

Directional Dependence of the Nuclear-Spin-Lattice Relaxation Time in Cubic Metals Caused by Divacancy Diffusion*

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We have calculated the dependence of the nuclear-spin-lattice relaxation time on the angle between the applied field and the crystal axes which would be caused by divacancy self-diffusion. The distinctive angular dependence found is expected to be useful in identifying the self-diffusion mechanisms in metals such as Na, Ag, and Al, for which it has been suggested that divacancy contributions to self-diffusion are important.

Ailion and Ho¹ have suggested a new technique which can be used to identify certain atomic self-diffusion mechanisms in solids. Their method involves measurement of the spin-lattice relaxation time in single crystals by means of a nuclear-magnetic-resonance (NMR) experiment in the rotating frame. The method depends upon the fact that an atom in jumping from one site to another can cause an increase in the disorder in the dipolar system. The increase in disorder is a maximum if the spins are originally aligned along their local fields. Such local alignment can be achieved by an adiabatic demagnetization carried out in a frame rotating with H_1 , the rf magnetic field, for reasons given in Refs. 1 and 2. The disorder in the dipolar system is transferred to the Zeeman system, resulting in a decrease in the magnetization of the sample that is measureable in NMR experiments.

The calculations^{2,3} of the spin-lattice relaxation time caused by self-diffusion are based on two assumptions. The first of these is that before a jump takes place both the dipolar and Zeeman systems can be described by a common spin temperature Θ . This means that the calculations are applicable when the time interval τ between jumps is large compared to the spin-spin relaxation time T_2 . This assumption leads to the formulation of important physical quantities as diagonal sums which can be easily evaluated. The second assumption is that the nuclear spins do not change their orientation during a jump. Because the duration of an atomic jump is of the order of 10^{-12} sec, much shorter than any spin-precession period, this assumption is well justified and allows the use of the sudden approximation. Immediately after a jump, the atom finds itself in a new local field with its spin preferentially oriented in the direction of the local field at its previous site. This implies a loss of order in the dipolar system. Slichter and Ailion^{2,3} recognized that the local fields at two sites are not completely independent and they defined a correlation parameter p . In fact they showed that $(T_{1p})_{\text{diff}}$, the diffusion contribution to

the spin-relaxation time constant, in the presence of a rotating field H_1 is given by

$$\frac{1}{(T_{1p})_{\text{diff}}} = \frac{2}{\tau} (1-p) \frac{H_L^2}{H_1^2 + H_L^2}, \quad (1)$$

where H_L is the local field. For vacancy diffusion, the condition $p=0$ means that the local fields at two sites are completely independent of each other, and $p=1$ implies that they are completely correlated. Ailion and Ho¹ have shown that the correlation parameter p is a function of the orientation of the static field H_0 with respect to the crystal axes, and of the self-diffusion mechanism. By measuring the angular dependence of p , one can thus identify the self-diffusion mechanism.

The angular dependence of p for vacancy, interstitial, and interstitialcy mechanisms has been calculated.¹ Recently, however, it has been reported⁴⁻⁷ that in certain metals divacancy self-diffusion may be a dominant diffusion mechanism. In this note we report the calculation of the angular dependence of p for divacancy self-diffusion which would be useful in identifying this mechanism. Following Ref. 2, we have carried out the calculation under the assumption that not only τ but also τ_v , the mean time between vacancy jumps ($\tau_v \ll \tau$ typically), is much longer than the spin-spin relaxation time T_2 . We will discuss the limitations of this assumption later. Slichter and Ailion² have shown that the average change in dipolar energy caused by a single atomic jump is given by

$$\langle \Delta \bar{E} \rangle = U \sum_{ij}' (A_{ij}^2 - A_{ij} A_{ijf}), \quad (2)$$

where

$$A_{ij} = \frac{1}{2} \gamma^2 \hbar^2 (1 - 3 \cos^2 \theta_{ij}) / R_{ij}^3, \quad (3)$$

i, j refer to lattice sites, R_{ij} is the internuclear separation, and θ_{ij} is the angle between the applied field and R_{ij} . A_{ijf} is the final value of A_{ij} , after the jump is completed, and U is a factor involving traces of spin operators. The prime over the sum indicates that it is restricted to occupied sites only. The above change in energy can also be written^{1,2}

TABLE I. Expressions for $1/(1-p_{dv})$ as a function of θ for fcc and bcc lattices in the case of divacancy diffusion.

Lattice	$1/(1-p_{dv})$
fcc	$\frac{17.2327 + 7.3623 \sin^2 2\theta}{12.2981 + 6.0066 \sin^2 2\theta}$
bcc	$\frac{3.7312 + 2.5958 \sin^2 2\theta}{2.6074 + 1.6059 \sin^2 2\theta}$

$$\langle \Delta \bar{E} \rangle = (2/N)(CH_L^2/\Theta)(1-p), \quad (4)$$

where C is the Curie constant and N is the total number of atoms. Equations (2) and (4) are related^{1,2} by

$$\frac{CH_L^2}{\Theta} \cong NU \sum_i A_{ij}^2, \quad (5)$$

$$p_{dv} = \frac{1}{G_1 G_2} \left[\sum_{q_1 q_2} \left(A_{q_1 r}^2 + A_{q_2 r}^2 - A_{q_2 r} A_{q_1 q_2} + \sum_i A_{i r} A_{i q_1} \right) / \sum_i A_{i r}^2 \right]. \quad (7)$$

We have calculated p_{dv} for fcc and bcc lattices, using the lattice sums calculated in Ref. 1, wherever possible. For the fcc lattice, we have considered nearest-neighbor divacancies and jumps to nearest-neighbor sites only. Results are given in Table I and the angular dependence of $1/(1-p)$ is shown in Fig. 1. Divacancy diffusion in the bcc lattice is more complicated. In this case when we consider only nearest-neighbor jumps, two kinds of processes are possible, and if one occurs then the other must also occur. In the first of these, the jump results in changing a nearest-neighbor divacancy to a next-nearest-neighbor divacancy while the second process corresponds to the reverse of the first. The rate of each of these processes taken separately would depend on the binding energies of the two types of divacancies. Using the binding energies of divacancies calculated by Johnson⁸ in α -iron as an example, it seems reasonable to assume that in many cases the individual rates of these two processes would not differ significantly, perhaps by an order of magnitude or less at temperatures of interest. In this case there may exist a sizable temperature regime in which both hopping processes are slow compared to the spin-spin relaxation rate. In this temperature regime, the angular dependence of the spin-lattice relaxation time will depend on an average over the two types of divacancy hopping. The results for p_{dv} in this case are given in Table I and the angular dependence of $1/(1-p)$ is shown in Fig. 2. In these calculations, the coordinate axes has been taken parallel to the $\langle 100 \rangle$ crystal direction, and θ is the angle between the z axis and the static field H_0 . Results for self-diffusion by a single va-

where now the sum is over all lattice sites.

We now consider divacancy self-diffusion. If we assume that the atom at a fixed position r jumps to a vacancy at q_1 , then the change in dipolar energy, averaged over all G_1 possible values of q_1 is

$$\langle \Delta \bar{E} \rangle = \frac{2U}{G_1} \sum_{i q_1}' (A_{i r}^2 - A_{i r} A_{i q_1}). \quad (6)$$

The factor of 2 appears since either i or j can be the jumping atom. We now convert Eq. (6) to a sum over all lattice sites by explicitly taking into account unoccupied sites. If we assume that the second vacancy is at q_2 which for bound divacancies has G_2 possible values, then we have to subtract terms $i = q_1, q_2$ from Eq. (6). Averaging over q_2 and using Eqs. (4) and (5), we find the correlation parameter for divacancy diffusion p_{dv} to be

cancy, interstitial, and interstitialcy mechanisms have been taken from Ref. 1.

Recent experimental evidence suggests that divacancies may contribute significantly to self-dif-

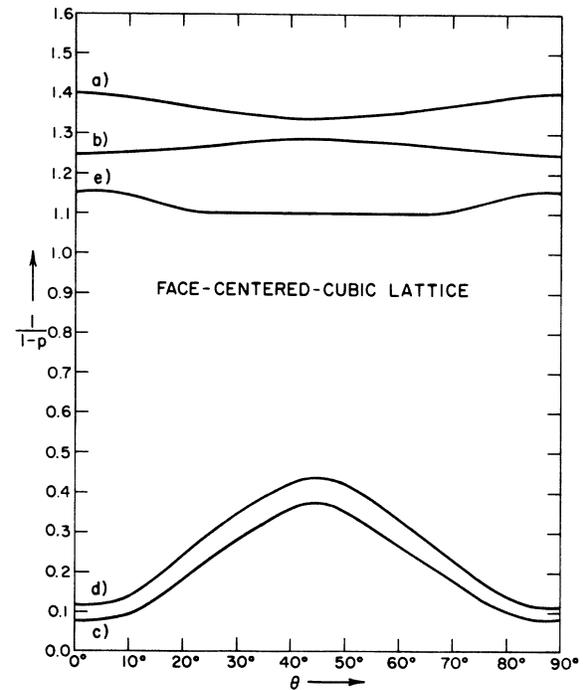


FIG. 1. Plot of $1/(1-p)$ vs θ for a fcc lattice in the case of diffusion by (a) divacancy, (b) vacancy, (c) interstitial, (d) interstitialcy ($\tau_i > T_2$), and (e) interstitialcy ($\tau_i < T_2$). For details of cases (b), (c), (d), and (e) see Ref. 1.

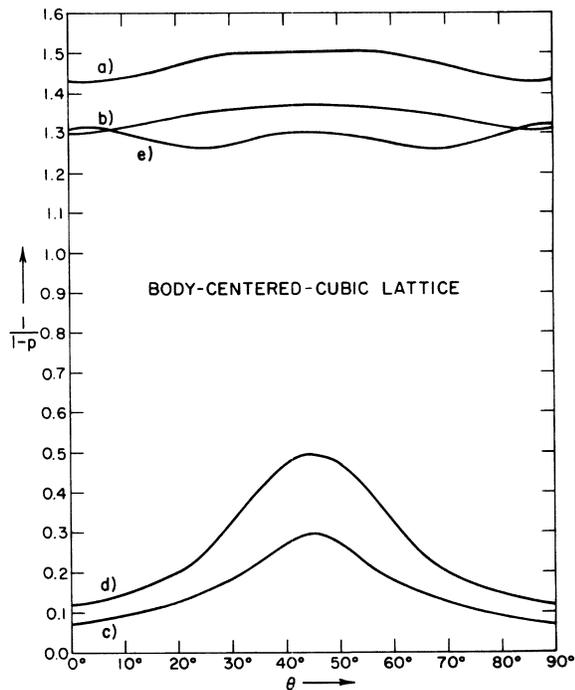


FIG. 2. Plot of $1/(1-p)$ vs θ for a bcc lattice in the case of diffusion by (a) divacancy, (b) vacancy, (c) interstitial, (d) interstitialcy ($\tau_i > T_2$), and (e) interstitialcy ($\tau_i < T_2$). For details of cases (b), (c), (d), and (e) see Ref. 1.

fusion in Na,^{4,5} particularly at temperatures approaching the melting point. Divacancies also seem to be important for self-diffusion in Ag,⁶ and may contribute to self-diffusion in Al⁷ and other metals. Deviations from a linear Arrhenius plot have been reported in all these metals, indicating that more than one diffusion mechanism is probably present. Application of the Ailion and Ho¹ tech-

nique, extended by the calculations presented here, may be able to provide far more information about the contributing mechanisms than is now available. However, several difficulties exist. In the first place, it appears likely that in some metals divacancy self-diffusion is important only at high temperature, i. e., temperatures approaching the melting point, although experimental results thus far are not definitive. If this should be so, the region of divacancy contribution would correspond to the region of motional narrowing, $\tau < T_2$, which would obscure any angular-dependent effects. At more moderate temperatures, i. e., 500–700 °K for aluminum, one finds that although $\tau > T_2$,⁹ our earlier assumption that $\tau_v < T_2$ is violated. The case of vacancy diffusion with $\tau_v < T_2$ has been discussed previously,^{1,2} and it has been argued effectively that the results in this case should very closely resemble the case $\tau_v > T_2$. More recently, Samuelson and Ailion¹⁰ have explicitly calculated vacancy-diffusion effects in the region $\tau_v < T_2$ and their results show negligible difference from the $\tau_v > T_2$ results. We expect this also to be the case for divacancy diffusion. Thus the results given above should prove useful if divacancy contributions are not strictly confined to the temperature region very near the melting temperature. A second difficulty is that NMR experiments cannot be performed on metal single crystals of reasonable size because rf electromagnetic fields can penetrate only very small distances. On the other hand, it should be possible to perform analogous nuclear-acoustic-resonance¹¹ (NAR) experiments since there is no such penetration problem with acoustic waves. We expect that measurements of angular dependence of the relaxation time in single crystals of metals using NAR experiments will be very useful in identifying the self-diffusion mechanisms occurring in them.

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