

Effect of the Translational-Diffusion Mechanism on the Low-Field NMR Spin-Lattice Relaxation Time in the Rotating Reference Frame: Calculation of the Order Parameter p^* †

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(Received 31 May 1967; revised manuscript received 7 December 1967)

The effect of the translational-diffusion mechanism on the low-field NMR spin-lattice relaxation time in the rotating reference frame is calculated for simple cubic, body-centered cubic, and face-centered cubic lattices. The results of these calculations suggest a new method for determining the preferred diffusion mechanism. Previously NMR has been able to provide a *direct measurement* of the activation energy only; a theory has always been needed to determine the jump frequency from the experimentally measured relaxation time. Recently Slichter and Ailion developed a new technique for the study of ultraslow diffusion which is applicable when the mean time τ between atomic jumps is less than the spin-lattice relaxation time T_1 . In their theory, an order parameter p appears in the relationship between the experimentally measured relaxation time and τ . This parameter p depends upon the diffusion mechanism and the angle θ , which describes the orientation of the crystal with respect to the external magnetic field. In this paper we have calculated p versus θ for vacancy diffusion, interstitialcy diffusion, and interstitial diffusion in bcc, fcc, and sc lattices for two cases. In the first case, we have assumed that τ_i , the mean time that an interstitial atom occupies a particular site between jumps, is longer than T_2 , the spin-spin relaxation time, and we have found that the angular dependence of p is quite different for different mechanisms. In the second case, we have assumed that $\tau_i < T_2$ and have found that the angular dependence of p for interstitialcy diffusion differs from the vacancy results by approximately 10% for the three lattices considered. These theoretical results, when combined with experimental measurements of the angular dependence of the low-field relaxation time, provide a method for the direct determination of the mechanism responsible for diffusion in these crystals.

I. INTRODUCTION

ONE of the most powerful tools for studying atomic motions is nuclear magnetic resonance. It has been used to study atomic diffusion^{1,2} and molecular rotations³ in a variety of substances. In many cases it has advantages over other techniques. For instance, it is not restricted to the study of the motion of atoms which have radioactive isotopes of convenient half-life, but can be used to observe the jumps of any paramagnetic nucleus regardless of whether or not that nucleus is radioactive. There are many nuclei which are paramagnetic, but which do not have convenient radioactive isotopes (e.g., Li⁷). A plot of the temperature dependence of the linewidth (or T_2) or a plot of the spin-lattice relaxation time versus reciprocal temperature provides a direct determination of the activation energy. By applying a theory like that of Bloembergen, Purcell, and Pound⁴ (BPP) or that of Torrey,⁵ the jump frequency can be determined from the experimentally

measured relaxation time. Even though the determination of the mechanism responsible for the diffusion is one of the most important problems connected with atomic motions, nuclear resonance has not in the past been able to provide a direct determination of the mechanism. It is the purpose of this paper to describe a new method for studying motions which will provide direct information about the nature of the atomic jumping process.

The temperature range over which diffusion can be studied by NMR has been greatly extended to very low temperatures by the development of a new method^{6,7} which measures the low-field spin-lattice relaxation time in a coordinate frame rotating at the Larmor frequency. The new technique is valid provided that τ , the mean time between atomic jumps, is less than T_1' , the spin-lattice relaxation time due to all mechanisms other than diffusion; whereas previous NMR techniques apply only to cases for which $\tau < T_2$. Since $T_2 \ll T_1'$ in a solid, this method has greatly extended the range of observation to very slow motions. The method has been applied to the observation of translational diffusion in metallic lithium^{8,9} in the temperature range from room temperature down to 185°K. At the latter temperature τ is of the order of 1 sec. The technique has also been applied to the study of molecular rota-

* This research was supported in part by the U. S. National Science Foundation, under Grant No. GP4302.

† This paper is based in part on the M.S. thesis presented by Pei-Pin Ho at the University of Utah, Salt Lake City (unpublished).

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¹ H. S. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1952).

² D. F. Holcomb and R. E. Norberg, *Phys. Rev.* **98**, 1074 (1955).

³ H. S. Gutowsky and G. E. Pake, *J. Chem. Phys.* **16**, 1164 (1948); **18**, 162 (1950).

⁴ N. Bloembergen, E. M. Purcell, and R. V. Pound, *Phys. Rev.* **73**, 679 (1948).

⁵ H. C. Torrey, *Phys. Rev.* **92**, 962 (1953); **96**, 690 (1954); H. A. Resing and H. E. Torrey, *ibid.* **131**, 1102 (1963).

⁶ D. C. Ailion and C. P. Slichter, *Phys. Rev. Letters* **12**, 168 (1964).

⁷ C. P. Slichter and D. C. Ailion, *Phys. Rev.* **135**, A1099 (1964).

⁸ D. C. Ailion and C. P. Slichter, *Phys. Rev.* **137**, A235 (1965).

⁹ D. C. Ailion, thesis, University of Illinois (unpublished).

tions in a number of chemical compounds^{10,11} and in gypsum.¹²

The above technique is based upon the realization that atomic jumping results in a loss of dipolar order and is thus a thermodynamically irreversible process. The loss of dipolar order resulting from a diffusion jump is a maximum if the nuclei are initially aligned along their individual local fields. Such alignment can be achieved by an adiabatic demagnetization of the system from a large external field to a small external field. This process results in the transfer of order from the Zeeman system to the dipolar system. After a nucleus undergoes a diffusion jump, it will in general find itself in a different local field and, as a result, there will be a loss of dipolar order. Following the jump, cross relaxation between the dipolar and Zeeman systems will transfer the loss of dipolar order to a loss of Zeeman order which can be observed experimentally as a decrease in the magnetization.¹³

As mentioned earlier, a theory is needed to relate the experimentally measured relaxation time to τ . The theories of BPP and of Torrey cannot be used in the case of weak fields as they are perturbation theories in which the dipolar Hamiltonian is treated as a perturbation on the eigenstates of the Zeeman Hamiltonian. This type of theory clearly does not apply when the external fields are less than or equal to the average dipolar fields. For this reason Slichter and Ailion developed a new theory⁷ which is applicable only if $\tau \gg T_2$. This theory, which thus complements the BPP theory, is based upon two assumptions. First, it is assumed that enough time elapses between any two diffusion jumps so that both the dipolar and Zeeman systems can be described by a common spin temperature prior to each jump. Since the time required for a spin temperature to be established is of the order of T_2 and since the time which any one nucleus spends on the average at any particular site is τ , this assumption is equivalent to assuming that $\tau \gg T_2$. The spin-temperature assumption allows us to use the density matrix and to formulate physical quantities as diagonal sums which can be evaluated without determining the eigenfunctions.¹⁴ The second assumption is that the sudden

approximation of quantum mechanics can be applied to the jumping process; i.e., we assume that the time the nucleus spends in the *actual process* of jumping is so short that, immediately after a diffusion jump, the spin will have the same orientation as it had immediately before the jump. Since the actual time which a nucleus spends in transit is of the order of the lattice vibration period ($\sim 10^{-12}$ sec) and the time required for the nucleus to change its orientation is of the order of the Larmor period ($\sim 10^{-8}$ sec in a field of 1 G), this assumption is clearly justified. Were it not so and were the nucleus to jump so slowly that it would have time to align itself along the new local field during the actual jumping time, the jumping would not result in a loss of dipolar order and would not be observable by magnetic resonance.

II. CALCULATION OF THE ENERGY CHANGE

Let us consider a spin system consisting of nuclei interacting with each other and with an external static field H_0 and a strong rf field H_1 . In a frame rotating with H_1 , we then have an effective Hamiltonian \mathcal{H} :

$$\mathcal{H} = \mathcal{H}_z + \mathcal{H}_d^0, \quad (1)$$

where

$$\mathcal{H}_z = \gamma \hbar [(H_0 - (\omega/\gamma))I_z + H_1 I_x], \quad (2)$$

and

$$I_z = \sum_j I_{zj}, \quad I_x = \sum_j I_{xj}. \quad (3)$$

Also

$$\mathcal{H}_d^0 = \frac{1}{2} \sum_{i,k} A_{ik} (3I_{zi}I_{zk} - \mathbf{I}_i \cdot \mathbf{I}_k), \quad (4)$$

where

$$A_{ik} = \frac{1}{2} \gamma^2 \hbar^2 \left(\frac{1 - 3 \cos^2 \theta_{ik}}{R_{ik}^3} \right). \quad (5)$$

Here, \mathcal{H}_d^0 is the secular part of the dipolar Hamiltonian; i.e., \mathcal{H}_d^0 is that part of the dipolar Hamiltonian which commutes with I_z .

The assumption that, prior to each jump, the dipolar and Zeeman parts of the spin system can be represented by a single temperature is equivalent to assuming that initially the system can be represented by a density operator ρ_i , given by

$$\rho_i = \frac{\exp[-(\mathcal{H}_d^0 + \mathcal{H}_z)/k\theta]}{Z}. \quad (6)$$

In the above formula, Z is the partition function. After the jump the dipolar Hamiltonian has changed to \mathcal{H}_d^0 and the temperature θ has changed to θ' . However, since we are assuming that the spin orientation is the same right after the jump as it was immediately before, \mathcal{H}_z is unchanged. We then have

$$\rho_f = \frac{\exp[-(\mathcal{H}_d^0 + \mathcal{H}_z)/k\theta']}{Z}. \quad (7)$$

a few G, it will be much easier to demagnetize H_1 than to demagnetize H_0 .

¹⁴ J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

¹⁰ D. W. McCall and D. C. Douglass, Appl. Phys. Letters **7**, 12 (1965).

¹¹ D. C. Douglass and G. P. Jones, J. Chem. Phys. **45**, 956 (1966).

¹² D. C. Look and I. J. Lowe, J. Chem. Phys. **44**, 2995 (1966).

¹³ It is experimentally difficult to demagnetize the spins from a large field ($\sim 10\,000$ G) to a field of order of the dipolar field (~ 1 G) in a time short compared to the spin-lattice relaxation time and yet long enough for the process to be adiabatic. For this reason, the nuclear relaxation is observed in a frame rotating at such a frequency as to exactly cancel the static magnetic field. [See C. P. Slichter and W. C. Holton, Phys. Rev. **122**, 1701 (1961).] Such a treatment is justified by the work of A. G. Redfield [*ibid.* **98**, 1787 (1955)], who showed that a nuclear spin system subject to an rf field which is strong enough to saturate the nuclear-resonance line should be described by a spin temperature in a frame rotating at the frequency of the rf field. This means that Curie's law will hold in the rotating frame, and the magnetization will be parallel to the rotating field H_1 . Since H_1 is typically only

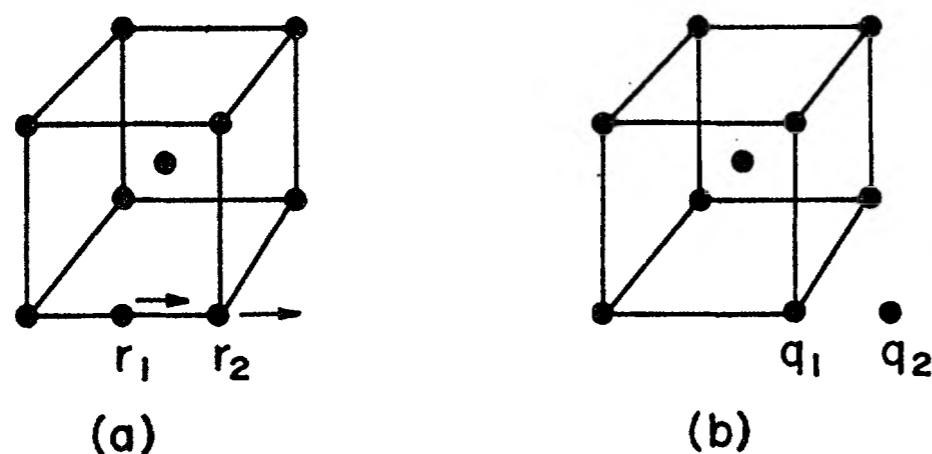


FIG. 1. (a) represents the situation in a bcc crystal before an interstitialcy jump and (b) represents the situation after the jump. r_1 and r_2 represent the initial positions of the jumping atoms and q_1 and q_2 represent their final positions.

For a system described by a temperature we can calculate the average energy \bar{E} from

$$\bar{E} = \text{Tr}(\mathcal{H}\rho). \quad (8)$$

The energy change which results from a single jump is then given by

$$\Delta\bar{E} = \text{Tr}(\mathcal{H}\rho_f) - \text{Tr}(\mathcal{H}\rho_i). \quad (9)$$

The assumption that the spin orientation is unchanged as a result of the jump tells us that

$$\rho_f = \rho_i = \rho. \quad (9')$$

We then have, in the high-temperature approximation,

$$\Delta\bar{E} = \text{Tr}(\mathcal{H}\rho_f - \mathcal{H}\rho_i) = \frac{1}{k\theta(2I+1)^N} \times [\text{Tr}(\mathcal{H}\rho_f^2) - \text{Tr}(\mathcal{H}\rho_i^2)]. \quad (10)$$

If there are N_0 jumping units each of which spends a mean time τ_0 between jumps, we have the result that the average rate of change of the dipolar energy due to jumping is

$$\frac{\partial \langle \mathcal{H}\rho \rangle}{\partial t} = \frac{N_0}{\tau_0} \langle \Delta E \rangle \cong -\frac{\langle \mathcal{H}\rho \rangle}{T_c}. \quad (11)$$

Slichter and Ailion⁷ have shown that the time T_c is the relaxation time that would be obtained if $H_1 = 0$.

We can define a local field H_L in the rotating frame by

$$\frac{CH_L^2}{\theta} = \frac{\text{Tr}(\mathcal{H}\rho^2)}{k\theta(2I+1)^N} = U \sum'_{i,j} A_{ij}^2, \quad (12)$$

where U is a factor involving the trace of the spin operators, N is the number of atoms, and C is the Curie constant. The prime indicates that we are summing only over occupied sites. If we assume that the number of unoccupied sites is small compared to the number of occupied sites, then

$$\frac{CH_L^2}{\theta} \cong NU \sum_i A_{ij}^2, \quad (13)$$

where the sum now includes all lattice sites and N represents the total number of atoms. Also

$$\frac{\text{Tr}(\mathcal{H}\rho^2)}{k\theta(2I+1)^N} = U \sum'_{ij} A_{ij}A_{ijf}, \quad (14)$$

where A_{ijf} is the value of A_{ij} after the jump. We then have that

$$\Delta\bar{E} = U \sum'_{ij} (A_{ij}^2 - A_{ij}A_{ijf}). \quad (15)$$

III. DETERMINATION OF p FOR τ_i (OR τ_v) $\gg T_2$

A. Vacancy Diffusion

In this section we will assume that diffusion takes place as a result of nearest-neighbor jumps. Let us consider a particular jump. Let r represent the initial site of the jumping nucleus and let q represent the final site. Then

$$\Delta\bar{E} = 2U \sum'_i (A_{ir}^2 - A_{ir}A_{iq}), \quad (16)$$

where we have used the fact that only the atom initially at r jumps. The factor of 2 arises since either i or j can be r .

Now in general there are a number G of different equally probable sites into which the nucleus at r can jump. (For nearest-neighbor vacancy diffusion, G is the number of nearest neighbors.) Since these are equally probable we should average over them. If we do so, we obtain

$$\langle \Delta\bar{E} \rangle = \frac{2U}{G} \sum'_{i,q} (A_{ir}^2 - A_{ir}A_{iq}). \quad (17)$$

Since, for vacancy diffusion, the atom at r must have a vacancy next to it, we can replace the sum over occupied sites by a sum over all lattice sites. If we subtract the term corresponding to $i=q$, we then get

$$\langle \Delta\bar{E} \rangle = \frac{2U}{G} \sum'_{i,q} (A_{ir}^2 - A_{ir}A_{iq}) - \frac{2U}{G} \sum_q A_{qr}^2 \quad (18a)$$

$$= 2U \sum'_i A_{ir}^2 - \frac{2U}{G} \sum_q (A_{qr}^2 + \sum'_i A_{ir}A_{iq}) \quad (18b)$$

$$= \frac{CH_L^2}{\theta} \frac{2}{N} (1-p), \quad (18c)$$

where

$$p = \frac{1}{G} \sum_q [A_{qr}^2 + \sum'_i A_{ir}A_{iq}] / \sum'_i A_{ir}^2. \quad (19)$$

This formula for p was first derived by Slichter and Ailion.⁷ If we substitute our expression (18c) into formula (11) we get

$$\frac{1}{T_c} = \frac{N_v}{\tau_v} \frac{2}{N} (1-p) = -\frac{2}{\tau} (1-p), \quad (20)$$

where we have replaced N_0 by N_v and τ_0 by τ_v and have used the fact that some atom must jump whenever a vacancy jumps and thus

$$N_v/\tau_v = N/\tau. \quad (21)$$

In the presence of a rotating field H_1 , Slichter and Ailion have shown that the magnetization will decay with a

time constant T given by

$$\frac{1}{T} = \frac{2}{\tau} (1-p) \frac{H_L^2}{H_1^2 + H_L^2}. \quad (22)$$

(The T used here corresponds to the $T_{1,p}$ used by Redfield¹³ and others.^{10,11})

B. Interstitialcy Diffusion

Interstitialcy diffusion occurs when an interstitial atom collides with an adjacent atom occupying a normal lattice site with the result that the initially interstitial atom moves to the normal site and the initially normal atom has moved to a new interstitial site.¹⁵ We are regarding the diffusion to be a simultaneous motion of the two atoms.¹⁶ This is shown in Fig. 1.

To calculate p we can use formula (15) but we must recognize now that in interstitialcy diffusion two atoms will have their dipolar energies changed. If r_1 and r_2 represent the initial positions of the jumping atoms and q_1 and q_2 represent their final positions, then the only terms which change are those for which either i or j is r_1 or r_2 (excepting, of course, the terms $i=r_1, j=r_2$ and $i=r_2, j=r_1$, since the interaction term between the two jumping atoms does not change). We then get

$$\Delta \bar{E} = 2U \sum_i' [(A_{ir_1^2} - A_{ir_1} A_{iq_1}) + (A_{ir_2^2} - A_{ir_2} A_{iq_2})]. \quad (23)$$

If we assume that the number of interstitial atoms is small compared to the number of normally occupied lattice sites, we can delete the prime in Eq. (23) and let the sum range over all normal lattice sites. (We are thus neglecting interactions between two interstitial atoms.) However, in the jump, the dipolar energy between the interstitial atom and the atom at r_2 does not change. Since this term has been included in the sum over i , we must explicitly subtract the term corresponding to $i=r_2$. We should further recognize that q_1 and r_2 refer to the same normal site, and r_1 and q_2 refer to interstitial sites. Let us replace the indices for the normal lattice site by q and the indices for the interstitial sites by r . Since we will average over different jump directions the

¹⁵ We have not performed our calculations for complexes of atoms like split interstitials, di-interstitials, or crowdions, but have limited our considerations in this paper to the motion of point defects like interstitial atoms and vacancies. However, if in a particular structure, complexes were thought to be responsible for the diffusion, the method of calculation considered here could be applied to that case.

¹⁶ We could alternatively regard the motion to consist of two steps, in each of which only one atom moves. In the first step, the normal atom moves to an interstitial site thereby leaving a vacancy between two interstitial atoms; in the second step, the initially interstitial atom jumps into the vacant site. If we calculate the energy changes for each step and add them, we will get the same total energy change as we get if we assume simultaneous motion of two atoms. We must be careful, however, to include the fact that the spin temperature prior to the second step is greater than it was prior to the first because of the heating which results from the first jump.

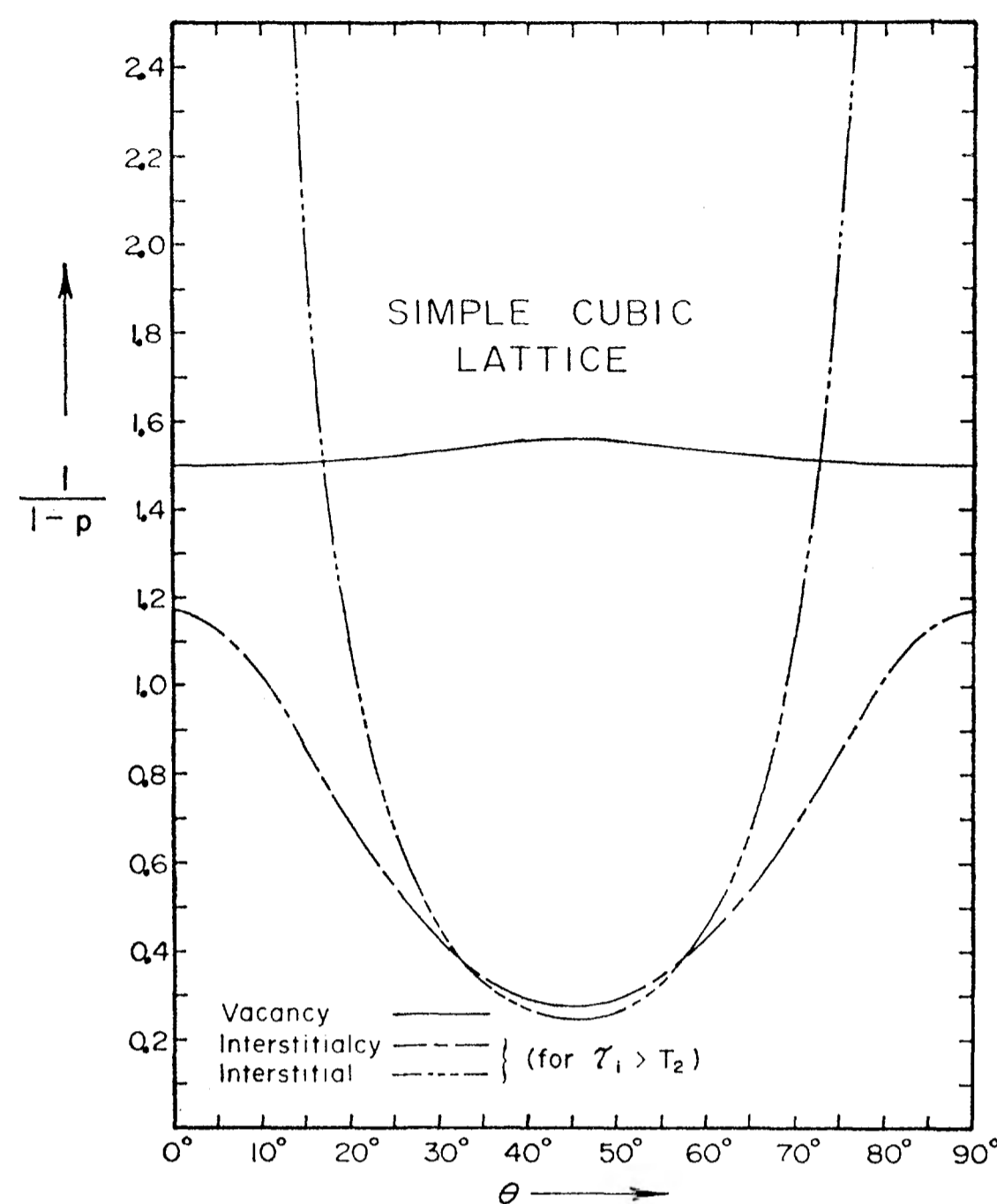


FIG. 2. A plot of $1/(1-p)$ versus θ for $\tau_i > T_2$ in a simple cubic crystal, assuming (a) vacancy diffusion, (b) interstitialcy diffusion, and (c) interstitial diffusion.

two interstitial sites can be treated equivalently. We then get

$$\langle \Delta \bar{E} \rangle = \frac{2U}{G} \sum_q [\sum_i (A_{ir^2} + A_{iq^2} - 2A_{ir} A_{iq}) - A_{qr^2}]. \quad (24)$$

We must also recognize that in a cubic crystal there may be a number G' of different but equally probable sites in which the interstitial atom can be situated. (In a bcc crystal in which the interstitial atom occupies the center of an edge as in Fig. 1, $G'=3$, corresponding to the cases in which the lines joining the interstitial atom to its nearest neighbors lie along the x , y , or z directions.) If we average over these different sites, we get

$$\langle \langle \Delta \bar{E} \rangle \rangle = \frac{2U}{GG'} \sum_{r,q} (\sum_i (A_{ir^2} + A_{iq^2} - 2A_{ir} A_{iq}) - A_{qr^2}). \quad (25)$$

The sum over i is a sum over all lattice sites. Now

$$\frac{CH_L^2}{\theta} \cong NU \sum_i A_{iq^2} = \frac{NU}{GG'} \sum_{i,r,q} A_{iq^2}. \quad (26)$$

We get $\langle \langle \Delta \bar{E} \rangle \rangle$ of the form (18c) only now p is given by

$$p = \left(\frac{1}{GG'} \sum_{r,q} A_{qr^2} + \frac{2}{GG'} \sum_{i,r,q} A_{ir} A_{iq} - \frac{1}{G'} \sum_{i,r} A_{ir^2} \right) / \frac{1}{G} \sum_{i,q} A_{iq^2}. \quad (27)$$

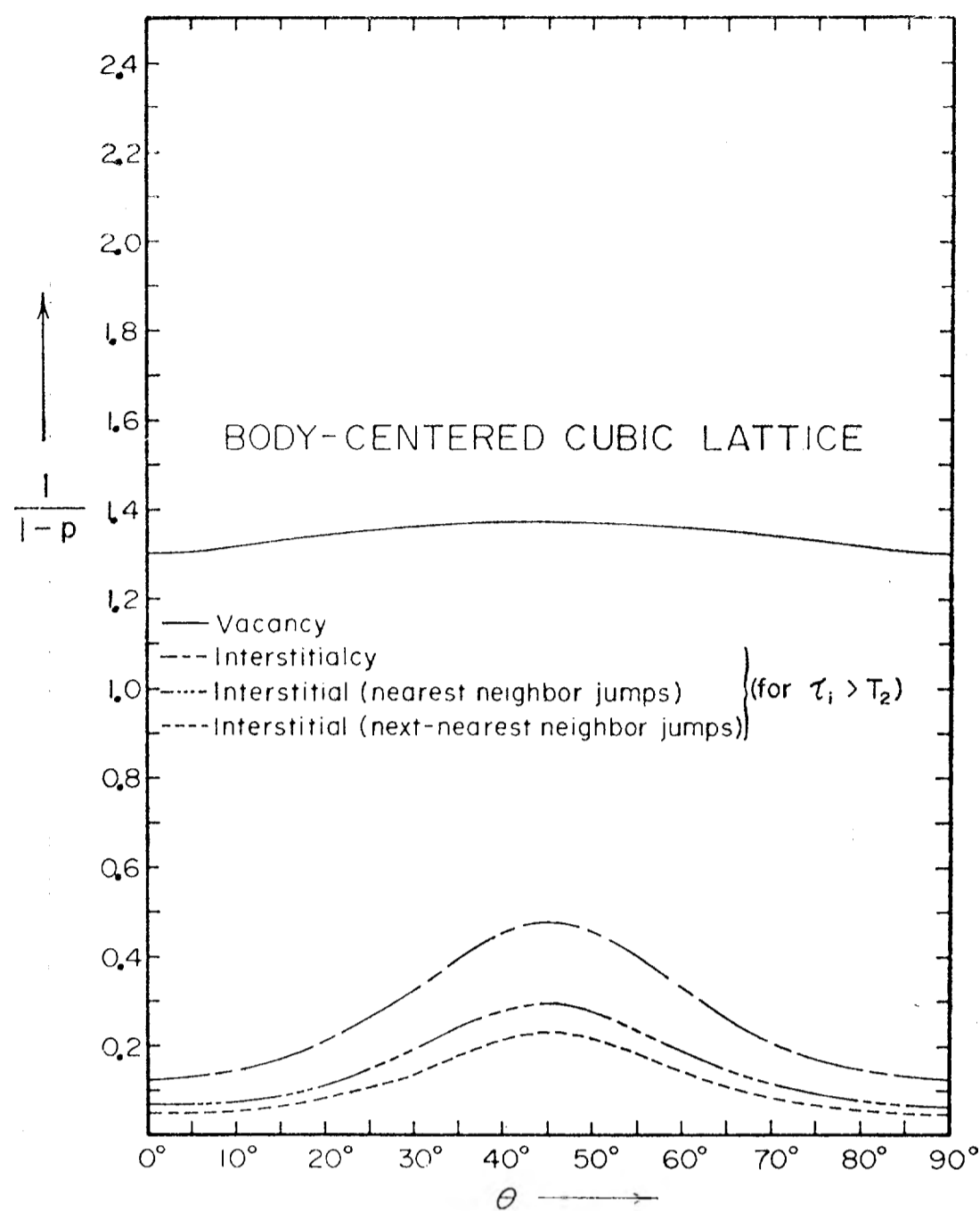


FIG. 3. A plot of $1/(1-p)$ versus θ for $\tau_i > T_2$ in a body-centered cubic crystal, assuming (a) vacancy diffusion, (b) interstitialcy diffusion, (c) interstitial diffusion (to nearest-neighbor interstitial sites), and (d) interstitial diffusion (to next-nearest-neighbor interstitial sites).

In this formula, r represents an interstitial site, q represents the normal lattice site into which the interstitial atom jumps, i ranges over all normal lattice sites, G is the number of atoms which are nearest neighbors to a given interstitial atom, and G' is the number of different sites in which the interstitial atom can appear.

C. Interstitial Diffusion

In this type of diffusion an interstitial atom jumps into one of the nearest-neighbor vacant interstitial sites. If we let r represent the initial site (an interstitial site) and q represent the final site (also an interstitial site), we then get for the mean energy change

$$\langle\langle\Delta\bar{E}\rangle\rangle = \frac{2U}{G'} \sum_{r,i} \left(A_{ir}^2 - \frac{1}{G} \sum_q A_{ir} A_{iq} \right). \quad (28)$$

Expression (28) can be written in the same form as Eq. (18c), if each term is multiplied and divided by $\sum_i A_{ij}^2$ where the indices i and j refer to normal lattice sites. Therefore

$$\langle\langle\Delta\bar{E}\rangle\rangle = 2U \sum_i A_{ij}^2 \times \left[\left(\frac{1}{G'} \sum_{i,r} A_{ir}^2 - \frac{1}{GG'} \sum_{i,q,r} A_{ir} A_{iq} \right) / \sum_i A_{ij}^2 \right]. \quad (29)$$

Also

$$\frac{CH_L^2}{\theta} \cong NU \sum_i A_{ij}^2. \quad (30)$$

Hence

$$\langle\langle\Delta\bar{E}\rangle\rangle = \frac{CH_L^2}{\theta} \frac{2}{N} (1-p). \quad (18c)$$

Therefore

$$p = \left(\sum_i A_{ij}^2 + \frac{1}{GG'} \sum_{i,r,q} A_{ir} A_{iq} - \frac{1}{G'} \sum_{i,r} A_{ir}^2 \right) / \sum_i A_{ij}^2. \quad (31)$$

IV. DETERMINATION OF p FOR τ_i (OR τ_v) $\ll T_2$

Only at very low temperatures will τ_i (or τ_v) be longer than T_2 , and at these temperatures it may be difficult to achieve an interstitial (or vacancy) concentration sufficiently great that $\tau < T_1'$, where τ is the mean time between jumps of a normal lattice atom. Only in a very pure sample will it be possible for T_1' to be sufficiently long so that the conditions $\tau_i > T_2$ and $\tau < T_1'$ can be satisfied simultaneously. For this reason we now extend our considerations to the region τ_i (or τ_v) $\ll T_2$.

A. Vacancy Diffusion

Since τ_v , the mean time a vacancy stays at a lattice site between jumps, is much less than τ , the atomic jump time, we have the possibility that $\tau_v \ll T_2 \ll \tau$ and there will be a trail of "hot" spins left behind the

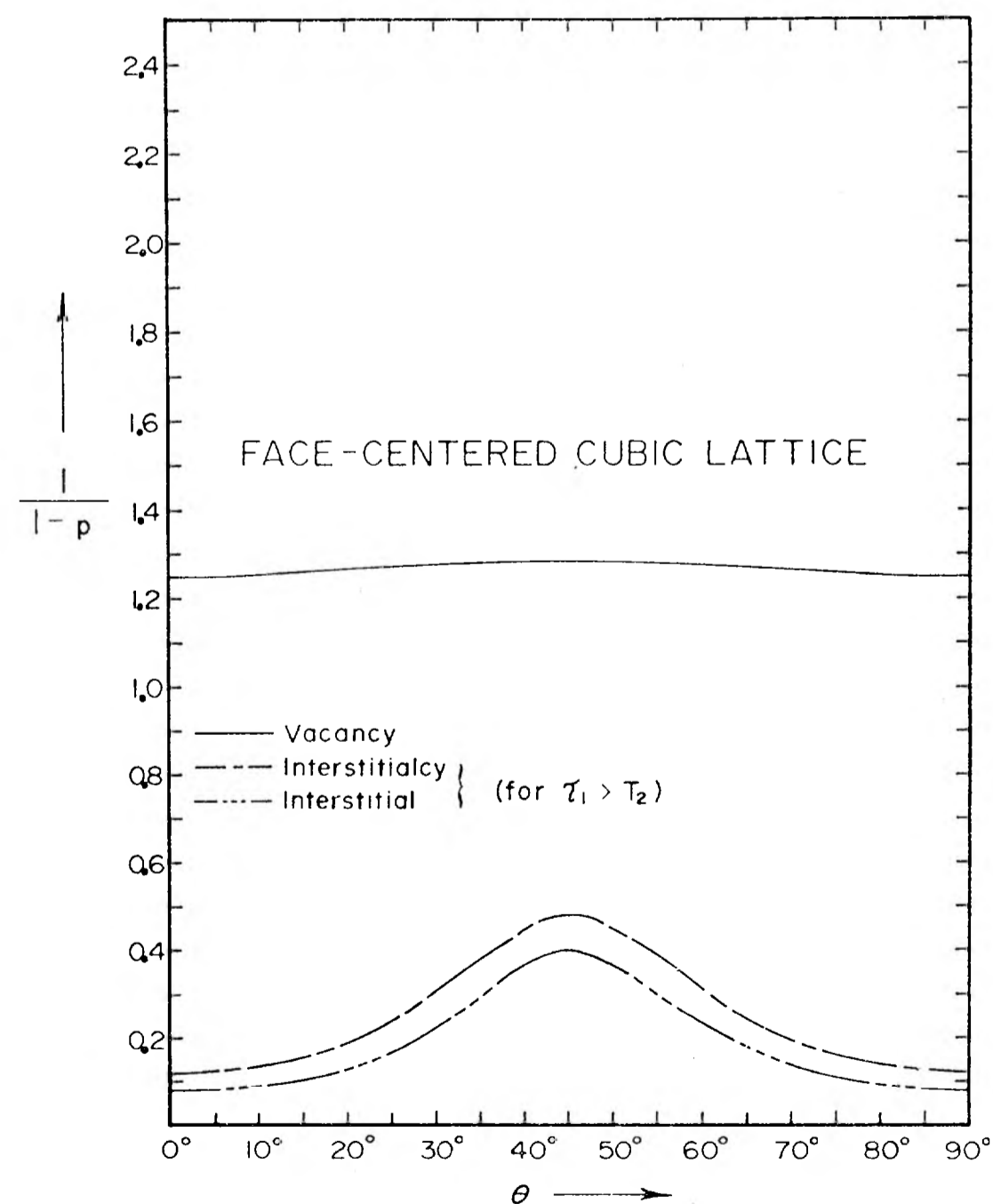


FIG. 4. A plot of $1/(1-p)$ versus θ for $\tau_i > T_2$ in a face-centered cubic crystal, assuming (a) vacancy diffusion, (b) interstitialcy diffusion, and (c) interstitial diffusion.

vacancy. (This phenomenon is discussed in detail in Refs. 7 and 8.) These "hot" spins will contribute considerably less to the dipolar energy than "cool" spins (i.e., spins at the mean dipolar temperature), so that we will have introduced an error by not distinguishing these spins from the normal "cool" spins. However, we can estimate an upper limit of the error introduced by omitting entirely these spins from the calculation of the dipolar energy. (This corresponds to assuming that these spins are at infinite temperature, certainly an upper limit.) We then find that the maximum error introduced by this source into the angular dependence of $1/(1-p)$ is only a few percent, which is very small compared to the differences exhibited in the curves of Figs. 2-4, and is even small (though not very small) compared to the 10% effects shown in Figs. 5-7. Therefore, we will consider the vacancy calculation given in Sec. III A of this paper to be essentially valid even if $\tau_i \ll T_2$.

B. Interstitialcy Diffusion

For interstitialcy diffusion there is a more serious error than the neglect of the trail of "hot" spins described above. In Sec. III B, we assumed that both the interstitial atom and the lattice atom which jump are at the same temperature θ prior to the "interstitialcy jump." If $\tau_i < T_2$, this treatment should not apply since, immediately before a jump, the lattice atom which will jump should be cool (as it has not jumped for a time τ), but the interstitial atom should be hot as it just completed a previous jump (on the average a time τ_i previously) and has not had time to cool off.

In Eqs. (24) and (25) above, the factor U implicitly contains the temperature θ in the denominator. Let

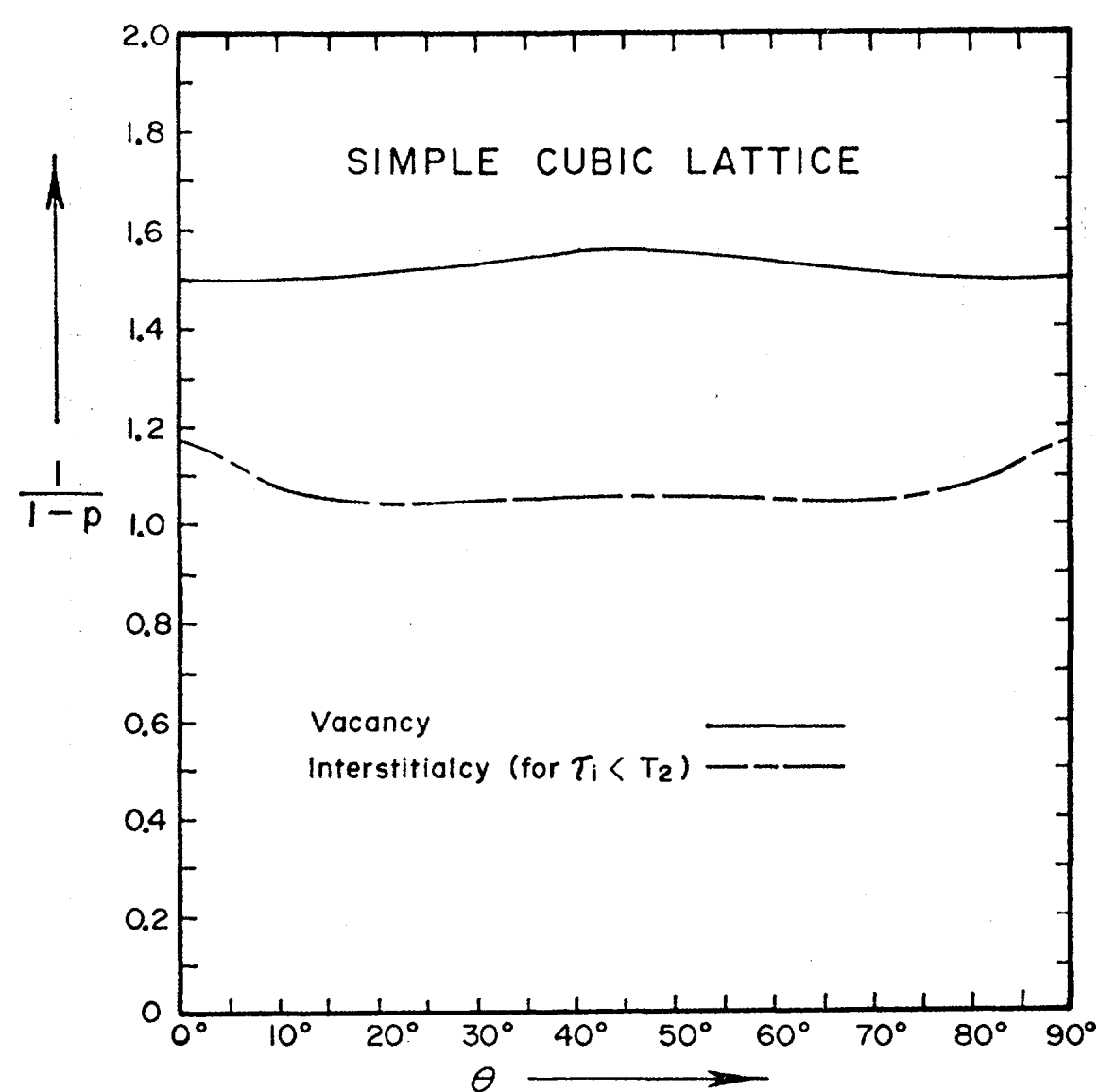


FIG. 5. A plot of $1/(1-p)$ versus θ for $\tau_i < T_2$ in a simple cubic crystal, assuming (a) vacancy diffusion and (b) interstitialcy diffusion.

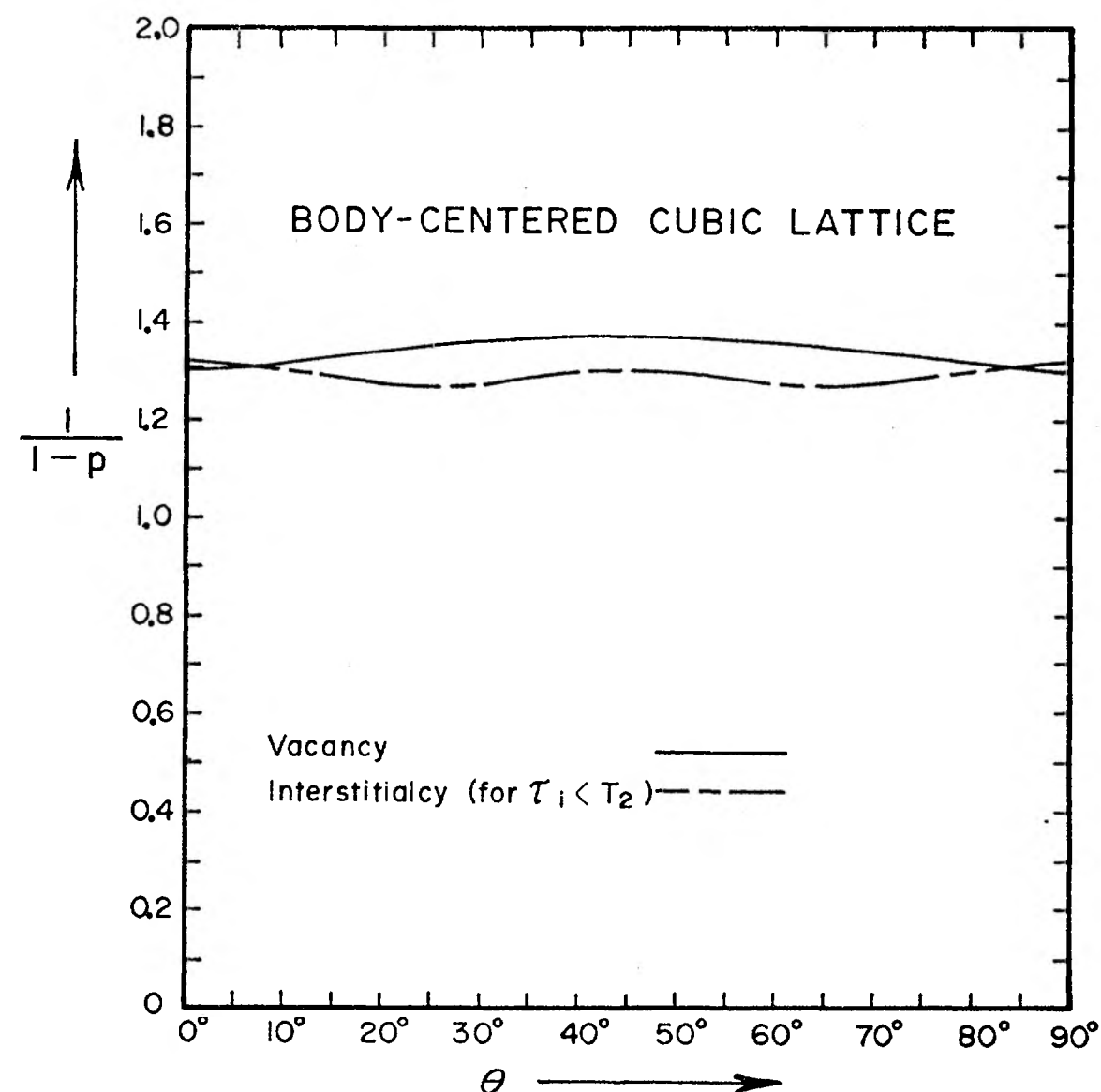


FIG. 6. A plot of $1/(1-p)$ versus θ for $\tau_i < T_2$ in a body-centered cubic crystal, assuming (a) vacancy diffusion and (b) interstitialcy diffusion.

us define a constant K by

$$U = K/\theta. \quad (32)$$

Then a correct expression replacing Eq. (25) would be

$$\langle\langle\Delta\bar{E}\rangle\rangle = \frac{2K}{GG'} \sum_{r,q} \left[\frac{\sum_i A_{iq}^2 - \sum_i A_{ir}A_{iq}}{\theta} + \frac{\sum_i A_{ir}^2 - A_{qr}^2 - \sum_i A_{ir}A_{iq}}{\theta'} \right]. \quad (33)$$

The first term represents the energy change of the initially normal lattice atom with respect to all atoms other than the neighboring interstitial, whereas the second term represents the energy change of the initially interstitial atom with respect to all lattice atoms other than the lattice atom which moves. θ is the initial temperature of the lattice atom (presumably the spin temperature of the entire system), whereas θ' is the initial temperature of the interstitial atom.

In order to derive a formula for p , we must first calculate θ' in terms of θ . This can be done by recognizing that the interstitial atom has been a lattice atom a time τ_i earlier, on the average, so that θ' also represents the *final* temperature of a jumping lattice atom [We note that if we replace θ' by θ in Eq. (33) we get Eq. (25).]

If we consider an atom at a lattice site q which jumps into an interstitial site r , we can calculate the mean energy $\langle\langle\bar{E}_f\rangle\rangle$ of the atom in the final site.

$$\begin{aligned} \langle\langle\bar{E}_f\rangle\rangle &= \text{Tr}(\rho_f \mathcal{H}_{df}) \\ &= - \left[\frac{2K}{GG'} \sum_{r,q} (\sum_i A_{ir}^2 - A_{qr}^2) \right] / \theta'. \quad (34) \end{aligned}$$

TABLE I. Results for vacancy diffusion.

	Simple cubic $\langle 100 \rangle$	Body-centered cubic jump direction $\langle 111 \rangle$	Face-centered cubic $\langle 110 \rangle$
$\sum_q A_{qr}^2$	$(\gamma^4 \hbar^4 / a^6)(3.0 - 2.25 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(0.0 + 4.74074 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(12.0 + 9 \sin^2 \theta)$
$\sum_i A_{ir}^2$	$(\gamma^4 \hbar^4 / a^6)(3.33902 - 2.07366 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(3.73129 + 2.59580 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(17.2327 + 7.36236 \sin^2 \theta)$
$\sum_{i,q} A_{ir} A_{iq}$	$(\gamma^4 \hbar^4 / a^6)(3.65865 - 1.68193 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(6.99067 + 1.97785 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(29.2149 + 14.7679 \sin^2 \theta)$
G	6	8	12
p	$\frac{1.109775 - 0.655322 \sin^2 \theta}{3.33902 - 2.07366 \sin^2 \theta}$	$\frac{6.99067 + 6.71859 \sin^2 \theta}{29.85032 + 20.76640 \sin^2 \theta}$	$\frac{41.2149 + 23.7679 \sin^2 \theta}{206.7924 + 88.34832 \sin^2 \theta}$
$1/1-p$	$\frac{3.33902 - 2.07366 \sin^2 \theta}{2.229245 - 1.418338 \sin^2 \theta}$	$\frac{29.85032 + 20.76640 \sin^2 \theta}{22.85965 + 14.04781 \sin^2 \theta}$	$\frac{206.7924 + 88.34832 \sin^2 \theta}{165.5775 + 64.5084 \sin^2 \theta}$

However, a fundamental assumption of our theory is that the spin orientation of the jumping atom is the same immediately after the jump as it was immediately before. This means that $\rho_f = \rho_i$. So, if we substitute into the above formula, we get

$$\langle \langle \bar{E}_f \rangle \rangle = \text{Tr}(\rho_i \mathcal{C}_{df}^0) = - \left[\frac{2K}{GG'} \sum_{r,q} \sum_i A_{ir} A_{iq} \right] / \theta. \quad (35)$$

By equating Eqs. (34) and (35), we get

$$\frac{1}{\theta'} = \frac{1}{\theta} \frac{\sum_{r,q} \sum_i A_{ir} A_{iq}}{\sum_{r,q} (\sum_i A_{ir}^2 - A_{qr}^2)}. \quad (36)$$

Thus

$$\begin{aligned} \langle \langle \Delta \bar{E} \rangle \rangle &= \frac{2U}{GG'} \left[\sum_{i,r,q} A_{iq}^2 - \sum_{i,r,q} A_{ir} A_{iq} \right. \\ &\quad + \frac{\sum_{i,r,q} A_{ir} A_{iq}}{\sum_{i,r,q} A_{ir}^2 - \sum_{r,q} A_{qr}^2} \\ &\quad \left. \times \left(\sum_{i,r,q} A_{ir}^2 - A_{qr}^2 - \sum_{i,r,q} A_{ir} A_{iq} \right) \right] \quad (37) \\ &= \frac{2U}{GG'} \left(\sum_{i,r,q} A_{iq}^2 \right) \left(1 - \frac{\sum_{i,r,q} A_{ir} A_{iq}}{\sum_{i,r,q} A_{ir}^2} \right) \\ &\quad \times \frac{\sum_{i,r,q} A_{ir} A_{iq}}{\sum_{i,r,q} A_{ir}^2 - \sum_{r,q} A_{qr}^2}. \quad (38) \end{aligned}$$

Therefore

$$p = \frac{\sum_{i,r,q} A_{ir} A_{iq}}{\sum_{i,r,q} A_{iq}^2} \frac{\sum_{i,r,q} A_{ir} A_{iq}}{\sum_{i,r,q} A_{ir}^2 - \sum_{r,q} A_{qr}^2}. \quad (39)$$

This is the formula for p which should apply to the case of interstitialcy diffusion when $\tau_i < T_2$. (Of course, we have neglected the fact that one of the neighbors of the interstitial atom is hot from previous jumping, as discussed above in Sec. IV A.)

C. Interstitial Diffusion

It should be observed that there is a fundamental difference between interstitial diffusion and the other two types of diffusion considered in this paper (vacancy and interstitialcy). In interstitial diffusion only the interstitial atoms jump and the normal stitial atoms do not jump, whereas in the other cases the normal atoms eventually jump. This means that, in the case of interstitial diffusion, there is the possibility of a "thermal bottleneck" in which the "hot" interstitial atom jumps again before it has had a chance to cool down. Nevertheless, if τ_i , the mean time between interstitial jumps, is long compared to T_2 , then the interstitial atom can "cool down" between jumps in which case each new jump will result in the energy change predicted in Eqs.

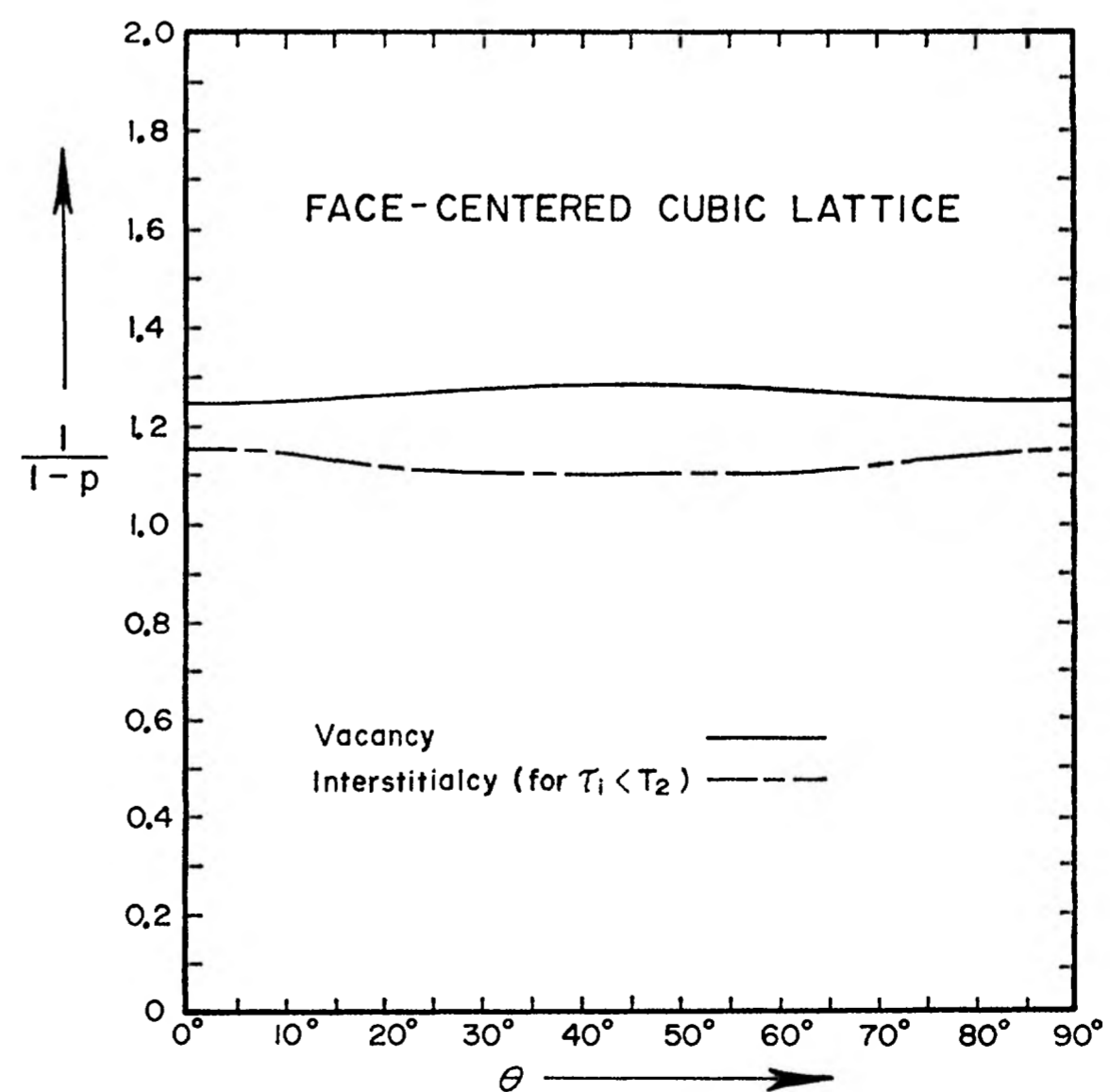


FIG. 7. A plot of $1/(1-p)$ versus θ for $\tau_i < T_2$ in a face-centered cubic crystal, assuming (a) vacancy diffusion and (b) interstitialcy diffusion.

TABLE II. Results for interstitialcy diffusion for $\tau_i > T_2$.

	Simple cubic $\langle 111 \rangle$	Body-centered cubic jump direction $\langle 100 \rangle$	Face-centered cubic $\langle 100 \rangle$
G'	1	3	1
G	8	2	6
$(1/GG') \sum_{r,q} A_{qr}^2$	$(\gamma^4 \hbar^4 / a^6)(0.0 + 0.592512 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(32.0 - 24 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(32.0 - 24 \sin^2 \theta)$
$(1/GG') \sum_{i,r,q} A_{ir} A_{iq}$	$(\gamma^4 \hbar^4 / a^6)(0.437010 + 0.123607 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(5.87674 - 0.891858 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(19.5129 - 8.97069 \sin^2 \theta)$
$(1/G') \sum_{i,r} A_{ir}^2$	$(\gamma^4 \hbar^4 / a^6)(0.392772 + 4.66933 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(69.9881 - 45.1034 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(196.458 - 140.077 \sin^2 \theta)$
$(1/G) \sum_{i,q} A_{iq}^2$	$(\gamma^4 \hbar^4 / a^6)(3.33902 - 2.07366 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(3.73129 + 2.59580 \sin^2 \theta)$	$(\gamma^4 \hbar^4 / a^6)(17.2327 + 7.36236 \sin^2 \theta)$
p	$0.481248 - 3.829604 \sin^2 \theta$ $3.33902 - 2.07366 \sin^2 \theta$	$-26.234620 + 19.319684 \sin^2 \theta$ $3.73129 + 2.59580 \sin^2 \theta$	$-125.432 + 98.136 \sin^2 \theta$ $17.2327 + 7.36236 \sin^2 \theta$
$1/1-p$	$3.33902 - 2.07366 \sin^2 \theta$ $2.857772 + 1.755944 \sin^2 \theta$	$3.73129 + 2.59580 \sin^2 \theta$ $29.965910 - 16.723884 \sin^2 \theta$	$17.2327 + 7.36236 \sin^2 \theta$ $142.665 - 90.774 \sin^2 \theta$

TABLE III. Results for interstitialcy diffusion for $\tau_i < T_2$.

	Simple cubic	Body-centered cubic	Face-centered cubic
p	$0.190978 + 0.108035 \sin^2 \theta + 0.015279 \sin^4 \theta$ $1.311474 + 12.798101 \sin^2 \theta - 8.453934 \sin^4 \theta$	$34.53607 - 10.48244 \sin^2 \theta + 0.79541 \sin^4 \theta$ $141.7446 + 19.8666 \sin^2 \theta - 54.7802 \sin^4 \theta$	$380.7533 - 350.0884 \sin^2 \theta + 80.4733 \sin^4 \theta$ $2834.055 - 789.521 \sin^2 \theta - 854.601 \sin^4 \theta$
1	$1.311474 + 12.798101 \sin^2 \theta - 8.453934 \sin^4 \theta$	$141.7446 + 19.8666 \sin^2 \theta - 54.7802 \sin^4 \theta$	$2834.055 - 789.521 \sin^2 \theta - 854.601 \sin^4 \theta$
$1-p$	$1.120497 + 12.690066 \sin^2 \theta - 8.469213 \sin^4 \theta$	$107.2085 + 30.3490 \sin^2 \theta - 55.5756 \sin^4 \theta$	$2453.302 - 439.433 \sin^2 \theta - 935.074 \sin^4 \theta$
$\left(\frac{1}{1-p}\right)_m / \left(\frac{1}{1-p}\right)_{\theta=0}^a$	0.8936 ^a	0.9611 ^a	0.9527 ^a

^a The minimum value of $1/(1-p)$ occurs at $\theta = 25^\circ$ for the sc and bcc lattices and at $\theta = 35^\circ$ for the fcc lattice.

(18c) and (31).¹⁷ However, in a real solid it may be difficult to satisfy $\tau_i > T_2$ at temperatures high enough for the motion to have an appreciable effect on the relaxation time. In that case the strong-collision-type calculation described in Sec. III C of this paper would not be valid. Nevertheless, if the mean time τ that a *lattice atom* must wait between successive encounters with interstitial atoms is long compared to T_2 , then the lattice atoms will achieve a common spin temperature prior to each encounter. We will thus get a narrowing of the resonance linewidth. However, the mean energy change of a *lattice atom* resulting from an encounter with an interstitial atom should be very much smaller than the energy change for vacancy or interstitialcy diffusion, since most of the atom's dipolar energy is not changed in the former case. Thus more encounters would be required to relax the magnetization, with the result that the rotating-frame relaxation time will be much longer than would be predicted for the strong collision

¹⁷ This would be valid only for spin- $\frac{1}{2}$ nuclei. For larger spins quadrupolar interactions should be taken into account. However, if $\tau_i \delta \omega_q \ll 1$, where $\delta \omega_q$ is the quadrupolar splitting, then the quadrupolar coupling will result in weak collisions for the jumping nuclei. These will be small compared to the strong effects of the dipolar coupling in the case of vacancy or interstitialcy diffusion.

cases.¹⁸ Also, more encounters would be required before motional narrowing could set in with the result that the "neck" of the T_2 curve will occur at a higher temperature. The rotating-frame relaxation-time minimum will still occur at the onset of motional narrowing, but this should occur at a higher temperature for interstitial diffusion than would be expected for vacancy or interstitialcy diffusion. Hence, it would be possible to distinguish interstitial diffusion from vacancy or interstitialcy diffusion only if the jump time τ can be measured by an independent technique (like radioactive tracers).

V. CALCULATION OF $(1/G') \sum_{i,r} A_{ir}^2$ AND $(1/GG') \sum_{i,r,q} A_{ir} A_{iq}$

As we saw in Eq. (5),

$$A_{ir} = \frac{1}{2} \gamma^2 \hbar^2 \frac{1 - 3 \cos^2 \theta_{ir}}{R_{ir}^3}, \quad (5')$$

where θ_{ir} is the angle between the applied field and the internuclear vector \mathbf{R}_{ir} .

¹⁸ The dependence of the mean time τ between encounters upon the measured relaxation time could be calculated by a method similar to that described in Ref. 5.

TABLE IV. Results for interstitial diffusion for $\tau_i > T_2$.

	Simple cubic $\langle 100 \rangle$	Body-centered cubic (nearest-neighbor jumps) $\langle 100 \rangle$	Body-centered cubic (next-nearest-neighbor jumps) jump direction $\langle 110 \rangle$	Face-centered cubic $\langle 110 \rangle$
G'	1	3	3	1
G	6	4	8	12
$(1/GG') \sum_{i,r,q} A_{ir} A_{iq}$	$(\gamma^4 h^4 / a^6) (0.219040 - 0.419273 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (13.6386 - 10.2291 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (-11.6052 + 8.70434 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (-21.8656 + 16.3974 \sin^2 \theta)$
$(1/G') \sum_i A_{ir}^2$	$(\gamma^4 h^4 / a^6) (0.392772 + 4.66933 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (69.9881 - 45.1034 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (69.9881 - 45.1034 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (196.458 - 140.077 \sin^2 \theta)$
$\sum_i A_{ij}^2$	$(\gamma^4 h^4 / a^6) (3.33902 - 2.07366 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (3.73129 + 2.59580 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (3.73129 + 2.59580 \sin^2 \theta)$	$(\gamma^4 h^4 / a^6) (17.2327 + 7.36236 \sin^2 \theta)$
p	$3.165288 - 7.162263 \sin^2 \theta$	$-52.61821 + 37.4701 \sin^2 \theta$	$-77.8620 + 56.4035 \sin^2 \theta$	$-201.0909 + 163.18676 \sin^2 \theta$
	$3.33902 - 2.07366 \sin^2 \theta$	$3.73129 + 2.59580 \sin^2 \theta$	$3.73129 + 2.59580 \sin^2 \theta$	$17.2327 + 7.36236 \sin^2 \theta$
	$3.33902 - 2.07366 \sin^2 \theta$	$3.73129 + 2.59580 \sin^2 \theta$	$3.73129 + 2.59580 \sin^2 \theta$	$17.2327 + 7.36236 \sin^2 \theta$
$1/(1-p)$	$0.173732 + 5.088603 \sin^2 \theta$	$56.34950 - 34.8743 \sin^2 \theta$	$81.5933 - 53.8077 \sin^2 \theta$	$218.3236 - 156.4544 \sin^2 \theta$

Now let us assume a rectangular coordinate system with axes parallel to the crystal's $\langle 100 \rangle$ direction. Suppose the applied field H_0 lay in the xz plane and made an angle θ with respect to the z axis. Then

$$\cos \theta_{ir} = \frac{\sin \theta X_{ir} + \cos \theta Z_{ir}}{R_{ir}}, \quad (40)$$

where X_{ir} and Z_{ir} are the x and z components of R_{ir} . If we restrict ourselves to cubic crystals for which terms linear in X_{ir} and Z_{ir} sum to zero, we get

$$\begin{aligned} \sum_{i,r} A_{ir}^2 = & \sum_{i,r} \frac{\gamma^4 h^4}{4R_{ir}^6} \left[1 - 6 \sin^2 \theta \left(\frac{X_{ir}}{R_{ir}} \right)^2 \right. \\ & - 6 \cos^2 \theta \left(\frac{Z_{ir}}{R_{ir}} \right)^2 + 9 \sin^4 \theta \left(\frac{X_{ir}}{R_{ir}} \right)^4 \\ & \left. + 9 \cos^4 \theta \left(\frac{Z_{ir}}{R_{ir}} \right)^4 + 54 \sin^2 \theta \cos^2 \theta \left(\frac{X_{ir} Z_{ir}}{R_{ir}^2} \right)^2 \right]. \quad (41) \end{aligned}$$

This is equivalent to formula (A4) of Ref. 8. Because of the cubic symmetry, we have that

$$\sum_{i,r} \frac{X_{ir}^2}{R_{ir}^2} = \sum_{i,r} \frac{Z_{ir}^2}{R_{ir}^2} \quad (42a)$$

and

$$\sum_{i,r} \frac{X_{ir}^4}{R_{ir}^4} = \sum_{i,r} \frac{Z_{ir}^4}{R_{ir}^4}. \quad (42b)$$

We then get

$$\begin{aligned} \frac{1}{G'} \sum_{i,r} A_{ir}^2 = & \frac{\gamma^4 h^4}{4G'} \sum_{i,r} \left(\frac{1}{R_{ir}} \right)^6 \left\{ \left[1 - 6 \left(\frac{Z_{ir}}{R_{ir}} \right)^2 + 9 \left(\frac{Z_{ir}}{R_{ir}} \right)^4 \right] \right. \\ & \left. + \frac{9}{2} \sin^2 \theta \left[3 \left(\frac{X_{ir} Z_{ir}}{R_{ir}^2} \right)^2 - \left(\frac{Z_{ir}}{R_{ir}} \right)^4 \right] \right\}. \quad (43) \end{aligned}$$

Similarly for $(1/GG') \sum_{i,r,q} A_{ir} A_{iq}$ we get

$$\begin{aligned} \frac{1}{GG'} \sum_{i,r,q} A_{ir} A_{iq} = & \frac{\gamma^4 h^4}{4GG'} \sum_{i,r,q} \frac{1}{R_{ir}^3 R_{iq}^3} \left\{ \left[1 - 3 \left(\frac{Z_{ir}}{R_{ir}} \right)^2 \right. \right. \\ & \left. \left. - 3 \left(\frac{Z_{iq}}{R_{iq}} \right)^2 + 9 \left(\frac{Z_{ir} Z_{iq}}{R_{ir} R_{iq}} \right)^2 \right] + \frac{9 \sin^2 \theta}{R_{ir}^2 R_{iq}^2} \right. \\ & \left. \times \left[\frac{1}{4} (Z_{ir}^2 - X_{ir}^2) (X_{iq}^2 - Z_{iq}^2) + X_{ir} X_{iq} Z_{ir} Z_{iq} \right] \right\}. \quad (44) \end{aligned}$$

For noncubic crystals, there would be an extra term proportional to $\sin^2 \theta$ in both Eqs. (43) and (44).

VI. RESULTS

We have calculated p versus θ for bcc, fcc, and sc lattices for vacancy, interstitialcy, and interstitial diffusion using the UNIVAC 1108 digital computer at the

TABLE V. $[1/(1-p)]_{\theta=\pi/4}/[1/(1-p)]_{\theta=0}$ for different mechanisms in different lattices for $\tau_i > T_2$.

	Simple cubic	Body-centered cubic	Face-centered cubic
Vacancy	1.0409	1.05032	1.0267
Interstitialcy	0.23472	3.8372	3.9240
Interstitial (nearest neighbors)	0.012603	4.4509	5.0365
Interstitial (next-nearest neighbors)		4.9797	

University of Utah computer laboratory to perform the lattice sums. Each of the programs was checked by hand calculation out to at least one atomic shell. The interstitial results have been calculated for $\tau_i > T_2$ only, whereas the interstitialcy results have been calculated for both cases: $\tau_i > T_2$ and $\tau_i < T_2$.

A. Vacancy Diffusion

For vacancy diffusion we assumed jumps to nearest-neighbor positions only. The results are summarized in Table I.

B. Interstitialcy Diffusion

For the sc lattice we assumed that the interstitial atom sits in the center of the primitive cell. For both the fcc and bcc lattices we assumed that the interstitial sites are at the center of the cube edges. Our results are contained in Table II (for $\tau_i > T_2$) and in Table III (for $\tau_i < T_2$).

C. Interstitial Diffusion

For interstitial diffusion, we calculated our parameters for jumps to the nearest vacant interstitial site. In the bcc case, we also performed a calculation assuming jumps to the next-nearest interstitial site. These results are summarized in Table IV.

The ratio of the maximum value of $1/1-p$ (at $\theta = \frac{1}{4}\pi$) to the minimum (at $\theta = 0$) for $\tau_i > T_2$ is plotted in Table V.

VII. CONCLUSIONS

In Figs. 2-4, we have plotted $1/1-p$ versus θ for each type of mechanism considered in each of our

¹⁹ We note that, in zero field, the angular dependence of T in Eq. (22) is identical to that of $1/(1-p)$. {We should bear in mind that this is not the case if H_1 is nonzero, for in that case we would have to correct for the angular dependence of the local field. Alternatively, it is easy to perform an adiabatic demagnetization of H_1 [see F. M. Lurie, thesis, University of Illinois (unpublished)] so that the relaxation is indeed observed in zero field.}

crystals. As we can see, in each crystal there are very striking differences among the results for the different mechanisms. These suggest a method for discriminating between different diffusion mechanisms for crystals with very long T_1 . The low-field relaxation time¹⁹ for a single crystal can be measured as a function of angle and compared with calculated results like the ones in Figs. 2-4. In this way incompatible mechanisms can be eliminated. (Of course, these results are valid only for spin- $\frac{1}{2}$ nuclei.¹⁷)

The results for vacancy and interstitialcy diffusion, valid for $\tau_i < T_2$, are plotted in Figs. 5-7. To distinguish these mechanisms from each other would require experimental precision of the order of 10% which is not too difficult to achieve. For $\tau_i < T_2$, a measurement of the temperature dependence of the rotating-frame relaxation time may distinguish interstitial diffusion from the other two mechanisms as discussed in Sec. IV C.

Experimental departures from the results described above may suggest mechanisms other than the ones considered here,²⁰ in which case additional calculations similar to those described in this paper would be necessary for these mechanisms.

Further calculations appropriate to other types of crystal structure are planned at the present time. In addition, experiments designed to verify these calculations are in progress in our laboratory.

ACKNOWLEDGMENTS

We wish to thank Professor B. G. Dick, Professor Earl Hygh, and, especially, Professor Peter Gibbs for reading the manuscript and making useful suggestions. Discussions with Professor C. P. Slichter about the effects of interstitial diffusion have been quite valuable. Professor Al Redfield was kind enough to check our calculations for interstitialcy diffusion for $\tau_i < T_2$. We are greatly obligated to Robert Huerta for writing the computer programs for all the lattice sums in this paper. One of the authors (P.-P. H.) is grateful to the Ministry of National Defense of the Republic of China for a scholarship grant to study in the United States.

²⁰ In α Fe, for instance, which is bcc, there is some evidence, based on radiation damage experiments [C. Erginsoy, G. H. Vinyard, and A. Englert, Phys. Rev. **133**, A595 (1964)] and Born-Mayer-type calculations [R. A. Johnson, Phys. Rev. **134**, A1329 (1964)] that the stable interstitial configuration could be a split interstitial aligned along the $\langle 110 \rangle$ direction. The calculations of H. B. Huntington [Phys. Rev. **91**, 1092 (1953)] and of R. A. Johnson and E. Brown [Phys. Rev. **127**, 446 (1962)] indicate that for Cu, which is fcc, a $\langle 100 \rangle$ split interstitial would have formation energy comparable to that of the so-called "body-centered interstitial" which we have considered here.