Table 1.

T/K	ν_1/MHz $m(\pm 3/2) \rightleftarrows m(\pm 1/2)$	ν_2/MHz $m(\pm 5/2) \rightleftarrows m(\pm 3/2)$	η	$\frac{e^2 q Q/h}{\text{MHz}}$
77	45.248 ± 0.005	83.478 ± 0.005	0.2580 ± 0.0001	281.892 ± 0.005
123	45.247 ± 0.005	83.561 ± 0.005	0.2562 ± 0.0001	282.128 ± 0.005
153	45.232 ± 0.005	83.619 ± 0.005	0.2544 ± 0.0001	282.280 ± 0.005
213	45.173 ± 0.005	83.749 ± 0.005	0.2495 ± 0.0001	282.581 ± 0.005
253	45.097 ± 0.005	83.850 ± 0.005	0.2444 ± 0.0001	282.789 ± 0.005
296	44.976 ± 0.005	83.960 ± 0.005	0.2372 ± 0.0001	282.977 ± 0.005
313	44.900 ± 0.005	83.994 ± 0.005	0.2334 ± 0.0001	282.992 ± 0.005
363	44.616 ± 0.005	84.043 ± 0.005	0.2204 ± 0.0001	282.838 ± 0.005
398	44.327 ± 0.005	83.994 ± 0.005	0.2087 ± 0.0001	282.401 ± 0.005

The small influence of $q(\mathrm{e})$ in periodates can be understood from the fact that for a I^{7+}-ion the Sternheimer factor γ_∞ should be small compared to I^-. Also for I^- in "ionic" crystals such as $\mathrm{NH_4TlI_4 \cdot 2\,H_2O}$ or $\mathrm{Me_2PtI_6}$, the main contribution of $e^2 q Q/h$ is due to $q(\mathrm{p})$.

The hydrogen bond plays an important role in the intramolecular interactions within crystalline $\mathrm{H_5IO_6}$. A comparison of the ^{127}I-NQR spectra in $\mathrm{D_5IO_6}$ and $\mathrm{H_5IO_6}$ will be quite interesting in this respect.

Nuclear Spin Relaxation by Defect Mechanisms of Self-Diffusion in Crystals

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The present paper shows how to incorporate the correlation between successive nuclear jumps, which are well known to play a role in defect mechanisms of self-diffusion in crystals, into the calculation of the correlation functions describing the temperature dependence of the nuclear spin relaxation in solids. The treatment is based on an extension of Torrey's theory of nuclear spin relaxation by randomly migrating nuclei. Explicit and detailed results are given for the monovacancy mechanisms of self-diffusion in an isotopically pure face-centred cubic crystal.

I. Introduction

Bloembergen, Purcell and Pound (BPP)[1] showed that the time dependent nuclear magnetic spin-spin coupling is one of the most powerful mechanisms for bringing about spin-lattice relaxation in liquids and solids. In monoatomic solids this time dependence is due to atomic diffusion which may be characterized by the (temperature dependent) mean time of stay of a nucleus on a given lattice site, τ, henceforth called the "mean jump time".

Information about diffusional motions may be obtained from the measurement of the temperature dependence of the spin lattice relaxation time either in the laboratory frame, T_1, where the splitting of the Zeeman-levels is due to the constant external magnetic field $\boldsymbol{H}_0$, or in the rotating frame $T_{1\varrho}$, where — in resonance — this splitting results from the rotating field with amplitude H_1. If relaxation is observed in relaxation fields $\boldsymbol{H}_0$ or $\boldsymbol{H}_1$ that are large compared with the internal local fields, the temperature variation of T_1 and $T_{1\varrho}$ may be interpreted by means of perturbation theory. In this way one obtains for T_1 due to the magnetic dipolar interaction of like spins[2]

$$\frac{1}{T_1} = \frac{3}{2}\,\gamma^4 \hbar^2 I(I+1)\left[J^{(1)}(\omega_0) + J^{(2)}(2\,\omega_0)\right]. \tag{1.1}$$

Here $J^{(q)}(\omega)$ is the Fourier-transform of the correlation function[2]

$$G^{(q)}(\tau) = \sum_j \langle F_{ij}^{(q)}(t)\, F_{ij}^{(q)*}(t+\tau)\rangle_t\,. \tag{1.2}$$

The $F^{(q)}(t)$ are functions depending on the relative distance and orientation of two spins i and j. q may assume the values 0, 1, or 2[2].

For the spin-lattice relaxation time in the rotating frame, $T_{1\varrho}$, Look and Lowe derived[3]

$$\frac{1}{T_{1\varrho}} = \frac{3}{8}\,\gamma^4 \hbar^2 I(I+1)\,J_0(2\,\omega_1)\,. \tag{1.3}$$

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[1] N. Bloembergen, E. M. Purcell and R. V. Pound, Phys. Rev. **73**, 679 [1948].

[2] A. Abragam, The Principles of Nuclear Magnetism, Clareedon Press, Oxford 1961.

[3] D. C. Look and I. J. Lowe, J. Chem. Phys. **44**, 2995 [1966].

ω_1 is the Larmor frequency due to the rotating field $H_1 (\omega_1 = \gamma H_1)$. As we see from Eqs. (1.1) and (1.3), the precise shape of the correlation functions $G^{(q)}(\tau)$ $(q = 0, 1, 2)$ enters into the relationship between the nuclear spin relaxation times and the mean jump time, τ. The shape of $G^{(q)}(\tau)$ depends strongly on the mechanism by which nuclear magnetization is carried from one lattice site to another.

A random walk model of self-diffusion, as treated by TORREY[4] (see Sect. II), is not quite realistic, since in most crystalline solids diffusion involves intrinsic point defects, e.g., vacant lattice sites. Even when the vacancies migrate randomly in direction and time, the nuclei do not, since the vacancies correlate the directions of successive nuclear jumps and the time interval after which these jumps occur.

As pointed out qualitatively by EISENSTADT and REDFIELD[5], these correlation effects cause the jumps of a given nucleus to be bunched into groups. Since we are dealing with temporal correlation functions the time scale for successive jumps enters into the correlation function and this bunching effect must be taken into account.

In Sections III to VI we calculate the correlation functions $G^{(q)}(\tau)$ taking into account the correlations between the jumps of a point defect and the jumps of a nucleus. Our starting point is Torrey's random walk model[4].

In Sect. VII the general considerations of the previous sections are applied to self-diffusion by a monovacancy mechanism in a face-centred cubic lattice.

II. Torrey's Model for Lattice Diffusion in Isotropic Bodies

Replacing the time average in Eq. (1.2) by an ensemble average, we may write for the correlation functions $G^{(q)}(\tau)$ (e.g., for $q = 1$) as follows[4]:

$$G^{(1)}(\tau) = \sum_j \langle F_{ij}^{(1)}(t)\, F_{ij}^{(1)*}(t+\tau)\rangle_t \tag{2.1}$$
$$= \iint f(\boldsymbol{r}_0)\, F_{ij}^{(1)}(\boldsymbol{r}_0)\, P(\boldsymbol{r}, \boldsymbol{r}_0, t)\, F_{ij}^{(1)*}(\boldsymbol{r})\, \mathrm{d}\boldsymbol{r}_0\, \mathrm{d}\boldsymbol{r}.$$

$(1/N)\, f(\boldsymbol{r}_0)\, \mathrm{d}\boldsymbol{r}_0$ is the probability that at zero time $(t = 0)$ spin j is located in the volume-element $\boldsymbol{r}_0$, $\boldsymbol{r}_0 + \mathrm{d}\boldsymbol{r}_0$ relative to spin i; thus $f(\boldsymbol{r}_0)$ is the initial spin-density.

$F_{ij}^{(1)}(\boldsymbol{r}_0)$ is given by the equation (see e.g. [2])

$$F_{ij}^{(1)}(\boldsymbol{r}_0) = \sin\Phi_{ij}\cos\Phi_{ij}\,(e^{i\varphi_{ij}}/r_{ij}^3)\,. \tag{2.2}$$

r_{ij}, Φ_{ij}, and φ_{ij} are the spherical coordinates of spin j relative to spin i. When internal motions occur, these coordinates are functions of the time. $P(\boldsymbol{r}, \boldsymbol{r}_0, t)$ is the probability that, if spin j was at zero time in the volume element $\boldsymbol{r}_0$, $\boldsymbol{r}_0 + \mathrm{d}\boldsymbol{r}_0$, at time t spin j is located in the element $\boldsymbol{r}$, $\boldsymbol{r} + \mathrm{d}\boldsymbol{r}$ relative to spin i.

For the calculation of $P(\boldsymbol{r}, \boldsymbol{r}_0, t)$ Torrey used the following model: All spin-positions are assumed to be statistically equivalent, i.e., at each position the same probability $P_1(\boldsymbol{r})\,\mathrm{d}\boldsymbol{r}$ exists that after one flight from this position the new position will be in the volume-element $\boldsymbol{r}$, $\boldsymbol{r} + \mathrm{d}\boldsymbol{r}$ relative to the previous position. The corresponding probability after n flights is designated by $P_n(\boldsymbol{r})$.

If spin i and spin j move in a random manner, spin i may be assumed to be fixed at the origin while spin j diffuses with double jump frequency. For this model $P(\boldsymbol{r}, \boldsymbol{r}_0, t)$ is equal to $P(\boldsymbol{r} - \boldsymbol{r}_0, 2t)$. This quantity may be calculated from CHANDRASEKHARS theory of random flights[6].

With

$$A(\boldsymbol{\rho}) = \int P_1(\boldsymbol{r})\, e^{i\boldsymbol{\rho}\boldsymbol{r}}\, \mathrm{d}\boldsymbol{r} \tag{2.3}$$

we may write

$$P(\boldsymbol{r} - \boldsymbol{r}_0, 2t) \tag{2.4}$$
$$= \frac{1}{8\pi^3}\int \exp\left[-i\,\boldsymbol{\rho}\left(\boldsymbol{r} - \boldsymbol{r}_0\right) - \frac{2t}{\tau}\left(1 - A(\boldsymbol{\rho})\right)\right]\mathrm{d}\boldsymbol{\rho}\,.$$

For isotropic diffusion $[A(\boldsymbol{\rho}) = A(\varrho)$ and $f(\boldsymbol{r}_0) = n$, i.e., the uniform spin-density is constant] Torrey's result ist

$$J_1(\omega) = \frac{8\pi n\tau}{15a^3}\int_0^\infty J_{3/2}^2(a\varrho)\,\frac{1 - A(\varrho)}{(1 - A(\varrho))^2 + (\omega\tau/2)^2}\,\frac{\mathrm{d}\varrho}{\varrho}\,. \tag{2.5}$$

a is the lower limit of the integration over $\boldsymbol{r}$ and $\boldsymbol{r}_0$ and may be interpreted as the distance of closest approach between two spins. $J_{3/2}(a\varrho)$ is the Bessel function of order 3/2.

All informations about the specific character of the random walk underlying Eq. (2.5) must be cast into $A(\varrho)$ [Eq. (2.3)].

For a nucleus walking randomly in direction but making jumps of equal length l Torrey assumed

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[4] H. C. TORREY, Phys. Rev. **92**, 962 [1953].

[5] M. EISENSTADT and A. G. REDFIELD, Phys. Rev. **132**, 635 [1963].

that $P_1(r)$ should be given by

$$P_1(r) = \delta(r-l)/4\pi l^2 . \qquad (2.6)$$

The corresponding $A(\varrho)$ is given by

$$A(\varrho) = \sin(l\varrho)/l\varrho . \qquad (2.7)$$

As pointed out by Torrey this model is an excellent approximation for the interpretation of NMR-measurements in powdered samples: In reality a nucleus may jump from each lattice site into one of the K equivalent nearest neighbour positions instead of the jumps to every point of a sphere underlying Torrey's model. But, for the application to powered samples, we would have to average the "true" correlation function for lattice diffusion in a single crystal with respect to the direction of the relaxation field. Because of mathematical difficulties this precise calculation may only be performed in the extreme case where $\omega_0\tau \gg 1$. In Torrey's model [Eq. (2.7)] the angular average is performed in an unprecise way. But the results of this approximation differ from the precise calculation by less than 1%.

III. Spatial and Temporal Correlation

In a defect mechanism of self-diffusion a wandering nucleus does not carry out a random motion, though the point-defect which causes these atomic jumps may walk randomly from one lattice site to the other. The influence of the correlation between the jumps of the wandering atom and the jumps of a point-defect on NMR is different from the well known "spatial" correlation, the nature of which may be detected from radio-active tracer-diffusion measurements (see e.g. [7]).

If a tracer-atom has just exchanged its site, say, with a vacancy, the probability that its next jump brings it back to its original position (which is now vacant) is larger than the probability that the next jump takes it to any other of the adjacent sites. A measure of the degree of this correlation is the correlation factor f defined by the relationship

$$D^{\mathrm{T}} = f \cdot D^{\mathrm{SD}} . \qquad (2.8)$$

D^{T}, the tracer self-diffusion coefficient, is defined as the diffusion coefficient of a tracer atom in the absence of concentration gradients of defects or atoms, and of temperature gradients or electric field gradients. D^{SD} is the macroscopic or "uncorrelated" self-diffusion coefficient.

In nuclear magnetic resonance we deal with temporal correlation functions and the fact that the individual jumps of a spin do not occur at constant time intervals must be taken into account. Consider the motion of a single nucleus: The probability per unit time for a displacement of this spin caused by a point defect is relatively small; it is determined by concentrations and jump frequencies of the defects. But after the initial jump a high probability exists that the same point-defect will cause one or two more jumps of the same nucleus shortly after the initial jump. After these correlated jumps of the nucleus a relatively long time will pass before the next point-defect causes jumps of this nucleus.

Following the nomenclature of EISENSTADT and REDFIELD [5] we call the individual displacements "jumps" while the series of jumps of a nucleus produced by the same point-defect is called an "encounter" between the point-defect and the nucleus. This aspect of the correlation between the random motion of the point defect and the motion of the nucleus is called "temporal correlation" analogous to the spatial correlation discussed above.

As we are dealing with correlation functions for the time dependence of the dipolar interaction between pairs of spins we must distinguish two aspects of the temporal correlation:

1. If the distance r_0 of the two spins i and j before an encounter is not more than a few jump distances, then the point defect is able to relate the jumps of the two spins. This effect is called "pair-correlation".

2. If r_0 is large compared with the lattice constant, then the point-defect is not able to relate the jumps of spin i to those of spin j.

There is always correlation between the successive jumps of a single spin if these jumps are caused by the same point-defect.

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[6] S. CHANDRASEKHAR, Revs. Mod. Phys. **15**, 1 [1943].

[7] A. D. LE CLAIRE in Physical Chemistry, An Advanced Treatise, Vol. X, Academic Press, W. Jost, ed., New York 1970, Chapter 5.

IV. A Model for Diffusion in Isotropic Bodies

In the high field region, to which this paper is restricted, perturbation theory may be applied to relate nuclear jumping to spin lattice relaxation, as long as the mean jump time τ is much smaller than the spin-lattice relaxation time due to processes other than diffusion, i.e., for $\tau < T_1^{\mathrm{rl}}$ (rl for "rigid lattice"). In physical terms this condition means that many nuclear jumps, or — in our model — many encounters must occur during the decay of a longitudinal non-equilibrium magnetization. Hence a single jump or encounter cannot be very effective in causing relaxation.

To estimate the details of the effect of an encounter between a point-defect and a pair of nuclei on the relaxation process we use the fact that the individual jumps within an encounter occur very rapidly after oneanother; i.e., the correlation time of these fluctuations within one encounter is much shorter than the time between two encounters. Hence all that enters into the correlation function is the change in relative orientation and distance of two spins due to an encounter with a point-defect.

Not all encounters result in a net displacement of the two spins relative to oneanother (e.g., if the last jumps of the encounter bring the nuclei back to their positions before the encounter). Because of the shortness of the time between these jumps we assume that these encounters do not cause relaxation and hence do not enter into the correlation function. The probability of the occurence of such encounters is denoted by $P(0)$.

Thus the number of jumps per second (in Torrey's model) must be replaced by the number of encounters per second which contribute to relaxation.

We denote the mean number of relative jumps of two spins during an encounter by Z and the mean time between two encounters by τ_{NMR}. Then the number of encounters per second is given by

$$\frac{1}{\tau_{\mathrm{NMR}}} = \frac{1}{\tau}\,\frac{1}{Z}\,(1 - P(0))\,. \tag{4.1}$$

In the following we neglect pair correlations and assume the jumps of the two spins of a pair to be independent of one-another. (How pair-correlations may be introduced into our model of diffusion will be pointed out in Sect. VI.)

This restriction permits us to assume spin i to be fixed in the origin while spin j diffuses with double jump-frequency. An encounter of spin j with a point-defect may result in different possible displacements l_j of spin j after the encounter relative to its position before the encounter. We further assume the single displacements to occur with different probabilities $P(l_j)$, which are the same ones for every lattice site.

For the calculation of $P(\boldsymbol{r}, \boldsymbol{r}_0, t)$ entering into the correlation functions $G^{(q)}(t)$ we use the following model for the diffusion process as seen in nuclear magnetic resonance in a high relaxation field:

We assume the diffusion process to be composed of encounters, the result of which is a displacement of spin j relative to its position before the encounter. The directions of the total displacements per encounter, l_j, are assumed to be random, while the occurence of a certain value of l_j is governed by the probabilities $P(l_j)$.

This model is very similar to Torrey's where all displacements are "jumps", while we are dealing with "encounters". The single steps of this random walk model result all in the same displacements l, while in our model different displacements may occur with different probabilities.

The present model approximates diffusional effects, observed by relaxation measurements in powdered samples, better than Torrey's model: e.g., in a face-centred cubic lattice the 12 possible jumps to the 12 nearest neighbour positions are replaced by jumps to random directions in Torrey's model, i.e., jumps may occur to any point of a sphere with radius equal to the nearest neighbour distance. In our model a spin may be displaced by more than only one nearest-neighbour distance as the result of an encounter, so that now more than only 12 directions may occur and therefore the model of random directions should even be a better approximation for a point-defect mechanism than for a random walk model.

V. Application of the Theory of Random Flights

CHANDRASEKHAR's "theory of random flights"[6] may be applied to the model for the calculation of $P(\boldsymbol{r}, \boldsymbol{r}_0, t)$ described above. For the probability $W_n(\boldsymbol{r} - \boldsymbol{r}_0)\,\mathrm{d}\boldsymbol{r}$ that after n encounters spin j is in the volume-element $\boldsymbol{r}, \boldsymbol{r} + \mathrm{d}\boldsymbol{r}$ relative to the starting point of the random walk we then have[6]

$$W_n(\boldsymbol{r}-\boldsymbol{r}_0)=\frac{1}{8\pi^3}\int\limits_{-\infty}^{+\infty} e^{-i\boldsymbol{\rho}(\boldsymbol{r}-\boldsymbol{r}_0)}A_n(\boldsymbol{\rho})\,\mathrm{d}\boldsymbol{\rho}\,, \quad (5.1)$$

where $A_n(\boldsymbol{\rho})$ is given by

$$A_n(\boldsymbol{\rho})=\prod_{j=1}^{n}\int P_j(\boldsymbol{r}_j)\,e^{i\boldsymbol{\rho}\boldsymbol{r}_j}\,\mathrm{d}\boldsymbol{r}_j\,. \quad (5.2)$$

$P_j(\boldsymbol{r}_j)$ denotes the probability that in the j-th encounter spin j is displaced by a vector $\boldsymbol{r}_j$ from its position before this encounter.

The motion of spin j is assumed to be isotropic, hence

$$A_n(\boldsymbol{\rho})=A_n(\varrho) \quad \text{and} \quad P_j(\boldsymbol{r}_j)=P_j(l_j)\,.$$

In the j-th encounter several total displacements l_j may occur with their respective probabilities $P(l_j)$. Hence we assume that

$$P_j(l_j)=\sum_{l_i>0}P(l_i)\,\frac{\delta(r_j-l_i)}{4\pi l_i^2}\,. \quad (5.3)$$

The sum goes over all l_i which are greater than zero and which can be achieved in one encounter. It converges very rapidly since the probabilities $P(l_i)$ become very small for values of l_i which are greater than about two jump distances (see Sect. VII).

With this form of $P_j(l_j)$ and Eq. (5.1) we obtain

$$W_n(\boldsymbol{r}-\boldsymbol{r}_0)=\frac{1}{8\pi^3}\int\limits_{-\infty}^{+\infty} e^{-i\boldsymbol{\rho}(\boldsymbol{r}-\boldsymbol{r}_0)}[A(\varrho)]^n\,\mathrm{d}\boldsymbol{\rho} \quad (5.4)$$

with

$$A(\varrho)=\sum_{l_i>0}P(l_i)\,\frac{\sin(\varrho l_i)}{\varrho l_i}\,. \quad (5.5)$$

Now we are able to calculate

$$P(\boldsymbol{r}-\boldsymbol{r}_0,2t)=\sum_n W_n(\boldsymbol{r}-\boldsymbol{r}_0)\,p_n(2t)\,, \quad (5.6)$$

where $p_n(2t)$ is the probability that the "jumping" nucleus j undergoes n encounters during the time $2t$.

If we assume a Poisson distribution for $p_n(2t)$,

$$p_n(2t)=\frac{1}{n!}\left(\frac{2t}{\tau_{\mathrm{NMR}}}\right)^n\exp\{-2t/\tau_{\mathrm{NMR}}\}\,, \quad (5.7)$$

then we obtain from Eq. (5.4), (5.5), and (5.6)

$$P(\boldsymbol{r},\boldsymbol{r}_0,t)=\frac{1}{8\pi^3}\int\exp\left[-i\,\boldsymbol{\rho}(\boldsymbol{r}-\boldsymbol{r}_0)-\frac{2t}{\tau_{\mathrm{NMR}}}(1-A(\varrho))\right]\mathrm{d}\boldsymbol{\rho}. \quad (5.8)$$

Eq. (5.8) has the same form as Torrey's Eq. (2.4). The difference of the two results is due to the fact that we replaced the mean time between successive nuclear jumps, τ, by the mean time between two successive encounters, τ_{NMR}, and that $A(\varrho)$ has a different form (see Eqs. (5.5) and (2.7)).

With the same modifications we may take over Torrey's result for the Fourier-transform of the correlation function $G^{(1)}(\tau)$:

$$J^{(1)}(\omega)=\frac{8\pi n\,\tau_{\mathrm{NMR}}}{15a^3}\int\limits_0^\infty J^2_{3/2}(a\,\varrho)\cdot\frac{1-A(\varrho)}{[1-A(\varrho)]^2+(\tfrac{1}{2}\omega\,\tau_{\mathrm{NMR}})^2}\,\frac{d\varrho}{\varrho} \quad (5.9)$$

$A(\varrho)$ and τ_{NMR} are given by the Eqs. (5.5) and (4.1), respectively. n denotes the spin density.

For the application of (5.9) to lattice diffusion in powdered samples the lower limit of integration over $\boldsymbol{r}_0$ and $\boldsymbol{r}$, a, must be determined from the normalization of the correlation function[4]. It may be derived easily that the value of a is the same for the two different models, namely $a=0.74335$[8].

VI. Pair Correlation

If the initial distance r_0 between the two spins of a pair before an encounter is comparable with the nearest-neighbour distance l, then the number of relative jumps per encounter is given by

$$Z=Z(0)+Z(r_0)\,. \quad (6.1)$$

$Z(0)$ denotes the number of jumps of a single spin during an encounter, while $Z(r_0)$ is the number of jumps of the other spin, a distance r_0 apart, which was assumed to rest in the origin (cf. Sect. IV and V). What we observe in a relaxation experiment is an average of the number of relative jumps and of the probabilities $P(l_i)$ over the initial distance r_0, since many encounters of a pair of nuclei with different point defects occur during the relaxation process (see Sect. IV). Hence the value of r_0 varies considerably during the relaxation process.

The average of Z and $P(l_i)$ may be performed as follows:

$$\bar{Z}=Z(0)+\sum_{r_0}(N(r_0)/N)(Z(r_0)\,, \quad (6.2)$$

$$\overline{P(l_i)}=\sum_{r_0}(N(r_0)/N)(P_{l_i}(r_0)\,. \quad (6.3)$$

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[8] H. C. Torrey, Phys. Rev. **96**, 690 [1954].

$N(r_0)$ denotes the number of spins a distance r_0 apart from a given reference spin, N the total number of spins, and depends thus on the lattice structure. By $P_{l_i}(r_0)$ we denote the probability that the change of the relative distance of a pair of spins due to an encounter is l_i, if the initial distance was r_0. $P_{l_i}(r_0)$ approaches the probabilities $P(l_i)$ with increasing r_0.

The calculation of $Z(r_0)$ and $P_{l_i}(r_0)$ would be a formidable task. Since, however, the value of $N(r_0)$ increases strongly with increasing r_0, while $Z(r_0)$ decreases to zero and $P_{l_i}(r_0)$ approaches the probabilities $P(l_i)$, we do not make a great mistake if we write

$$\bar{Z} = \bar{Z}(0) \tag{6.4}$$

and

$$\overline{P(l_i)} = P(l_i). \tag{6.5}$$

Eqs. (6.4) and (6.5) are equivalent to neglecting pair correlation.

VII. Monovacancy Diffusion in fcc-Crystals

In the following we shall neglect pair correlation (see the previous section) and demonstrate the principles of the calculation of the diffusion quantities needed for the evaluation of the Fourier spectrum of the correlation function [Eq. (5.9)] for an encounter between a monovacancy and a nucleus. For simplicity this nucleus will be called "tracer", though it is identical with the other nuclei of the sample.

VII.1. Calculation of $Z(0)$

The following definitions will help us to calculate the mean number of jumps per encounter, $Z(0)$:

By A_n we denote the probability that — within an encounter — the n-th jump of the tracer does (still) occur, while by $B(n)$ we denote the probability that an encounter consists of precisely n jumps.

We assume that $A_1 = 1$, i.e., the initial jump of the encounter is to occur surely, otherwise there is no encounter.

After the first jump of the tracer the vacancy continues its random walk through the crystal. With a certain probability it causes another jump of the tracer. This probability is given by the probability A_1 and by the probabilities $W(j)$ of the vacancy sitting on one of the neighbouring sites j of the tracer some time after the initial jump. Hence

$$A_2 = A_1 \frac{1}{K} \sum_{j1} W(j). \tag{7.1}$$

The sum runs over all lattice sites which are neighbours of the tracer after its first jump. K is the number of nearest neighbours of the respective lattice (e.g. $K = 12$ for fcc lattice).

After the second tracer jump again the same probabilities $W(j)$ exist, provided equivalent sites are given the same numbers as after the initial jump. Hence

$$A_3 = A_1 A_2 (1/K) \sum_j W(j) = [(1/K) \sum_j W(j)]^2. \tag{7.2}$$

In this way we may write for the probability A_n

$$A_n = [(1/K) \sum_j W(j)]^{n-1}. \tag{7.3}$$

The probability $B(n)$ that an encounter consists of precisely n jumps is given by

$$B(n) = A_n [1 - (1/K) \sum_j W(j)]. \tag{7.4}$$

This relationship means that the n-th jump must still occur, but then the encounter must be finished. As an encounter must consist either of one or two... or n jumps, the condition

$$\sum_{n=1}^{\infty} B(n) = 1 \tag{7.5}$$

must hold.

Eqs. (7.4) and (7.3) anable us to calculate $Z(0)$ from the equation

$$Z(0) = \sum_{n=1}^{\infty} [n\, B(n)]. \tag{7.6}$$

The sum (7.6) converges so strongly that we extend it to infinity, though in practice the encounter does not consist of more than two or three jumps. The result is

$$Z(0) = 1/[1 - (1/K) \sum_j W(j)]. \tag{7.7}$$

Hence by calculating the probabilities for the stay of a vacancy on the neighbouring sites of the tracer we are able to calculate $Z(0)$.

VII.2. Calculation of $P(l_i)$

For the probability $P(l_i)$ that after an encounter between the tracer and a vacancy the tracer is a distance l_i away from its lattice site before the encounter we can write

$$P(l_i) = \sum_n P_n(l_i) [1 - (1/K) \sum_j W(j)]. \tag{7.8}$$

Table 1. The quantities occuring in this table are defined in Sect. VII.

$n = 1$		$n = 2$		$n = 3$		
l_j	$P_1(l_j)$	l_j	$P_2(l_j)$	l_i	$P_{3,l_j}(l_i)$	$P_2(l_j) \cdot P_{3,l_j}(l_i)$
$\sqrt{2}a_0$	1	0	$(1/K)\,W(1)$	$\sqrt{2}a_0$	1	$(1/K)\,W(1)$
		$\sqrt{2}a_0$	$(4/K)\,W(2)$	0	$(1/K)\,W(2)$	$(4/K^2\,(W(2))^2$
				$\sqrt{2}a_0$	$(1/K)\,[W(1) + W(2) + W(3) + W(4)]$	$(4/K^2)\,W(2)\,[W(1) + W(2) + W(3) + W(4)]$
				$2a_0$	$(1/K)\,[W(2) + W(4)]$	$(4/K^2\,W(2)\,[W(2) + W(4)]$
				$\sqrt{6}a_0$	$(1/K)\,[W(3) + W(4) + W(5) + W(2)]$	$(4/K^2)\,W(2)\,[W(2) + W(3) + W(4) + W(5)]$
				$2 \cdot \sqrt{2}a_0$	$(1/K)\,W(4)$	$(4/K^2)\,W(2) \cdot W(4)$
		$2a_0$	$(2/K)\,W(3)$	$\sqrt{2}a_0$	$(1/K\,[W(1) + 2W(2) + W(3)]$	$(2/K^2)\,W(3)\,[W(1) + 2W(2) + W(3)]$
				$\sqrt{6}a_0$	$(1/K)\,[2W(2) + 2W(4)]$	$(4/K^2)\,W(3)\,[W(2) + W(4)]$
				$\sqrt{10}a_0$	$(1/K)\,[W(3) + 2W(4) + W(5)]$	$(2/K^2)\,W(3)\,[W(3) + 2W(4) + W(5)]$
		$\sqrt{6}a_0$	$(4/K)\,W(4)$	$\sqrt{2}a_0$	$(1/K)\,[W(1) + W(2)]$	$(4/K^2)\,W(4)\,[W(1) + W(2)]$
				$2a_0$	$(1/K)\,W(2)$	$(4/K^2)\,W(2)\,W(4)$
				$2\sqrt{2}a_0$	$(1/K)\,[W(2) + W(4)]$	$(4/K^2)\,W(4)\,[W(2) + W(4)]$
				$\sqrt{6}\,a_0$	$(1/K)\,[W(2) + W(3)]$	$(4/K^2)\,W(4)\,[W(2) + W(3)]$
				$\sqrt{10}a_0$	$(1/K)\,[W(3) + W(4)]$	$(4/K^2)\,W(4)\,[W(4) + W(3)]$
				$\sqrt{12}a_0$	$(1/K)\,W(4)$	$(4/K^2)\,(W(4))^2$
				$\sqrt{14}a_0$	$(1/K)\,[W(4) + W(5)]$	$(4/K^2)\,[W(4) + W(5)]$
		$2\sqrt{2}a_0$	$(1/K)\,W(5)$	$\sqrt{2}a_0$	$(1/K)\,W(1)$	$(1/K^2)\,W(1)\,W(5)$
				$\sqrt{6}a_0$	$(4/K)\,W(2)$	$(4/K^2)\,W(5)\,W(2)$
				$\sqrt{10}a_0$	$(2/K)\,W(3)$	$(2/K^2)\,W(5)\,W(3)$
				$\sqrt{14}a_0$	$(4/K\,W(4)$	$(4/K^2)\,W(5)\,W(4)$
				$3\sqrt{2}a_0$	$(1/K)\,W(5)$	$(1/K^2)\,(W(5))^2$

$P_n(l_i)$ is the probability that n tracer jumps occur within an encounter and that after these n jumps the tracer is at a distance l_i from its starting point. The second term in the sum is the probability that after these n jumps of the tracer the encounter is finished. The probabilities $P_n(l_i)$ decrease strongly with increasing n (see Table 1). Therefore the sum over n converges very well.

In Fig. 1 we show three planes of an fcc lattice. After its initial jump the tracer, initially sitting on site 1, is on site 0, while the vacancy, initially on site 0, now is on site 1. The 12 neighbouring sites of the tracer after the initial jump are denoted by 1 to 5. Because of the symmetry of all possible vacancy paths with respect to the direction 1—0, the probabilities for the vacancy sitting, say, on either one of the two sites 3 are the same ones.

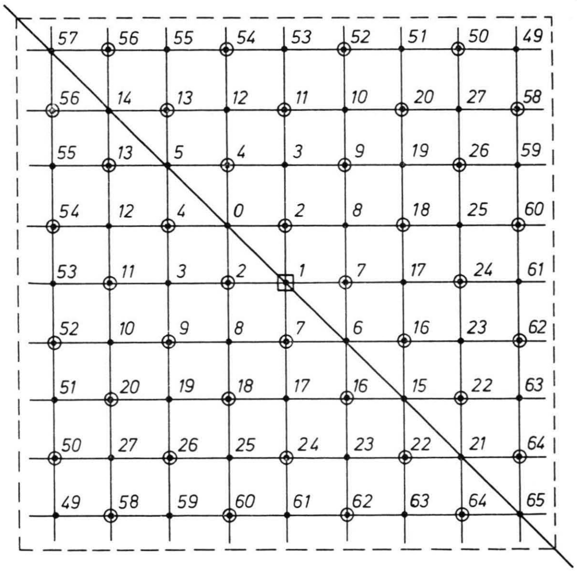

Fig. 1. Three planes of an fcc lattice. The nearest-neighbour distance is $\sqrt{2}\,a_0$. Points (●) denote lattice sites in the plane of the paper. Circles (⊙) denote sites in planes a distance $\pm\,a_0$ apart from the plane of the paper (see also Sect. VII).

If we denote the cube edge of a unit cell of the fcc lattice by $2a_0$, the nearest neighbour distance is $l = \sqrt{2}\,a_0$. After the initial tracer jump only $l_i = \sqrt{2}\,a_0$ may occur, the respective probability is $P_1(\sqrt{2}a_0) = 1$.

After its second jump the tracer may sit on one of the sites 1 to 5. The respective values of l_i, referred to the initial tracer site, 1, are $l_i' = 0$, $\sqrt{2}\,a_0$, $2a_0$, $\sqrt{6}\,a_0$, and $2 \cdot \sqrt{2}\,a_0$. The probabilities $P_2(l_j)$ are listed in Table 1.

The probabilities $P_3(l_i)$ depend on the probabilities $P_2(l_j)$, that after two jumps the tracer was a distance l_j apart from its starting point:

$$P_3(l_i) = \sum_{l_j} P_2(l_j)\, P_{3,l_j}(l_i)\,. \tag{7.9}$$

$P_{3,l_j}(l_i)$ denotes the probability that after three jumps the tracer is a distance l_i away from its starting point, if, after two jumps, it was a distance l_j away.

For the calculation of $P_{3,l_j}(l_i)$ we make use of the fact that after each jump of the tracer its neighbouring lattice sites may be denoted with respect to the previous jump direction in the same manner as after the initial tracer jump; i.e., if we denote the vacant lattice site after the first tracer jump by 1, then the vacant site will have the number 1 after all further tracer jumps. Hence the probabilities $P_2(l_j)$ and $P_{3,l_j}(l_i)$ may be reduced to the calculation of the probabilities $W(j)$ of the vacancy sitting on one of the neighbouring lattice sites of the tracer after its initial jump (see Table 1).

VIII. Numerical Results

The probabilities $W(j)$ $(j = 1, 2, \ldots, 5)$ were calculated along the lines outlined by Bardeen and Herring (see, e.g. [7]) for the calculation of directional correlation factors. In these calculations the tracer-site may be treated as a centre of symmetry. In our problem paths of the vacancy through the tracer site are not allowed to contribute to $W(j)$, and therefore the tracer site is not a centre of symmetry.

The accuracy of the values of the $W(j)$ depends on the boundary of random return of the vacancy (dashed line in Figure 1). By defining the boundary in such a way that the vacancy must make at least five jumps to cross the boundary we obtained an accuracy of a few percent for the values of $W(j)$. Within the boundary we have 97 different lattice sites and the calculation of the $W(j)$ requires the inversion of a 97 × 97 matrix.

The results are shown in Table 2:

Table 2

$Z(0) = 1.26,$
$P(0) = 0.077,$
$P(\sqrt{2}a_0) = 0.897,$
$P(2a_0) = 0.013,$
$P(\sqrt{6}a_0 = 0.018,$
$P(2\sqrt{2}a_0) = 0.0028.$

Hence an encounter consists of an average of 1.26 jumps. If the boundary of random return is drawn at a larger distance from the vacancy, the value of $Z(0)$ may increase by a few percent. For the evaluation of the correlation function we used the value $Z(0) = 1.32$ which was calculated by Mehrer by the computer simulation of the random walk of a vacancy (Monte Carlo method)[9].

For not more than about 40 random jumps Mehrer obtained the value $Z(0) = 1.26$ which is in good agreement with our approximation where the vacancy must make at least 10 jumps to cross the boundary and return to the tracer-site randomly, i.e., on the average the vacancy will make about 30 to 40 jumps before its random return. Mehrer's value was calculated from the simulation of 300 random jumps of the vacancy.

By a different method of calculation, Eisenstadt and Redfield[5] obtained a value of 1.347 for $Z(0)$ which is in fair agreement with the value used in our calculations.

Our results for $P(l_i)$ show that about 89,7 percent of all encounters end with unit-displacements while 7,7% do not contribute to relaxation.

With these values of the diffusion parameters we can evalute the Fourier-transform $J^{(1)}(\omega)$ of the correlation function [see Eqs. (5.5) and (5.9)]. For that purpose we write Eq. (5.9) in a slightly modified form. For the spin density n we introduce

$$n = n_0\, c/(2a_0)^3 \tag{8.1}$$

where n_0 is the number of spins in a unit cell with cube edge $2a_0$ and c the fraction of occupied lattice sites. Defining a constant k due to Torrey[8] by

$$k = a/l = a/\sqrt{2}a_0 = 0.74335 \tag{8.2}$$

and changing the variable of integration over ϱ by means of the relation

$$x = a\,\varrho\,, \tag{8.3}$$

we may write for the Fourier-transform of the correlation function

$$J^{(1)}(\omega) = \frac{\sqrt{2}\,\pi\, c}{15\, k^3 a_0{}^6\, \omega} \cdot \mathrm{Int}(\omega\tau) \tag{8.4}$$

with

$$\mathrm{Int}(\omega\tau) = \int_0^\infty J_{3/2}^2(x) \cdot \frac{\left[1 - A\left(\frac{x}{a}\right)\right] \cdot \frac{Z(0)}{1-P(0)} \cdot \omega\tau}{\left[1 - A\left(\frac{x}{a}\right)\right]^2 + \left[\frac{Z(0)}{1-P(0)} \cdot \frac{\omega\tau}{2}\right]^2} \cdot \frac{\mathrm{d}x}{x} \tag{8.5}$$

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[9] H. Mehrer, Private Communication.

and

$$A(x) = \sum_{l_i > 0} P(l_i) \frac{\sin\left(\frac{x}{k} \cdot \frac{l_i}{l}\right)}{\frac{x}{k} \cdot \frac{l_i}{l}} . \tag{8.6}$$

The integral $\operatorname{Int}(\omega\tau)$ was calculated by numerical integration for various values of the parameter $\omega\tau$. In Fig. 2 the τ-dependence of $\operatorname{Int}(\omega\tau)$ for a given value of ω is compared with the values of the integral occuring in Torrey's theory [see, e.g., Eq. (2.5)] and with a Debye-spectrum $\frac{2}{3} \cdot \omega\tau/(1+\omega^2\tau^2)$ describing the relaxation properties of a Markoffian process and resulting from a simple exponential correlation function. [The factor of $\frac{2}{3}$ in the Debye-spectrum results from the separation of the prefactor similarly to equation (8.4).]

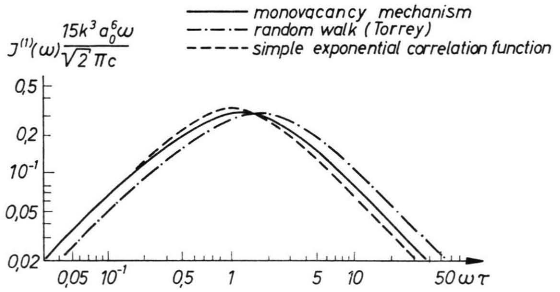

Fig. 2. Fourier spectra for a Markoffian process (simple exponential correlation function), Torrey's random walk model, and for a monovacancy mechanism of self-diffusion in a face-centred cubic lattice (see also Sect. VIII).

The values of the spectra $J^{(0)}(\omega)$ and $J^{(2)}(\omega)$ may be obtained from the values of $J^{(1)}(\omega)$ (Fig. 2) by means of the relationship[2, 4]

$$J^{(0)}(\omega) : J^{(1)}(\omega) : J^{(2)}(\omega) = 6 : 1 : 4 . \tag{8.7}$$

IX. Discussion

The most significant difference between Torrey's and the present results for monovacancy diffusion may be seen from Fig. 2: τ-values determined from the linear parts of the spectra differ about 30 percent from oneanother. This difference is due to the fact that the mean time between successive nuclear jumps was replaced by the mean time between different encounters.

In the present model the $\omega\tau$-value for which the Fourier spectrum has a maximum as well as the shape of the spectrum depend on the diffusion mechanism. For a monovacancy mechanism, explicitly treated in this paper, the maximum occurs for $\omega\tau \simeq 1.3$. The shape of the spectrum is similar to the shape for Torrey's random walk model, the maximum of which occurs for $\omega\tau \cong 1.7$, however *.

Within the accuracy of our calculations the high-temperature asymptote ($\omega\tau \ll 1$) of the monovacancy model coincides with the Debye spectrum. Hence we may conclude that for very rapid diffusion there are only small differences between the influence of Markoffian processes and that of monovacancy diffusion on nuclear magnetic relaxation. In the surroundings of the maximum ($\omega\tau \simeq 1$) or at lower temperatures ($\omega\tau \gg 1$), however, the differences between the two models are considerable.

The application of the present results to the analysis of self-diffusion in aluminium will be treated in a separate paper[10].

Acknowledgements

I would like to thank Professor A. Seeger, Dr. F. Noack, and Dr. H. Mehrer for numerous helpful discussions.

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* It is to be noted that the maximum of the quantity Ψ listed in Torrey's papers[4,8] occurs for a different value of $\omega\tau$ than the maximum of the correlation function shown in Fig. 2 since the correlation function is proportional to the product $\omega\tau \cdot \Psi$.

[10] A. Seeger, D. Wolf, and H. Mehrer, Phys. Stat. Sol., to be published.