PHYSICAL REVIEW B VOLUME 6, NUMBER 9 1 NOVEMBER 1972

Spin Diffusion in the Heisenberg Magnets at Infinite Temperature

Tohru Morita*
Department of Physics, Ohio University, Athens, Ohio 45701
(Received 4 February 1972)

A theoretical criterion for the occurrence of the spin diffusion is given in terms of the "friction function" or "memory function" which occurs in the kinetic equation of the Fourier-space transform $I(\vec{k}, t)$ of the two-time spin-pair correlation function. The friction function in the limit of $\vec{k} \to 0$ is determined with the aid of the short-time expansion of the two-time spin-pair correlation function for the square, sc, and bcc isotropic Heisenberg magnets at infinite temperature, and the criterion is checked. The spin diffusion constants for spin 1/2 are $0.860Ja^2$, $0.619Ja^2$, and $0.509Ja^2$, respectively, for these lattices, where J is the exchange integral and a is the lattice constant. The spin diffusion constants for larger spins are also provided. It should be noted that $0.509Ja^2$ is in complete agreement with the experimental value $(0.525 \pm 0.06)Ja^2$ for the bcc solid He^3. For the one-dimensional isotropic Heisenberg magnet and for the square, sc, and bcc XY magnets, the friction function could not be determined in the present calculation. Suggested values of the spin diffusion constant are given for these lattices. Comparison is made with the results of Windsor's computer-simulation calculation. There exists no spin diffusion for the one-dimensional XY model.

I. INTRODUCTION

It has not been clear theoretically whether spin diffusion occurs in the Heisenberg magnets, even though the formulas are provided by which one can calculate the spin diffusion constant, assuming its occurrence. In the present paper, a theoretical criterion is given for the occurrence of the spin diffusion in the Heisenberg magnet, and it is checked for the isotropic Heisenberg magnet and the XY magnet. Discussions are restricted to infinite temperature.

If the spin diffusion occurs, the Fourier-space transform

$$I(\vec{k}, t) = N^{-1} \langle S_{\vec{k}}^{z}(t) S_{-\vec{k}}^{z}(0) \rangle$$

of the two-time spin-pair correlation function behaves as follows:

$$I(\vec{k}, t) = (\text{const}) e^{-Dk^2 t} \qquad (1.1)$$

for small wave vector $\vec{k}$ and large time t, where D is the spin diffusion constant. Mori and Kawasaki,[1] assuming that

$$\ddot{I}(\vec{k}, t) \equiv \frac{d^2 I(\vec{k}, t)}{dt^2}$$

takes appreciable value of $O(k^2)$ only before a short correlation time τ_c, gave a formula

$$D = -\lim_{\vec{k}\to 0} k^{-2} I(\vec{k}, 0)^{-1} \int_0^{\tau_c} \ddot{I}(\vec{k}, t)\, dt\,. \qquad (1.2)$$

In evaluating D with the aid of this formula, Mori and Kawasaki assumed a Gaussian distribution function for $\ddot{I}(\vec{k}, t)$. Then D is calculated from the knowledge of the terms of $O(t^2)$ and $O(t^4)$ of the short-time expansion of $I(\vec{k}, t)$.

On the other hand, Resibois and De Leener[2] investigated the following kinetic equation, which is valid at infinite temperature:

$$\frac{d}{dt} I(\vec{k}, t) = -\int_0^t \Gamma(\vec{k}, t-t') I(\vec{k}, t')\, dt'\,. \qquad (1.3)$$

They gave the following formula:

$$D = \frac{1}{2} \left(\frac{\partial^2}{\partial \vec{k}^2} \int_0^\infty \Gamma(\vec{k}, t)\, dt \right)_{\vec{k}=0}, \qquad (1.4)$$

which is easily obtained by substituting (1.1) into (1.3) and assuming $\Gamma(\vec{k}, t)$ decays to zero. We see that (1.2) and (1.4) are equivalent by taking another time derivative of (1.3). Resibois and De Leener used a solution of an approximate integral equation in place of $\Gamma(\vec{k}, t)$ of (1.4). Bennett and Martin[3] also discussed the spin diffusion with the aid of the function $\Gamma(\vec{k}, t)$ or its Fourier-time transform.

In the present paper, we investigate the kinetic equation (1.3) for small $\vec{k}$ and show (i) that the spin diffusion occurs, if there exists a positive value k_c and if the friction function $\Gamma(\vec{k}, t)$ for $|\vec{k}| < k_c$ is so short ranged that conditions (A) and (B) given below are satisfied for its Laplace transform $\Gamma_p(\vec{k})$, and then the value D occurring in the condition (B) is the spin diffusion constant. It is further shown (ii) that the spin diffusion constant D can be calculated by the following formula:

$$D = \int_0^\infty \Psi(t)\, dt\,, \qquad (1.5)$$

$$\Psi(t) = -\lim_{\vec{k}\to 0} [\ddot{I}(\vec{k}, t)/k^2 I(\vec{k}, 0)]\,. \qquad (1.6)$$

Condition (*A*). There exists a negative number s such that $\Gamma_p(\vec{k})$ is an analytic function of p when $\mathrm{Re}\,p > s$ and $|\vec{k}| < k_c$.

Condition (*B*). $\Gamma_p(\vec{k})$ is $O(k^2)$ if $\mathrm{Re}\,p > s$ and $\lim_{\vec{k}\to 0} \lim_{p\to 0} \Gamma_p(\vec{k})/k^2 \equiv D$ is not zero.

In a recent paper,[4] the short-time expansion coefficients of the two-time spin-pair correlation function of the Heisenberg magnets of spin $\frac{1}{2}$ at infinite temperature have been given up to $O(t^{10})$ for the linear chain and up to $O(t^8)$ for the square and sc lattices. The coefficients for the bcc lattice have been obtained up to $O(t^8)$, and the expansion coefficients for an arbitrary spin for these lattices have been obtained up to $O(t^6)$.[5] By using those coefficients, we express $\Psi(t)$ defined by (1.6) as a product of a Gaussian distribution function and a power series in time t. We check the convergence of the result when the power series is truncated. Based on this result, we discuss the conditions (A) and (B) for $\Gamma(\vec{k}, t)$, and give an estimate of D for these lattices.

In Sec. II, we sketch a derivation of the conditions (A) and (B) and the formula (1.5). In Sec. III, $\Gamma(\vec{k}, t)$ and $\Psi(t)$ are obtained for the isotropic Heisenberg magnet and the XY magnet at infinite temperature for the linear, square, sc, and bcc lattices. Results are given and discussed in Sec. IV. Comparison with previous works and experiments is given in Sec. V.

II. BASIC THEOREM

We are concerned with $I(\vec{k}, t)$ which is a two-time correlation function of $S_{\vec{k}}^z(t)$ and $S_{-\vec{k}}^z(t)$:

$$I(\vec{k}, t) = N^{-1} \langle S_{\vec{k}}^z(t) S_{-\vec{k}}^z(0) \rangle , \tag{2.1}$$

where N is the total number of spins in the system and

$$S_{\vec{k}}^z(t) = e^{iHt} S_{\vec{k}}^z e^{-iHt} , \quad S_{\vec{k}}^z = \textstyle\sum_j s_j^z e^{i\vec{k}\cdot\vec{R}_j} .$$

The Liouville equation for $S_{\vec{k}}^z(t)$,

$$\frac{d}{dt} S_{\vec{k}}^z(t) = i[H, S_{\vec{k}}^z(t)],$$

is reduced to the generalized Langevin equation[6]

$$\frac{d}{dt} S_{\vec{k}}^z(t) = -\int_0^t \Gamma(\vec{k}, t-t') S_{\vec{k}}^z(t')\, dt' + R_{\vec{k}}^M(t) \qquad (t>0) , \tag{2.3}$$

where

$$\Gamma(\vec{k}, t) = \langle R_{\vec{k}}^M(t) R_{\vec{k}}^{M*}(0) \rangle \tag{2.4}$$

and

$$\langle R_{\vec{k}}^M(t) S_{-\vec{k}}^z(0) \rangle = 0, \quad t > 0 . \tag{2.5}$$

In deriving (2.3), use is made of the fact that

$$\langle \dot{S}_{\vec{k}}^z(0) S_{-\vec{k}}^z(0) \rangle = 0$$

at infinite temperature. By taking the correlation of (2.3) with $S_{-\vec{k}}^z(0)$, we have

$$\frac{d}{dt} I(\vec{k}, t) = -\int_0^t \Gamma(\vec{k}, t-t') I(\vec{k}, t')\, dt' . \tag{2.6}$$

This equation is solved by the Laplace transform. By denoting the Laplace transforms of $I(\vec{k}, t)$ and $\Gamma(\vec{k}, t)$ as $I_p(\vec{k})$ and $\Gamma_p(\vec{k})$, respectively, one has

$$I_p(\vec{k}) = \sigma^{(0)}(0)/[p + \Gamma_p(\vec{k})] , \tag{2.7}$$

where $\sigma^{(0)}(0) = I(\vec{k}, 0) = \frac{1}{3} S(S+1)$ for spin S at infinite temperature.

The inverse Laplace transform of (2.7) gives

$$I(\vec{k}, t) \simeq \sigma^{(0)}(0)\, e^{-Dk^2 t} \qquad (t \to \infty) \tag{2.8}$$

for small $\vec{k}$, if (A) the abscissa of convergence $s(\vec{k})$ of the Laplace transform $\Gamma_p(\vec{k})$ is negative, and (B) $\Gamma_p(\vec{k})$ is $O(k^2)$ if $\mathrm{Re}\, p > s$, and

$$\lim_{\vec{k}\to 0} \lim_{p \to 0} \Gamma_p(\vec{k})/k^2 = D$$

is not zero. Here s is such a negative number that $0 > s > s(\vec{k})$ for small values of $\vec{k}$. An existence of such an s is guaranteed under the condition (A).

If we could calculate $\Gamma(\vec{k}, t)$ and show that the above conditions (A) and (B) are satisfied for its Laplace transform $\Gamma_p(\vec{k})$, we predict the occurrence of the spin diffusion and give the spin diffusion constant D by

$$D = \lim_{\vec{k}\to 0} \lim_{p \to 0} \Gamma_p(\vec{k})/k^2 .$$

If $\Gamma_p(\vec{k})/k^2$ is found to be a continuous function of $\vec{k}$, we can exchange the order of the limits and have

$$D = \lim_{p\to 0} \lim_{\vec{k} \to 0} \Gamma_p(\vec{k})/k^2 . \tag{2.9}$$

The Laplace transform $\ddot{I}_p(\vec{k})$ of the second derivative of the $I(\vec{k}, t)$ with respect to time t is given by

$$\ddot{I}_p(\vec{k}) = p^2 I_p(\vec{k}) - pI(\vec{k}, 0) - \dot{I}(\vec{k}, 0) = -I(\vec{k}, 0)\, \frac{p\Gamma_p(\vec{k})}{p + \Gamma_p(\vec{k})} . \tag{2.10}$$

When $\Gamma_p(\vec{k})$ is of $O(k^2)$, the limit of $\vec{k} \to 0$ of this equation gives

$$\lim_{\vec{k}\to 0} \frac{\Gamma_p(\vec{k})}{k^2} = -\lim_{\vec{k}\to 0} \frac{\ddot{I}_p(\vec{k})}{k^2 I(\vec{k}, 0)} \equiv \Psi_p . \tag{2.11}$$

Thus the formula (2.9) is also written as follows:

$$D = -\lim_{p\to 0} \lim_{\vec{k}\to 0} \frac{\ddot{I}_p(\vec{k})}{k^2 I(\vec{k}, 0)} \equiv \Psi_0 . \tag{2.12}$$

It should be noted that the order of the limits in (2.12) cannot be changed because

$$\lim_{p\to 0} \ddot{I}_p(\vec{k}) = -\dot{I}(\vec{k}, 0) = 0 .$$

The inverse Laplace transform of (2.11) gives

$$\lim_{\vec{k}\to 0} \frac{\Gamma(\vec{k}, t)}{k^2} = -\lim_{\vec{k}\to 0} \frac{\ddot{I}(\vec{k}, t)}{k^2 I(\vec{k}, 0)} \equiv \Psi(t) . \tag{2.13}$$

Equation (2.12) is now written as follows:

$$D = \int_0^\infty \Psi(t)\, dt , \tag{2.14}$$

where

$$\Psi(t) = -\lim_{\vec{k}\to 0} [\ddot{I}(\vec{k}, t)/k^2 I(\vec{k}, 0)] . \tag{2.15}$$

This is the required equation (1.5) .

III. $\Gamma(\vec{k},t)$ AND $\Psi(t)$

The short-time expansion of $I(\vec{k}, t)$ at infinite temperature is obtained from the short-time expansion of the two-time spin-pair correlation function $\sigma(\vec{R}_{if}, t) \equiv \langle s_i^z(t) S_f^z(0) \rangle$ by a Fourier-space transform:

$$I(\vec{k}, t) = I_\alpha^{(0)}(\vec{k}) + \sum_{n=1}^{\infty} \frac{(-1)^n I_\alpha^{(2n)}(\vec{k})}{(2n)!\,(2z_S)^n} \tau^{2n} . \quad (3.1)$$

Here

$$\tau^2 = 2z_S J^2 t^2 , \quad z_S = \tfrac{4}{3} z S(S+1) , \quad (3.2)$$

where z is the coordination number of the lattice and J is the exchange integral;

$$I_\alpha^{(0)}(\vec{k}) = \sigma_\alpha^{(0)}(0) = \tfrac{1}{3}S(S+1) ,$$
$$I_\alpha^{(2n)}(\vec{k}) = \textstyle\sum_i \sigma_\alpha^{(2n)}(\vec{R}_{if})\, e^{i\vec{k}\cdot\vec{R}_{if}} . \quad (3.3)$$

The values of $\sigma_\alpha^{(2n)}(\vec{R}_{if})$ have been given in Tables IV–VI of Ref. 4 for the Heisenberg magnets of spin $\frac{1}{2}$ at infinite temperature, for the linear, square, and sc lattices. The values for the bcc lattice are given in Table III of Ref. 5. For the isotropic Heisenberg magnet $\alpha = t$; and for the XY magnet $\alpha = 0$ and J must be replaced by $J_\perp$. For an arbitrary spin S, $\sigma_\alpha^{(2n)}$ is expanded in powers of $\frac{1}{3}S(S+1)$:

$$\sigma_\alpha^{(2n)}(\vec{R}_{if}) = \textstyle\sum_p \sigma_{\alpha,p}^{(2n)}(\vec{R}_{if})\,[\tfrac{1}{3}S(S+1)]^p ,$$

and the coefficients $\sigma_{\alpha,p}^{(2n)}(\vec{R}_{if})$ have been calculated for $2n \le 6$.[5]

The coefficients $I_\alpha^{(2n)}(\vec{k})$ are related with the so-called moments $\langle \omega^{2n} \rangle_{\vec{k}}$, which are the expansion coefficients of $I(\vec{k}, t)/I(\vec{k}, 0)$, by

$$\langle \omega^{2n} \rangle_{\vec{k}} = J^{2n} I_\alpha^{(2n)}(\vec{k}) / I_\alpha^{(0)}(\vec{k}) .$$

By expanding the exponential in the summation of (3.3) and noting the sum rule

$$\textstyle\sum_i \sigma_\alpha^{(2n)}(\vec{R}_{if}) = 0 , \quad (3.4)$$

we have

$$I_\alpha^{(2n)}(\vec{k}) = k^2 a^2 M_\alpha^{(2n)} + O(k^4) \quad (3.5)$$

for an arbitrary direction of $\vec{k}$, where

$$M_\alpha^{(2n)} = \textstyle\sum_i \sigma_\alpha^{(2n)}(\vec{R}_{if}) X_{if}^2 / a^2 . \quad (3.6)$$

X_{if} is the x component of $\vec{R}_{if}$ and a is the lattice constant. The values of $M_\alpha^{(2n)}$ for spin $\frac{1}{2}$ are listed in Table I. For an arbitrary spin, we have

$$M_\alpha^{(2n)} = \textstyle\sum_p M_{\alpha,p}^{(2n)} [\tfrac{1}{3}S(S+1)]^p . \quad (3.7)$$

The coefficients $M_{\alpha,p}^{(2n)}$ are listed in Table II, where $M_{\alpha,p}^{(2n)}$ ($\alpha = 0, 2, 4$) are the contributions of $J_\parallel^{\alpha} J_\perp^{2n-\alpha}$: If $J_\parallel \ne J_\perp$, $M_{\alpha,p}^{(2n)}$ in the above expression must be replaced by $\sum_{\alpha=0}^{2n} M_{\alpha,p}^{(2n)} J_\parallel^{\alpha} J_\perp^{2n-\alpha} / J^{2n}$. By taking the second derivative of (3.1), we have

TABLE I. Values of $M_\alpha^{(2n)} = I_\alpha^{(2n)}(\vec{k})/k^2a^2 = \langle\omega^{2n}\rangle_{\vec{k}}\, 4J^{2n}k^2a^2$ as $\vec{k} \to 0$ for the Heisenberg magnets of spin $\frac{1}{2}$ at infinite temperature.

Lattice	$M_t^{(2)}$	$M_t^{(4)}$	$M_t^{(6)}$	$M_t^{(8)}$	$M_t^{(10)}$
		Isotropic Heisenberg magnet			
Linear	0.5	1.0	9.0 ($\rho_4 = 1.50$)	170.0 ($\rho_6 = 2.83$)	4948.0 ($\rho_8 = 5.89$)
Square	0.5	5.0	175.0 ($\rho_4 = 1.17$)	11 350.0 ($\rho_6 = 1.51$)	
sc	0.5	9.0	549.0 ($\rho_4 = 1.13$)	61 138.0 ($\rho_6 = 1.40$)	
bcc	0.5	13.0	1125.0 ($\rho_4 = 1.11$)	179 334.0 ($\rho_6 = 1.36$)	
		XY magnet			
Lattice	$M_0^{(2)}$	$M_0^{(4)}$	$M_0^{(6)}$	$M_0^{(8)}$	$M_0^{(10)}$
Linear	0.5	0.0	0.0	0.0	0.0
Square	0.5	2.0	32.0 ($\rho_4 = 1.33$)	1064.0 ($\rho_6 = 2.22$)	
sc	0.5	4.0	128.0 ($\rho_4 = 1.33$)	8288.0 ($\rho_6 = 2.16$)	
bcc	0.5	6.0	288.0 ($\rho_4 = 1.33$)	28 128.0 ($\rho_6 = 2.17$)	

$$\ddot{I}(\vec{k}, t) = -J^2 \left(I_\alpha^{(2)}(\vec{k}) + \sum_{n=1}^{\infty} \frac{(-1)^n I_\alpha^{(2n+2)}(\vec{k})}{(2n)!\,(2z_S)^n} \tau^{2n} \right) . \quad (3.8)$$

Substitution of (3.8), (3.1), and (3.5) with (3.3) into (2.15) gives

$$\Psi(t) = J^2 a^2 I_\alpha^{(0)}(0)^{-1} \left(M_\alpha^{(2)} + \sum_{n=1}^{\infty} \frac{(-1)^n M_\alpha^{(2n+2)}}{(2n)!\,(2z_S)^n} \tau^{2n} \right) . \quad (3.9)$$

In a separate paper,[7] the short-time expansion of $\Gamma(\vec{k}, t)$ is obtained from the expansion (3.1) of $I(\vec{k}, t)$ as follows:

$$\Gamma(\vec{k}, t) = \Gamma_\alpha^{(0)}(\vec{k}) + \sum_{n=1}^{\infty} \frac{(-1)^n \Gamma_\alpha^{(2n)}(\vec{k})}{(2n)!\,(2z_S)^n} \tau^{2n} , \quad (3.10)$$

where

$$\Gamma_\alpha^{(0)}(\vec{k}) = I_\alpha^{(2)}(\vec{k}) / I_\alpha^{(0)}(\vec{k}) ,$$
$$\Gamma_\alpha^{(2)}(\vec{k}) = \frac{I_\alpha^{(4)}(\vec{k})}{I_\alpha^{(0)}(\vec{k})} - \left(\frac{I_\alpha^{(2)}(\vec{k})}{I_\alpha^{(0)}(\vec{k})} \right)^2 ,$$

etc. It is noted that the expansion coefficients of $\Gamma(\vec{k}, t)/k^2$ are equal to the corresponding expansion coefficients of $\Psi(t)$ plus a term of $O(k^2)$. It follows from this fact that, when one could obtain $\Psi(t)$ which is valid for all times, from the short-time expansion (3.9), he could also obtain $\Gamma(\vec{k}, t)$ which is valid for all times, from the corresponding expansion (3.10), if $\vec{k}$ is very small. If the Laplace transform Ψ_p of the obtained $\Psi(t)$ has a negative abscissa of convergence and $\Psi_0 > 0$, $\Gamma(\vec{k}, t)$ obtained in a similar way would also satisfy the same properties, if $\vec{k}$ is very small. Thus by taking ad-

TABLE II. Expansion coefficients of $\Psi(t)$ of order t^{2n-2} and $[\frac{1}{3}S(S+1)]^p$; cf. (3.9) and (3.7). $M_{t,p}{}^{(2n)}$ for the isotropic Heisenberg magnet, and $M_{0,p}{}^{(2n)}$ for the XY magnet.

$2n$	p	$M_{t,p}{}^{(2n)}$	$M_{0,p}{}^{(2n)}$	$M_{2,p}{}^{(2n)}$	$M_{4,p}{}^{(2n)}$
			Linear chain		
2	2	8.0	8.0		
4	2	−16.0	−6.4	−9.6	
4	3	128.0	25.6	102.4	
6	2	89.6	$68.04+\frac{5}{7}$	$-19.32-\frac{3}{7}$	$39.88+\frac{5}{7}$
6	3	−2508.8	$-710.52-\frac{3}{7}$	$-1004.84-\frac{1}{7}$	$-792.44-\frac{3}{7}$
6	4	10905.6	$1743.44+\frac{2}{7}$	$5615.48+\frac{3}{7}$	$3545.68+\frac{2}{7}$
			Square lattice		
2	2	8.0	8.0		
4	2	−16.0	−6.4	−9.6	
4	3	384.0	153.6	230.4	
6	2	89.6	$68.04+\frac{5}{7}$	$-19.32-\frac{3}{7}$	$39.88+\frac{5}{7}$
6	3	−6348.8	$-2246.52-\frac{3}{7}$	$-2284.84-\frac{1}{7}$	$-1816.44-\frac{3}{7}$
6	4	68761.6	$16079.44+\frac{2}{7}$	$33775.48+\frac{3}{7}$	$18905.68+\frac{2}{7}$
			sc lattice		
2	2	8.0	8.0		
4	2	−16.0	−6.4	−9.6	
4	3	640.0	281.6	358.4	
6	2	89.6	$68.04+\frac{5}{7}$	$-19.32-\frac{3}{7}$	$39.88+\frac{5}{7}$
6	3	−10188.8	$-3782.52-\frac{3}{7}$	$-3564.84-\frac{1}{7}$	$-2840.44-\frac{3}{7}$
6	4	179865.6	$46799.44+\frac{2}{7}$	$86511.48+\frac{3}{7}$	$46553.68+\frac{2}{7}$
			bcc lattice		
2	2	8.0	8.0		
4	2	−16.0	−6.4	−9.6	
4	3	896.0	409.6	486.4	
6	2	89.6	$68.04+\frac{5}{7}$	$-19.32-\frac{3}{7}$	$39.88+\frac{5}{7}$
6	3	−14028.8	$-5318.52-\frac{3}{7}$	$-4844.84-\frac{1}{7}$	$-3864.44-\frac{3}{7}$
6	4	342681.6	$93903.44+\frac{2}{7}$	$162287.48+\frac{3}{7}$	$86489.68+\frac{2}{7}$

vantage of the continuity of the coefficients $\Gamma_\alpha{}^{(2n)}(\vec{k})/k^2$ with respect to $\vec{k}$, we can conclude the conditions (A) and (B) for $\Gamma(\vec{k}, t)$. It is, therefore, sufficient to discuss the properties of $\Psi(t)$ and Ψ_p.

In analyzing the two-time spin-pair correlation function and its Fourier-space transform[8] or the friction functions for these quantities,[7] we introduced the Gaussian distribution function by using the first two terms of the expansion. For (3.9), we have

$$J^2a^2[M_\alpha{}^{(2)}/I_\alpha{}^{(0)}(0)]e^{-\tau^2/2\tau_G{}^2}, \tag{3.11}$$

where

$$\tau_G{}^2 = 2z_S M_\alpha{}^{(2)}/M_\alpha{}^{(4)}. \tag{3.12}$$

If an expansion

$$1-\frac{m_2}{2!}X^2+\frac{m_2}{4!}X^4-\frac{m_6}{6!}X^6+\frac{m_8}{8!}X^8-+\cdots \tag{3.13}$$

can be expressed by a Gaussian distribution function $e^{-\alpha X^2}$, the ratio of the coefficients

$$\rho_4 \equiv \frac{m_4}{3m_2{}^2}, \quad \rho_6 \equiv \frac{m_6}{5.3m_2{}^3}, \quad \rho_8 \equiv \frac{m_8}{7.5.3m_2{}^4}, \ \cdots \tag{3.14}$$

must be unity. The values of ρ_{2n} for the expansion of $\Psi(t)$ given by (3.9) are included in Table I for spin $\frac{1}{2}$. ρ_4 for $S=\frac{1}{2}$ and $S=1\sim\infty$ are given in Table III. We express $\Psi(t)$ as a product of (3.11)

TABLE III. Parameter ρ_4 for $\Psi(t)$. For the Gaussian distribution function $\rho_4=1$.

Isotropic Heisenberg magnet			XY magnet		
Lattice	$S=\frac{1}{2}$	$S=1\sim\infty$	Lattice	$S=\frac{1}{2}$	$S=1\sim\infty$
Linear	1.50	$1.81\sim1.78$	Linear		$8.67\sim7.10$
Square	1.17	$1.22\sim1.24$	Square	1.33	$1.65\sim1.82$
sc	1.13	$1.16\sim1.17$	sc	1.33	$1.49\sim1.58$
bcc	1.11	$1.13\sim1.14$	bcc	1.33	$1.43\sim1.49$

and a power series of τ^2:

$$\Psi(t)=J^2a^2\frac{M_\alpha{}^{(2)}}{I_\alpha{}^{(0)}(0)}e^{-\tau^2/2\tau_G{}^2}\left(1+\sum_{n=1}^{\infty}\frac{\xi_\alpha{}^{(2n)}}{(2n)!(2z_S)^n}\tau^{2n}\right). \tag{3.15}$$

The factor $M_\alpha{}^{(2)}/I_\alpha{}^{(0)}(0)$ is equal to $\frac{8}{3}S(S+1)$ for the isotropic Heisenberg and XY magnets of the lattices under consideration at infinite temperature. $\tau_G{}^2$ is so chosen that $\xi_\alpha{}^{(2)}$ is zero. The parameter $\tau_G{}^2$ and the coefficients $\xi_\alpha{}^{(2n)}$ for spin $\frac{1}{2}$ are listed in Table IV. For an arbitrary spin S, $\tau_G{}^2$ and $\xi_\alpha{}^{(4)}/(4z_S)^2$ are calculated with the aid of the following formulas:

$$\tau_G{}^2=\left(\frac{M_\alpha{}^{(4)}}{2z_S M_\alpha{}^{(2)}}\right)^{-1}, \tag{3.16}$$

$$\frac{\xi_\alpha{}^{(4)}}{(2z_S)^2}=\frac{M_\alpha{}^{(6)}}{(2z_S)^2 M_\alpha{}^{(2)}}-3\left(\frac{M_\alpha{}^{(4)}}{2z_S M_\alpha{}^{(2)}}\right)^2, \tag{3.17}$$

where

$$\frac{M_\alpha{}^{(4)}}{2z_S M_\alpha{}^{(2)}}=\frac{1}{8zM_{\alpha,2}{}^{(2)}}\left[M_{\alpha,3}{}^{(4)}+M_{\alpha,2}{}^{(4)}\left(\frac{S(S+1)}{3}\right)^{-1}\right], \tag{3.18}$$

$$\frac{M_\alpha{}^{(6)}}{(2z_S)^2 M_\alpha{}^{(2)}}=\frac{1}{(8z)^2 M_{\alpha,2}{}^{(2)}}\left[M_{\alpha,4}{}^{(6)}+M_{\alpha,3}{}^{(6)}\left(\frac{S(S+1)}{3}\right)^{-1}+M_{\alpha,2}{}^{(6)}\left(\frac{S(S+1)}{3}\right)^{-2}\right].$$

TABLE IV. Values of $\tau_G{}^2=2z\,M_\alpha{}^{(2)}/M_\alpha{}^{(4)}$ and the coefficients $\xi_\alpha{}^{(2n)}$ of Eqs. (3.15) and (3.19) for spin $\frac{1}{2}$.

Isotropic Heisenberg magnet						
Lattice	$\tau_G{}^2$	$\xi_t{}^{(0)}$	$\xi_t{}^{(2)}$	$\xi_t{}^{(4)}$	$\xi_t{}^{(6)}$	$\xi_t{}^{(8)}$
Linear	2.0	1	0	6	−40	936
Square	0.8	1	0	50	−200	
sc	0.6667	1	0	126	−776	
bcc	0.6154	1	0	222	−8448	

XY magnet					
Lattice	$\tau_G{}^2$	$\xi_0{}^{(0)}$	$\xi_0{}^{(2)}$	$\xi_0{}^{(4)}$	$\xi_0{}^{(6)}$
Square	2.0	1	0	16	−208
sc	1.5	1	0	64	−1216
bcc	1.3333	1	0	144	−4416

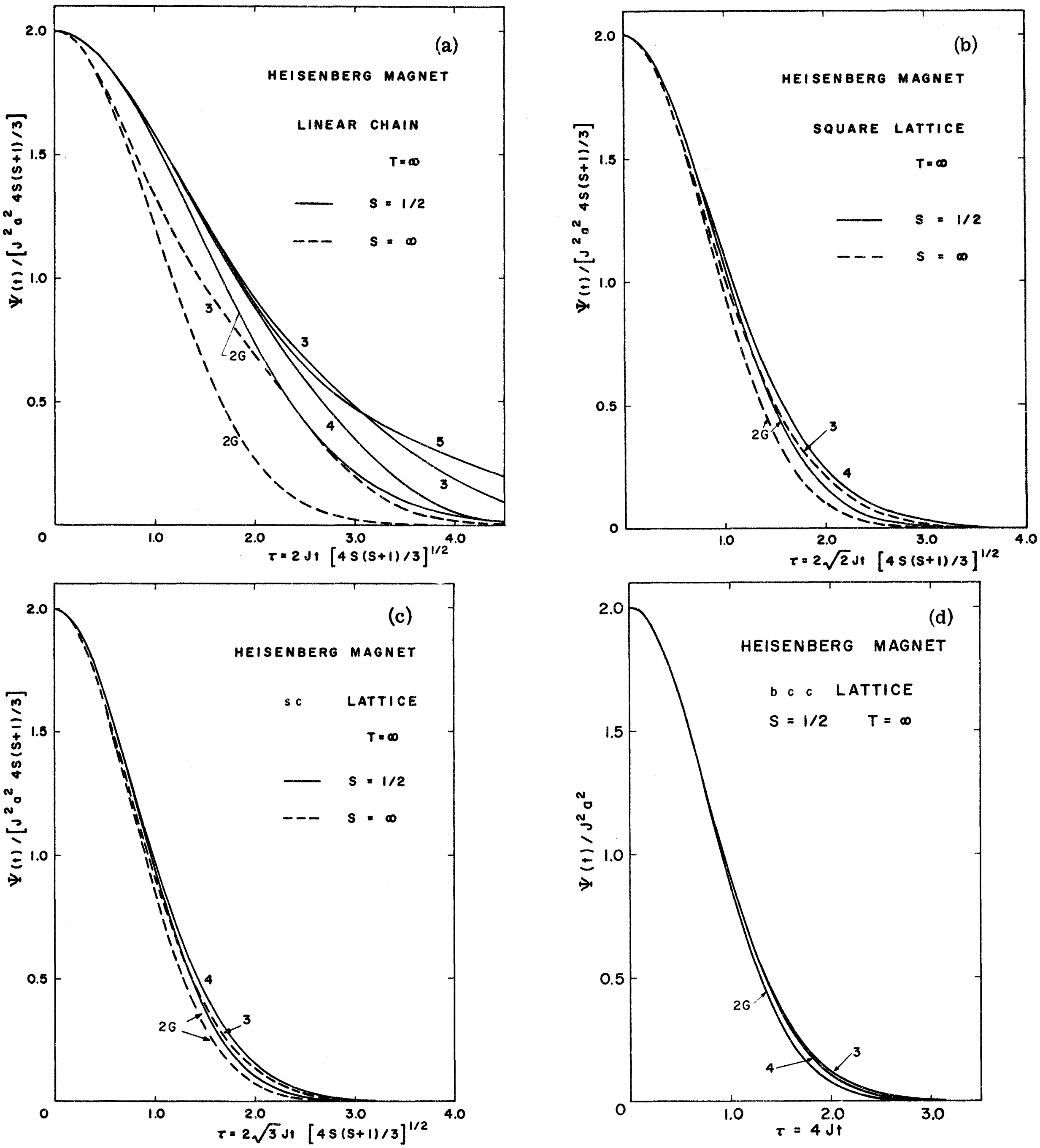
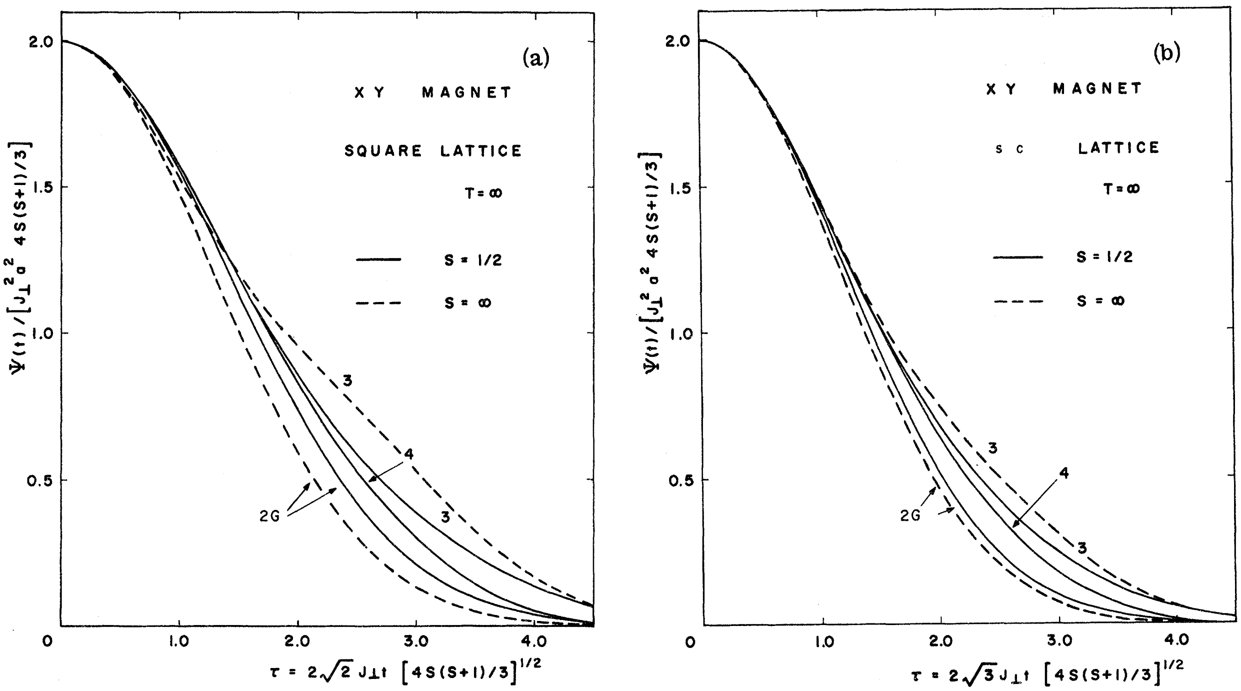


FIG. 1. $\Psi(t)$ given by (3.15) as a function of $\tau=(2z_S)^{1/2}Jt$ for the isotropic Heisenberg magnet at infinite temperature; (a) linear chain, (b) square lattice, (c) sc lattice, and (d) bcc lattice. Label n ($n=2$, 3, 4, 5) indicates that the power series on the right-hand side of (3.15) is truncated at nth term. As $\xi_\alpha{}^{(2)}$ is zero, we have the Gaussian distribution function for $n=2$; label G is associated in addition to 2 to indicate this fact.

The values of $M_{\alpha,p}{}^{(2n)}$ are found in Table II; $\alpha=t$ for the isotropic Heisenberg magnet and $\alpha=0$ for the XY magnet.

The time integral of $\Psi(t)$ given by (3.15) is calculated by

$$\int_0^\infty \Psi(t)\,dt = Ja^2\,\frac{M_\alpha{}^{(2)}}{I_\alpha{}^{(0)}(0)}\left(\frac{\pi}{2}\right)^{1/2}\frac{\tau_G}{(2z_S)^{1/2}}\times\left(1+\sum_{n=1}^{\infty}\frac{\xi_\alpha{}^{(2n)}\,\tau_G{}^{2n}}{n!\,(4z_S)^n}\right). \quad (3.19)$$



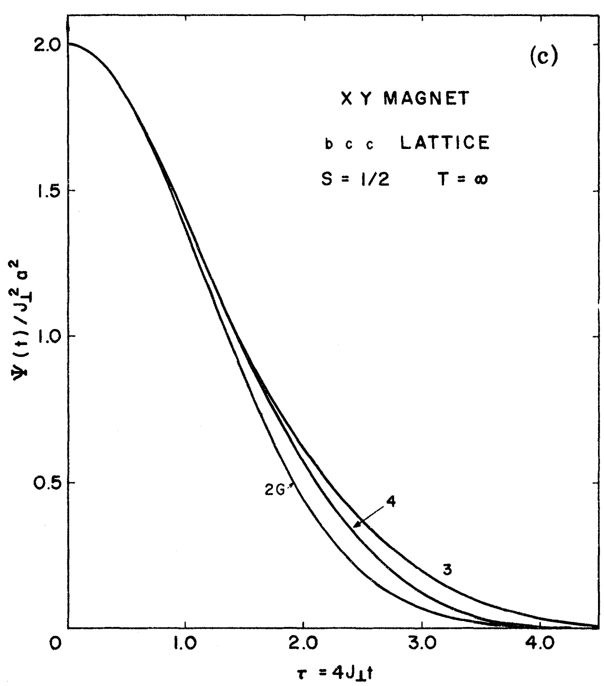


FIG. 2. $\Psi(t)$ given by (3.15) for the XY magnet at infinite temperature; (a) square lattice, (b) sc lattice, (c) bcc lattice.

IV. RESULTS AND DISCUSSIONS

The limiting function $\Psi(t)$ is calculated by using the formula (3.15), where the power series on the right-hand side is truncated to the exactly known terms. Curves are shown in Fig. 1 for the isotropic Heisenberg magnet of the linear, square, sc, and bcc lattices and in Fig. 2 for the XY magnet of the square, sc, and bcc lattices. The number n ($n=2$, 3, 4, 5) denotes that the curve is obtained by truncating the power series in the large parens of (3.15) at the term of $O(\tau^{2n})$. As $\xi_\alpha^{(2)}=0$, the curve for $n=2$ is for the Gaussian distribution function. The values of the integral $\int_0^\infty \Psi(t)\,dt$ are obtained with the aid of the formula (3.19) and are listed in Tables V and VI, where "n term" has the same meaning as n associated with the curves in the figures. In Figs. 1(b) and 1(c), the curve for $n=3$ is not given for $S=\frac{1}{2}$, for the difference of that curve with the curve for $n=4$ is so small that they collapse to the same line. As seen from Table IV, $\xi_\alpha^{(6)}$ is negative and hence the curve 4 is always below curve 3. From Figs. 1(b)–1(d), we conclude a satisfactory convergence of the present expansion for the isotropic Heisenberg magnet of spin $\frac{1}{2}$ for the square, sc, and bcc lattices. The values of ρ_4 and ρ_6 for the isotropic Heisenberg magnet of spin $\frac{1}{2}$ given in Table I are near to unity for the square, sc, and bcc lattices, suggesting a convergence starting from the Gaussian distribution function. Table III shows that the values of ρ_4 for these systems are almost the same also for larger spins, and we can expect a satisfactory convergence for larger spins for the isotropic Heisenberg magnet of these lattices.

As mentioned in Sec. III, $\Gamma(\vec{k}, t)$ has expansion coefficients of $O(k^2)$. As the differences of the expansion coefficients $\Gamma(\vec{k}, t)/k^2$ and those of $\Psi(t)$ are

TABLE V. $D/Ja^2=\int_0^\infty \Psi(t)\,dt/Ja^2$ for spin $\frac{1}{2}$. N term ($N=2$, 3, 4, 5) denotes the values of the integral when the sum in (3.19) is terminated at $n=N-1$.

Lattice	Two term (Gaussian)	Three term	Four term	Five term	D/Ja^2
		Isotropic Heisenberg magnet			
Linear	1.772	2.105	1.920	2.190	~2.1
Square	0.793	0.842	0.839		0.840
sc	0.591	0.620	0.618		0.619
bcc	0.492	0.512	0.507		0.509
		XY magnet			
Square	1.253	1.410	1.325		~1.4
sc	0.886	0.997	0.953		~1.0
bcc	0.724	0.814	0.776		~0.8

TABLE VI. $\int_0^\infty \Psi(t)\,dt\,(Ja^2)^{-1}[\frac{4}{3}S(S+1)]^{-1/2}$ for spin larger than $\frac{1}{2}$. The values will be very good estimates for $D(Ja^2)^{-1}\,[\frac{4}{3}S(S+1)]^{-1/2}$ for the isotropic Heisenberg magnets of the square, sc, and bcc lattices.

Isotropic Heisenberg magnet (three term) Lattice	$S=1$	$S=\frac{3}{2}$	$S=\frac{5}{2}$	$S=\frac{7}{2}$	$S=\infty$	XY magnet (three term) Lattice	$S=1\sim\infty$
Linear	1.813	1.717	1.659	1.640	1.618		
Square	0.810	0.800	0.794	0.792	0.790	Square	1.47~1.49
sc	0.605	0.601	0.598	0.598	0.596	sc	1.02~1.03
bcc	0.503	0.501	0.499	0.499	0.498	bcc	0.81~0.83

of $O(k^2)$, we can expect the same convergence for $\Gamma(\vec{k},t)/k^2$ as for $\Psi(t)$ when k is very small. The determined function $\Psi(t)$ is a product of a Gaussian distribution function and a polynomial. Its Laplace transform Ψ_p is expressed in terms of the parabolic-cylinder function[9] and is an entire function. For small k, $\Gamma(\vec{k},t)/k^2$ will take the same form as $\Psi(t)$ and hence $\Gamma_p(\vec{k})/k^2$ will be an entire function, satisfying the condition (A). The value $\lim_{p\to 0}\lim_{\vec{k}\to 0}\Gamma_p(\vec{k})/k^2$ must be $\lim_{p\to 0}\Psi_p$ which is nonzero as listed in Table III. Thus condition (B) is also satisfied. We now conclude that the spin diffusion occurs for the isotropic Heisenberg magnet of spin $\frac{1}{2}$ at infinite temperature, for the square, sc, and bcc lattices. The obtained spin diffusion constants are listed in Table V for these lattices. The result of the three-term approximation given in Table VI will give reliable values of the spin diffusion constant D for these systems of higher spins.

As shown in Figs. 1(a) and 2(a)–2(c), convergence of the expansion (3.15) is not satisfactory for the linear Heisenberg magnet and the square, sc, and bcc XY magnets. Since we have no theoretically determined function $\Psi(t)$, we cannot discuss analytic properties of the Laplace transform Ψ_p. We are not sure whether the spin diffusion occurs for these systems. The last column for the linear isotropic Heisenberg magnet and XY magnet in Table V and the part for these systems in Table VI give the suggested values of the spin diffusion constant, if the spin diffusion occurs for these lattices.

For the one-dimensional XY magnet of spin $\frac{1}{2}$, the exact $I(\vec{k},t)$ is known[10]:

$$I(\vec{k},t)=\tfrac{1}{4}J_0(4J_\perp t\sin\tfrac{1}{2}k)\ . \tag{4.1}$$

This function oscillates at large t and cannot describe the spin diffusion. The Laplace transform of (4.1) is

$$I_p(\vec{k})=\tfrac{1}{4}[p^2+(4J_\perp\sin\tfrac{1}{2}k)^2]^{-1/2}\ . \tag{4.2}$$

Substituting this into (2.7), we have

$$\Gamma_p(\vec{k})=[p^2+(4J_\perp\sin\tfrac{1}{2}k)^2]^{1/2}-p\ . \tag{4.3}$$

This $\Gamma_p(\vec{k})$ has a branch point on the imaginary axis and does not satisfy condition (A). If one calculates $\Psi(t)$, one obtains $\Psi(t)=2J_\perp^2a^2$ which is independent of time; cf. Table I.

In the present analysis, we considered the isotropic Heisenberg magnet and the *isotropic XY* magnet. In these systems, $S_{\vec{k}}^z$ for $\vec{k}=0$ commutes with the total Hamiltonian, and $I(\vec{k},t)$ does not decay when $\vec{k}=0$ and $I(\vec{k},t)$ for very small k decays

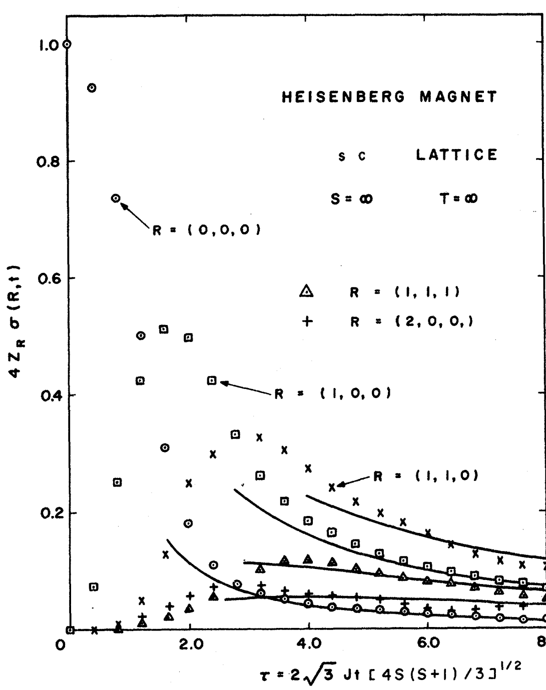


FIG. 3. Comparison of the asymptotic behavior of the two-time spin-pair correlation of classical spin for the sc lattice; ⊙, ⊡, ×... are due to computer-simulation calculation of Windsor, and the solid lines represent the solution of the diffusion equation. $Z_{\vec{R}}$ is the total number of neighbors with a relative coordinate equivalent to $\vec{R}$, including $\vec{R}$ itself. $Z_{\vec{R}}=1$ when $\vec{R}=(0,0,0)$.

TABLE VII. Comparison of the asymptotic behaviors of $4\sigma(\vec{R}, t)$ for the isotropic Heisenberg magnet at infinite temperature, obtained by the computer simulation calculation for classical spin (W) and by the spin diffusion (S-D). The values of the computer simulation for the linear and square lattices are read from graphs in Fig. 5 of Ref. 13. The values for the sc lattice are taken from Table I of Ref. 13.

Linear chain $D=1.62Ja^2[\frac{4}{3}S(S+1)]^{1/2}$

	$\vec{R}=(0)$		(1)		(2)		(3)		(4)		(5)	
τ	W	S-D	W	S-D	W	S-D	W	S-D	W	S-D	W	S-D
4.0	0.165	0.157	0.265	0.290	0.274	0.269	0.197	0.249	0.082	0.230	0.025	0.213
5.0	0.143	0.140	0.246	0.264	0.224	0.248	0.187	0.233	0.143	0.219	0.054	0.206
6.0	0.124	0.128	0.220	0.243	0.216	0.231	0.168	0.219	0.149	0.208	0.094	0.198

Square lattice $D=0.79Ja^2[\frac{4}{3}S(S+1)]^{1/2}$

	$\vec{R}=(0, 0)$		(1, 0)		(1, 1)		(2, 0)		(2, 1)		(2, 2)	
τ	W	S-D	W	S-D	W	S-D	W	S-D	W	S-D	W	S-D
4.0	0.078	0.071	0.230	0.228	0.206	0.182	0.119	0.116	0.217	0.186	0.024	0.048
6.0	0.053	0.048	0.183	0.164	0.141	0.141	0.107	0.105	0.167	0.180	0.072	0.058
8.0	0.026	0.036	0.111	0.127	0.128	0.114	0.099	0.091	0.174	0.163	0.057	0.058

sc lattice $D=0.596Ja^2[\frac{4}{3}S(S+1)]^{1/2}$

	$\vec{R}=(0, 0, 0)$		(1, 0, 0)		(1, 1, 0)		(1, 1, 1)		(2, 0, 0)	
τ	W	S-D	W	S-D	W	S-D	W	S-D	W	S-D
4.0	0.043	0.039	0.185	0.164	0.272	0.228	0.117	0.106	0.058	0.055
6.0	0.025	0.022	0.105	0.101	0.161	0.159	0.080	0.083	0.032	0.049
8.0	0.013	0.014	0.068	0.070	0.103	0.116	0.049	0.065	0.038	0.040
Error	0.005		0.013		0.018		0.014		0.013	

sc lattice

	$\vec{R}=(2, 1, 0)$		(2, 1, 1)		(2, 2, 0)		(2, 2, 1)		(2, 2, 2)	
τ	W	S-D	W	S-D	W	S-D	W	S-D	W	S-D
4.0	0.162	0.153	0.112	0.107	0.025	0.026	0.007	0.036	0.013	0.004
6.0	0.205	0.153	0.137	0.120	0.025	0.037	0.054	0.058	0.006	0.009
8.0	0.119	0.135	0.137	0.112	0.072	0.039	0.119	0.065	0.026	0.013
Error	0.025		0.025		0.018		0.025		0.014	

very slowly. We discussed whether this slow decay can be accounted by the spin diffusion. Recently attention has been called to the nonergodic nature of the one-dimensional *anisotropic XY* model.[11] For this system $S_{\vec{k}}^z$ for $\vec{k}=0$ does not commute with the total Hamiltonian, and hence $I(\vec{k}, t)$ decays to a value different from the initial value at $t=0$ even for $\vec{k}=0$. This implies that the behavior of $I(\vec{k}, t)$ cannot be described by the spin diffusion for this system.

V. COMPARISON OF THE VALUES OF D

First we compare our result with the experiment for the bcc solid He^3. The value obtained by Thompson *et al.*[12] is $D=(0.525\pm0.06)Ja^2$ in our unit. Our result $D=0.509Ja^2$ for spin $\frac{1}{2}$ is in complete agreement with the experiment.

In the next place, we compare our results with Windsor's computer-simulation calculation for classical spin ($S=\infty$).[13] When the spin diffusion occurs, the asymptotic behavior of $I(\vec{k}, t)$ is given by (2.8) for small k. The asymptotic behavior of the two-time spin-pair correlation function $\sigma(\vec{R}, t)$ is given by an inverse Fourier transform of that expression. The result is

$$\sigma(\vec{R}, t) \simeq [a/(4\pi Dt)^{d/2}]\, e^{-R^2/4Dt} , \tag{5.1}$$

where d is the dimension of the lattice. This result (5.1) is obtained by using the expression (2.8) in place of $I(\vec{k}, t)$ also for large k and then by extending the region of the integration over $\vec{k}$ to the whole space. By considering that both $I(\vec{k}, t)$ and the expression (2.8) for large k decay to zero fast, we confirm that it cannot affect the asymptotic behavior. Figure 3 shows the comparison of this asymptotic behavior with the results of the computer-simulation calculation for the sc lattice. An agreement is observed at $\tau \geq 5.0$. The numerical values at $\tau=4.0$, 6.0, and 8.0 are compared in Table VII. Similar comparisons for the linear chain and the square lattice are included in Table

VII. D/Ja^2 used in (5.1) are 1.62, 0.790, and 0.596 times $[\frac{4}{3}S(S+1)]^{1/2}$ for the linear, square, and sc lattice, respectively. Fairly good agreement suggests the occurence of the spin diffusion also for the isotropic Heisenberg magnet of spin $S=\infty$ for the linear chain. As the convergence of the present expansion is similar for finite S and for the XY magnet of the square, sc, and bcc lattices, the spin diffusion may occur for these cases too. It is recalled that Gulley *et al.*[14] checked the spin diffusion constant previously given, in a similar way for the sc lattice.

Finally we compare our results with previous theoretical values. As mentioned in the Introduction, Mori and Kawasaki[1] essentially suggested to use formula (1.5) and to approximate $I(\vec{k}, t)$ for small k by a Gaussian distribution function. The second column [two term (Gaussian)] of Table V gives the values obtained by this method for the case of spin $\frac{1}{2}$. Those values are very good estimates to the values determined in the present work, which are listed at the last column of the same table. For large spins, the situation is not changed. The values obtained by Bennett and Martin[3] and Resibois and De Leener[2] are 20% less than the present values.

ACKNOWLEDGMENTS

The author is grateful to Professor E. R. Hunt and Dr. T. Horiguchi for valuable discussions. Computation was performed with the aid of computer IBM 360/44 of Computer Center, Ohio University.

*Senior foreign scientist of NSF and Ohio University (1971–1972). Present address: Department of Applied Science, Faculty of Engineering, Tohoku University, Sendai, Japan.

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PHYSICAL REVIEW B VOLUME 6, NUMBER 9 1 NOVEMBER 1972

Electronic Shielding of Pr^{3+} and Tm^{3+} Ions in Crystals*

Paul Erdös and Jack H. Kang†

Department of Physics, The Florida State University, Tallahassee, Florida 32306

(Received 22 February 1972)

The relativistic wave functions, the electronic shielding factors $\sigma_i (i=2,4,6)$, the quadrupole antishielding factors and quadrupole polarizabilities are calculated for Pr^{3+} and Tm^{3+} ions. Two different theoretical schemes, the variational and the outward-integration methods are used. The results are compared with each other and with experimental values derived mainly from Mössbauer spectroscopy.

I. INTRODUCTION

For the study of rare-earth and actinide ions in crystals a first estimate of the crystal field effect is often obtained by considering a bare crystal field reduced through shielding.[1] Other quantities of interest that are due to shielding are the nuclear quadrupole antishielding factor, as well as the quadrupole polarizability.

Two different schemes have been developed to deal with the shielding problem. One is a numerical integration method, the other a variational method. The aim of this paper is to compare the results of these two methods with each other in