with the recent work of Parker *et al.*[1] $f\Delta K$ is usually used to distinguish diffusion mechanisms,[12] assuming that $\Delta K\sim 1$. f for divacancy self-diffusion is 0.48.[13] The recent results for the isotope effect in argon are consistent with a divacancy mechanism and $\Delta K\sim 1$, provided that f for the Kr tracer is close to the self-diffusion value, as is indicated by Parker's calculations.[1]

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