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Short-Range Order Effect on the Magnetic Anisotropy near the Transition Point*

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The temperature dependence of the magnetic anisotropy with tetragonal symmetry is studied classically for antiferromagnets near T_N, by developing a refined statistical theory. It appears that the magnetic anisotropy has a singularity of $(T-T_N)^{-1/2}$, where T_N denotes the Néel point to be determined from the exchange energy. Because the actual Néel point T_N^* shifts from T_N to the higher temperature by T_A which is proportional to the anisotropy constant, the magnetic anisotropy at T_N^* remains finite with an estimate of $\sim(T_A/T_N)^{1/2}$ times the powder susceptibility at T_N^*. The theoretical results are in good agreement with the experiments made by Stout *et al.* The other short-range order effects are also discussed. Especially, the theory predicts that the peak of the powder susceptibility appears above T_N, in agreement with the measment. In the course of the treatment,

$$\varphi(x)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{dk_1dk_2dk_3}{1-x\cos^2(k_1/2)\cos^2(k_2/2)\cos^2(k_3/2)}$$

and its derivative, which play an important role in the present theory, are plotted for $0\leqq x\leqq 1$.

I. INTRODUCTION

THE temperature dependence of the magnetic anisotropy of ferromagnets and antiferromagnets at low temperature has been well understood theoretically.[1] But, there is no theoretical contribution to the temperature dependence of the magnetic anisotropy near the transition point, except a treatment based on the Weiss approximation which is misleading in antiferromagnets.

Specifically, we shall consider in this paper the magnetic anisotropy of MnF_2 and FeF_2 near the Néel point T_N, which has been studied in detail experimentally.[2,3] Concerning the magnetic anisotropy of orthorhombic symmetry, a slight generalization will be necessary, of course, because our treatment concerns the magnetic anisotropy of tetragonal symmetry. If the magnetic anisotropy is of cubic symmetry, there will be no singular feature as discussed in this paper. In ferromagnets the temperature dependence of the magnetic anisotropy can be treated in a simpler manner.

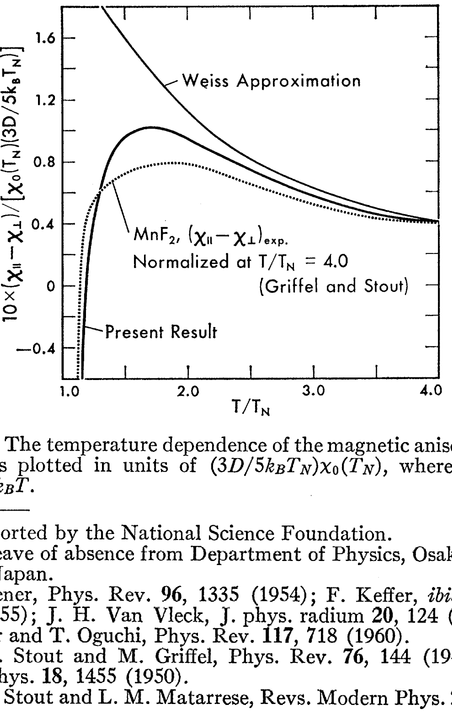

FIG. 1. The temperature dependence of the magnetic anisotropy. $\chi_{\parallel}-\chi_{\perp}$ is plotted in units of $(3D/5k_BT_N)\chi_0(T_N)$, where $\chi_0(T)=N\mu^2/3k_BT$.

The temperature dependence of the magnetic anisotropy of MnF_2 and FeF_2 are sketched below.

(1) MnF_2.[2] The experimental curve is shown in Fig. 1. At high temperatures the magnetic susceptibility parallel to the c axis $\chi_{\parallel}$ is larger than that perpendicular to the c axis $\chi_{\perp}$. With decreasing temperature, the magnetic anisotropy $\chi_{\parallel}-\chi_{\perp}$ goes up toward a maximum at a temperature $\sim 2T_N$. It decreases below $\sim 2T_N$ and changes its sign at $\sim 1.1T_N$.

(2) FeF_2.[3] The general features of this compound are similar to those of MnF_2 except for one point. That is, the anisotropy goes to zero below T_N, namely, at $\sim(9/10)T_N$; hence the maximum of $\chi_{\parallel}-\chi_{\perp}$ appears at a rather low temperature $\sim 1.2T_N$.

The behavior of $\chi_{\parallel}-\chi_{\perp}$ at high temperatures can be predicted from the molecular-field approximation of Weiss,[4] according to which $\chi_{\parallel}-\chi_{\perp}$ is proportional to the square of the powder susceptibility χ^2 in paramagnetic regions, and hence the maximum anisotropy should appear at T_N, in great disagreement with the measurements (see Fig. 1). This discrepancy comes from the fact that the molecular-field approximation neglects the cluster formation of spins coupled by the exchange interaction which increases with decreasing temperature and covers whole spins in the lattice at T_N. The anisotropy energy of coupled spins will be given by the anisotropy energy per spin times the number of coupled spins which increases roughly as $T_N/(T-T_N)$. Due to a large anisotropy energy associated with the cluster, the

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[1] C. Zener, Phys. Rev. **96**, 1335 (1954); F. Keffer, *ibid.* **100**, 1692 (1955); J. H. Van Vleck, J. phys. radium **20**, 124 (1959); F. Keffer and T. Oguchi, Phys. Rev. **117**, 718 (1960).

[2] J. W. Stout and M. Griffel, Phys. Rev. **76**, 144 (1949); J. Chem. Phys. **18**, 1455 (1950).

[3] J. W. Stout and L. M. Matarrese, Revs. Modern Phys. **25**, 338 (1953).

[4] F. Keffer, Phys. Rev. **87**, 608 (1952).

spin cluster will orient more frequently along the easy direction of the magnetization, namely, the c axis, than along the other directions, even above T_N. This effect tends to make $\chi_\perp$ larger than $\chi_\parallel$ because $\chi_\parallel - \chi_\perp$ is negative below T_N, according to the Van Vleck-Néel theory. As a result the effect of the anisotropy energy on the magnetic susceptibility proves to consist of two competing contributions. The first part comes from the response of spin to the magnetic field as a single spin, which tends to make $\chi_\parallel > \chi_\perp$. The second one comes from the response of the spin as a member of a cluster, which tends to make $\chi_\parallel < \chi_\perp$. The second part will prove to be $\sim (1/\pi)[T_N/(T-T_N)]^{1/2}$ times as effective as the first part. This tells us that the change of sign of $\chi_\parallel - \chi_\perp$ will occur at roughly

$$(1/\pi)[T_N/(T-T_N)]^{1/2} \sim 1,$$

in agreement with the measured result for MnF_2.

The sketch given above concerns the theoretical prediction when the anisotropy energy is very small compared to the exchange energy. This is just the case for MnF_2, but not for FeF_2. In the former, the anisotropy energy comes mainly from the magnetic dipole interaction,[4] whose magnitude is of the order to $10^{-3}k_BT_N$. Here k_B denotes the Boltzmann constant. In the latter, the anisotropy energy comes from the crystalline field energy, whose magnitude is of the order of $10^{-1}k_BT_N$.[5] This anisotropy energy makes the Néel point shift appreciably to the higher temperature. Therefore, the transition may appear at a temperature higher than the temperature at which $\chi_\parallel - \chi_\perp$ changes sign. However, our theory fails to predict a sufficient shift of T_N to achieve agreement with the measured $\chi_\parallel - \chi_\perp$ for FeF_2, using a reasonable magnitude of the anisotropy constant. For MnF_2, the shift of the Néel point T_A makes $\chi_\parallel - \chi_\perp$ finite at the actual Néel point, which is estimated to be $\sim -(T_A/T_N)^{1/2}\chi_c(T_N)$. Here $\chi_c(T_N)$ denotes the powder susceptibility at T_N. This estimate is between 2 and 3 times as large as the measured value.

The effect of the anisotropy energy on the magnetic susceptibility is rather subtle in an antiferromagnet. However, the anisotropy field, which sublattices see separately, will be much stronger. Very recently, Heller and Benedek[6] found the linewidth of F^{19} resonance in MnF_2 to be strongly anisotropic with respect to the direction of the applied field in temperature regions from $1.1T_N$ to T_N. This strong anisotropy is closely related to a strong anisotropy field acting on the sublattice.[7]

Assuming the anisotropy energy to be of the crystalline-field type, we shall treat the problem classically. In Sec. II the general expression for the magnetic susceptibility is given in terms of the spin-pair correlation function, up to the term linear with respect to the anisotropy constant. The correlation function is evaluated in Sec. III, and the temperature dependence of $\chi_\parallel - \chi_\perp$ is discussed in Sec. IV. The main result is given in Fig. 1. In Sec. V the other short-range order effect is discussed. In particular it may be noted that the peak of the theoretical powder susceptibility appears above T_N, in agreement with experiment. This is because a considerable amount of the short-range order, 28%, remains at T_N according to our theory. The relation of the present theory to the others is also discussed in Sec. V.

II. THE LOCAL SUSCEPTIBILITY FOR THE SYSTEM WITH ANISOTROPY ENERGY

We assume that the spin $\mathbf{S}$ is a classical vector with a magnitude of $[S(S+1)]^{1/2}$ and that the anisotropy energy is of the crystalline-field type with tetragonal symmetry. The total energy of the system is given by

$$E = E_{\mathrm{ex}} + E_{\mathrm{an}}; \tag{1}$$

$$E_{\mathrm{ex}} = A \sum_{nn} \cos\gamma_{jl}, \tag{2}$$

$$E_{\mathrm{an}} = -D \sum_j (\tfrac{3}{2}\cos^2\theta_j - \tfrac{1}{2}), \tag{3}$$

where A denotes the coupling constant proportional to the exchange integral, D the anisotropy constant, γ_{jl} the angle between the directions of two nearest-neighbor spins, θ_j the angle the spin j makes with the tetragonal axis, and $\sum_{nn}$ the sum over nearest-neighbor pairs.

Let $\chi(\mathbf{l}-\mathbf{j})$ be the magnetization of the spin $\mathbf{l}$ induced by a unit magnetic field acting on spin $\mathbf{j}$. Its formal expression up to the term linear in the magnetic field is

$$\chi(\mathbf{l}-\mathbf{j}) = (\mu^2/k_BT)\langle\cos\theta_l \cos\theta_j\rangle_{\mathrm{ex+an}}. \tag{4}$$

Here $\langle\cdots\rangle_{\mathrm{ex+an}}$ means the average over the ensemble for the system with both exchange and anisotropy energies, and μ is the magnetic moment, $g\mu_B[S(S+1)]^{1/2}$.

The local susceptibility $\chi(\mathbf{l}-\mathbf{j})$ is the most fundamental quantity for our study because the following relations can be shown easily:

$$\sum_j \chi(\mathbf{l}-\mathbf{j}) + \sum_\nu \chi(\mathbf{l}-\boldsymbol{\nu}) = (1/N)\chi, \tag{5}$$

$$\sum_j \chi(\mathbf{l}-\mathbf{j}) - \sum_\nu \chi(\mathbf{l}-\boldsymbol{\nu}) = (1/N)\chi', \tag{6}$$

where $\mathbf{l}$, $\mathbf{j}$ belong to the "+" sublattice and $\boldsymbol{\nu}$ to the "−" sublattice, and N denotes the total number of spins. χ represents the uniform susceptibility and χ' the susceptibility to be obtained in the case when +, − sublattices are subjected to a staggered field $+\mathbf{H}$, $-\mathbf{H}$, respectively. The Néel point is then determined by the temperature at which χ' becomes infinite.

The expansion of Eq. (4) up to terms linear in D is given by

$$\chi(\mathbf{l}-\mathbf{j}) = (\mu^2/k_BT)[\langle\cos\theta_l \cos\theta_j\rangle + (D/k_BT) \times \sum_m \langle\cos\theta_l \cos\theta_j (\tfrac{3}{2}\cos^2\theta_m - \tfrac{1}{2})\rangle + \cdots], \tag{7}$$

where $\langle\cdots\rangle$ denotes the average over the exchange

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[5] M. Tinkham, Proc. Roy. Soc. (London) **A236**, 535 (1956).

[6] P. Heller and G. B. Benedek, Phys. Rev. Letters **8**, 428 (1962).

[7] T. Moriya, Tech. Rept. of Institute for Solid State Physics, Ser. A, No. 42, 1962 [Prog. Theoret. Phys. (Kyoto) (to be published)].

system. In deriving the above equation, we used the relation

$$\langle(\tfrac{3}{2}\cos^2\theta-\tfrac{1}{2})\rangle=0, \tag{8}$$

which is justified by the isotropic nature of the exchange interaction. If we fix the orientation of spin $\mathbf{j}$ in the differential solid angle $d\omega$ at $\omega(\theta,\varphi)$, the average value of the z component of spin $\mathbf{l}$ is proportional to $\cos\theta_j$, namely,

$$\langle\cos\theta_l\rangle_{\omega_j}=\tilde{f}(\mathbf{l}-\mathbf{j})\cos\theta_j. \tag{9}$$

By multiplying (9) by $\cos\theta_j(d\omega_j/4\pi)$ and integrating over ω_j, we have

$$\langle\cos\theta_j\cos\theta_l\rangle=\langle\cos^2\theta_j\rangle\tilde{f}(\mathbf{l}-\mathbf{j}). \tag{10}$$

The factor $d\omega_j/4\pi$ represents the probability of finding spin $\mathbf{j}$ in $d\omega_j$ at ω_j. In (10)

$$\tilde{f}(0)=1, \tag{11}$$

and $\langle\cos^2\theta\rangle=\frac{1}{3}$.

By making use of (9), we express the second term in (7) in terms of $\tilde{f}$:

$$\langle\cos\theta_l\cos\theta_j(\tfrac{3}{2}\cos^2\theta_m-\tfrac{1}{2})\rangle_{\omega_m}=\tilde{f}(\mathbf{j}-\mathbf{m})\times\tilde{f}(\mathbf{l}-\mathbf{m})\cos^2\theta_m(\tfrac{3}{2}\cos^2\theta_m-\tfrac{1}{2}),$$

where spin $\mathbf{m}$ is fixed in $d\omega_m$ at ω_m. By multiplying the above expression by $d\omega_m/4\pi$ and integrating over ω_m, we have

$$\langle\cos\theta_l\cos\theta_j(\tfrac{3}{2}\cos^2\theta_m-\tfrac{1}{2})\rangle=(2/15)\tilde{f}(\mathbf{j}-\mathbf{m})\tilde{f}(\mathbf{l}-\mathbf{m}). \tag{12}$$

If we substitute (10) and (12) into (7), the result becomes

$$\chi(\mathbf{l}-\mathbf{j})=(\mu^2/3k_BT)[\tilde{f}(\mathbf{l}-\mathbf{j})+\tfrac{2}{5}(D/k_BT)g(\mathbf{l}-\mathbf{j})], \tag{13}$$

where $g(\mathbf{l}-\mathbf{j})$ is defined by

$$g(\mathbf{l}-\mathbf{j})=\textstyle\sum_m\tilde{f}(\mathbf{j}-\mathbf{m})\tilde{f}(\mathbf{l}-\mathbf{m}). \tag{14}$$

If $\mathbf{l}\neq\mathbf{j}$, (13) gives the correct expression for $\chi(\mathbf{l}-\mathbf{j})$. If $\mathbf{l}=\mathbf{j}$, a particular consideration is necessary because the left-hand side of (12) now becomes

$$\langle\cos^2\theta_j(\tfrac{3}{2}\cos^2\theta_m-\tfrac{1}{2})\rangle. \tag{15}$$

In the case where $\mathbf{j}=\mathbf{m}$, (15) becomes 2/15; otherwise it reduces to the correlation function of a quadrupole which is a very small effect.[8] Hence, we can write safely

$$\chi(0)=(\mu^2/3k_BT)[\tilde{f}(0)+\tfrac{2}{5}(D/k_BT)]. \tag{16}$$

It may be noted that the effect of anisotropy energy on $\chi(\mathbf{l}-\mathbf{j})$ is quite different for the two cases $\mathbf{l}\neq\mathbf{j}$ and $\mathbf{l}=\mathbf{j}$ because $g(0)$ deviates appreciably from unity as it approaches T_N, as will be seen later.

III. EVALUATION OF $\tilde{f}(\mathbf{l}-\mathbf{j})$

Our problem is now reduced to the problem of the propagation of order, which was originally discussed for the Ising model by Zernike.[9] The exact solution has been given for the two-dimensional Ising ferromagnet by Kaufman and Onsager.[10] See Elliott and Marshall[11] for a quantum-statistical treatment based on the Heisenberg model with spin $\frac{1}{2}$.

The formal expression for a correlation function $\tilde{f}(\mathbf{l}-\mathbf{j})$ is given by

$$\tilde{f}(\mathbf{l}-\mathbf{j})=(3/Z)\int\cdots\int\cos\theta_j\cos\theta_l\times\prod_{nn}K(\omega_s,\omega_t)d\omega_1\cdots d\omega_N, \tag{17}$$

where Z is the partition function, and

$$K(\omega_s,\omega_t)=\exp(-\beta\cos\gamma_{st});\quad \beta=A/k_BT. \tag{18}$$

The function $K(\omega_s,\omega_t)$ is bilinearly expanded in terms of the normalized spherical harmonics of ω, $\psi_{lm}(\omega)$:

$$K(\omega_s,\omega_t)=\lambda_0+4\pi\sum_{l=1}^{\infty}\sum_{m=-l}^{l}(-)^l\lambda_l\psi_{l,m}(\omega_s)\psi_{l,-m}(\omega_t), \tag{19}$$

where the term

$$\lambda_l(\beta)=(\pi/2\beta)^{1/2}I_{l+\frac{1}{2}}(\beta) \tag{20}$$

is the spherical Bessel function with imaginary argument. λ_l/λ_0 decreases as β^l with increasing temperature.

The partition function Z is given by the integration of $\prod K(\omega_s,\omega_t)$ over all angles of spins. We expand the product in a power series of λ_l, and draw a bond between a neighboring pair (s,t) if $K(\omega_s,\omega_t)$ contributes a factor $\lambda_l(l\neq 0)$ to a term in the series. Then each term in the series corresponds to a graph with some bonds in the lattice. Because of the orthogonal property of $\psi_{lm}(\omega)$, every term with open polygons composed of bonds vanishes after integration. Thus the first term of the series proves to be $(4\pi)^N(\lambda_0)^{\gamma_0N/2}$, γ_0 being the number of nearest neighbors. The next term comes from the graph with a closed polygon composed of 3 (fcc) or 4 (sc, bcc) bonds which will be neglected. In this approximation the integral in (17) now can be evaluated. The nonvanishing contributions come from graphs with open polygons with ends $\mathbf{l},\mathbf{j}$. If a graph is an open polygon with n bonds, its contribution to (17) proves to be $(-)^n(\lambda_1/\lambda_0)^n$. By summing up such contributions over all possible graphs, we get an approximate evaluation of (17):

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[8] By the procedure used in Sec. III, we get

$$\Sigma_m\langle\cos^2\theta_j(\tfrac{3}{2}\cos^2\theta_m-\tfrac{1}{2})\rangle=(2/15)/(1-\gamma_0\lambda_2/\lambda_0),$$

where, for a bcc lattice, we estimate $\gamma_0\lambda_2/\lambda_0\cong(1/15\gamma_0)(T_N/T)^2\leqq 1/120$.

[9] F. Zernike, Physica **7**, 565 (1940).

[10] B. Kaufman and L. Onsager, Phys. Rev. **76**, 1244 (1949); see also a review article, G. F. Newell and E. Montroll, Revs. Modern Phys. **25**, 353 (1953).

[11] R. J. Elliott and W. Marshall, Revs. Modern Phys. **30**, 75 (1958).

$$f(\mathbf{l}-\mathbf{j})=\sum_{n=0}^{\infty}(-)^n Q_n(\mathbf{l}-\mathbf{j})(\lambda_1/\lambda_0)^n. \tag{21}$$

$Q_n(\mathbf{l}-\mathbf{j})$ represents the number of ways by which we can get from $\mathbf{j}$ to $\mathbf{l}$ through n bonds. This should be done without any overlapping of bonds. Due to the translational symmetry of the lattice, $Q_n(\mathbf{l}-\mathbf{j})$ can be expanded in a Fourier series:

$$Q_n(\mathbf{l}-\mathbf{j})=(1/N)\sum_k \Gamma_n(\mathbf{k})\exp[-i\mathbf{k}\cdot(\mathbf{l}-\mathbf{j})]. \tag{22}$$

Here $\mathbf{k}$ is the wave vector of the lattice which is taken over N values of the first Brillouin zone of the lattice. If we disregard the exclusion of overlapping bonds, $\Gamma_n(\mathbf{k})$ is given by[12]

$$\Gamma_n(\mathbf{k})=\gamma_{\mathbf{k}}{}^n. \tag{23}$$

Here

$$\gamma_k=\sum_\delta \exp(i\mathbf{k}\cdot\boldsymbol{\delta}), \tag{24}$$

where $\boldsymbol{\delta}$ is the vector to the nearest neighbors. See Fisher and Sykes[13] for an attempt to find the exact asymptotic form of Q_n.

Substituting (22) with (23) into (21), we get, after summation,

$$f(\mathbf{l}-\mathbf{j})=(1/N)\sum_{\mathbf{k}}\exp[-i\mathbf{k}\cdot(\mathbf{l}-\mathbf{j})]/(1+\alpha\gamma_k/\gamma_0), \tag{25}$$

where

$$\alpha=\gamma_0(\lambda_1/\lambda_0). \tag{26}$$

In deriving (25), we introduced two kinds of errors. First, we neglected the contribution from graphs with closed polygons in both the numerator and denominator of (17). This approximation overestimates $\tilde{f}(\mathbf{l}-\mathbf{j})$ of (17) for sc and bcc lattices for the following reasons. In the lattice mentioned, the closed polygon contributes a positive value or factor to the integral. If we insert a closed polygon into a lattice that includes an open polygon without any overlapping of bonds, the number of graphs proves to be smaller than that of a lattice without the open polygon. This effect makes the numerator of (17) smaller than the denominator. Second, we erroneously took into account graphs with overlapping bonds, bringing about an overestimation of Q_n.[13a]

$f(\mathbf{l}-\mathbf{j})$ thus overestimated is now normalized so as to satisfy (11) by setting

$$\tilde{f}(\mathbf{l}-\mathbf{j})=f(\mathbf{l}-\mathbf{j})/f(0). \tag{27}$$

$f(0)$ is larger than unity, as shown above.

Substituting (25) and (27) into (14), we have

$$g(\mathbf{l}-\mathbf{j})=\{1/[f(0)]^2\}(1/N)\sum_{\mathbf{k}} \\ \times\exp[-i\mathbf{k}\cdot(\mathbf{l}-\mathbf{j})]/(1+\alpha\gamma_k/\gamma_0)^2, \tag{28}$$

where we made use of

$$(1/N)\sum_{\mathbf{j}}\exp(i\mathbf{k}\cdot\mathbf{j})=1 \text{ for } \mathbf{k}=0, \text{ and } 0 \text{ otherwise}. \tag{29}$$

IV. TEMPERATURE DEPENDENCE OF MAGNETIC ANISOTROPY

By substituting (13) and (16) into (5) and (6), we have

$$\begin{pmatrix}\chi\\ \chi'\end{pmatrix}=\frac{N\mu^2}{3k_BT}\left\{\sum_j \tilde{f}(\mathbf{l}-\mathbf{j})\begin{pmatrix}+\\ -\end{pmatrix}\sum_\nu \tilde{f}(\mathbf{l}-\boldsymbol{\nu})\right. \\ \left.+\frac{2}{5}\frac{D}{k_BT}\left[1+\sum_j{}' g(\mathbf{l}-\mathbf{j})\begin{pmatrix}+\\ -\end{pmatrix}\sum_\nu g(\mathbf{l}-\boldsymbol{\nu})\right]\right\}, \tag{30}$$

where $\sum_j{}'$ is the sum over $\mathbf{j}$ except $\mathbf{j}=\mathbf{l}$. $\tilde{f}$ is given by (27) with (25) and g by (28).

The sum in (30) is carried out with the help of (29). We shall begin with the evaluation of χ. The sum in (29) should be taken over whole spins, while in the sum $\sum_j{}' g(\mathbf{l}-\mathbf{j})$ the summand for $\mathbf{j}=\mathbf{l}$ should be excluded. Hence,

$$\sum_j{}' g(\mathbf{l}-\mathbf{j})+\sum_\nu g(\mathbf{l}-\boldsymbol{\nu})=[f(0)]^{-2}(1+\alpha)^{-2}-g(0).$$

By this method we obtain

$$\chi=\frac{N\mu^2}{3k_BT}\left\{\frac{1}{f(0)}\frac{1}{1+\alpha}\right. \\ \left.+\frac{2}{5}\frac{D}{k_BT}\left[\frac{1}{[f(0)]^2}\frac{1}{(1+\alpha)^2}+1-g(0)\right]\right\}. \tag{31}$$

In order to evaluate χ', we shall refer to the bcc lattice appropriate for MnF_2 and FeF_2. Referring to the reciprocal lattice of the sublattice, namely, simple cubic (sc), we have

$$\gamma_k/\gamma_0=\cos(k_1/2)\cos(k_2/2)\cos(k_3/2). \tag{32}$$

The first Brillouin zone of a bcc lattice is covered by the $\mathbf{k}$ values satisfying $-\pi\leqq k_1$, $k_2\leqq\pi$, and $-2\pi\leqq k_3\leqq 2\pi$. The sum in the expression for χ' is easily carried out if we rewrite the sum, for example,

$$\sum_j \tilde{f}(\mathbf{l}-\mathbf{j})-\sum_\nu \tilde{f}(\mathbf{l}-\boldsymbol{\nu})$$

as

$$\sum_m \tilde{f}(\mathbf{l}-\mathbf{m})\exp[i\boldsymbol{\kappa}\cdot(\mathbf{l}-\mathbf{m})],$$

where $\boldsymbol{\kappa}=(0,0,2\pi)$, and $\mathbf{m}$ is taken over whole spins. If we note that $\gamma_\kappa=-\gamma_0$, χ' becomes

$$\chi'=\frac{N\mu^2}{3k_BT}\left\{\frac{1}{f(0)}\frac{1}{1-\alpha}\right. \\ \left.+\frac{2}{5}\frac{D}{k_BT}\left[\frac{1}{[f(0)]^2}\frac{1}{(1-\alpha)^2}+1-g(0)\right]\right\}. \tag{33}$$

The Néel point is given by the temperature with the divergence of χ'. By (20) λ_1/λ_0 is the Langevin function $L(\beta)$. Hence, T_N is determined by

$$L(A/k_BT_N)=1/\gamma_0, \tag{34}$$

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[12] For instance, W. Opechowski, Physica **25**, 476 (1959).

[13] M. E. Fisher and M. F. Sykes, Phys. Rev. **114**, 45 (1959).

[13a] *Note added in proof.* All terms to contribute to the numerator of (17) are positive (negative) if $\mathbf{j}$, $\mathbf{l}$ belong to the same (different) sublattice(s). This is because the number of steps for going from $\mathbf{j}$ to $\mathbf{l}$ is always even (odd).

using (20) and (26). From (34) we get $A/k_BT_N=0.379$, which agrees well with the corresponding Weiss-approximation value, 0.375.

The effect of the anisotropy energy is to cause T_N to shift to a higher temperature. The principal part of χ' near T_N is approximated by

$$(N\mu^2/3k_BT)[f(0)(1-\alpha)-(2/5)D/k_BT]^{-1},$$

whence T_N proves to be determined by

$$L(A/k_BT_N)=(1/\gamma_0)-\tfrac{2}{5}[1/\gamma_0 f(0)](D/k_BT). \qquad (35)$$

Now let us look into the uniform susceptibility χ. Equation (31) gives the susceptibility $\chi_{\parallel}$ along the z axis which is assumed to be the easy direction of spin orientation. The susceptibility $\chi_{\perp}$ perpendicular to the easy direction, can be obtained if we replace the factor $\frac{2}{5}$ in the second term of (31) by $-\frac{1}{5}$. Hence

$$\chi_{\parallel}-\chi_{\perp}=\frac{N\mu^2}{3k_BT}\times\frac{3}{5}\frac{D}{k_BT}\left\{\frac{1}{[f(0)]^2}\frac{1}{(1+\alpha)^2}+1-g(0)\right\}. \qquad (36)$$

The first term in the braces of (36) gives the value of $\chi_{\parallel}-\chi_{\perp}$ derived from the Weiss approximation,[14] assuming $f(0)$ to be unity. The powder susceptibility χ_c is simply given by the first term in (31), which also reduces to the result obtained by the Weiss approximation by assuming $f(0)$ to be unity.

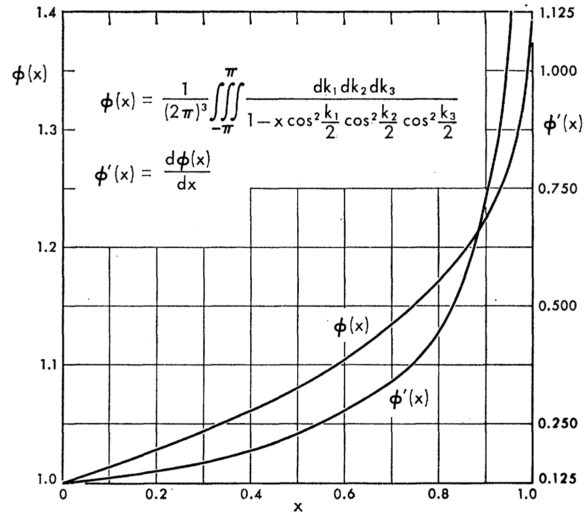

FIG. 2. Curves for $\varphi(x)$ and $\varphi'(x)$ vs x. The definition of $\varphi(x)$ is given in the figure.

By making use of (25) and (28), we obtain

$$f(0)=\varphi(x),\quad g(0)=[\varphi(x)+2x\varphi'(x)]/[\varphi(x)]^2, \qquad (37)$$

where

$$\varphi(x)=\frac{1}{(2\pi)^3}\iiint_{-\pi}^{\pi}\frac{dk_1dk_2dk_3}{1-x(\gamma_k/\gamma_0)^2}, \qquad (38)$$

$x=\alpha^2$, and $\varphi'(x)=d\varphi(x)/dx$.

The behavior of $\varphi(x)$ and $\varphi'(x)$ can be seen in Fig. 2. As x moves from 0 to 1, $\varphi(x)$ increases from 1 to $\varphi(1)=1.3932$ (Watson's value[15]). $\varphi'(x)$ starts from 0.125 at $x=0$ and increases until it diverges as

$$\varphi'\sim\pi^{-1}(1-x)^{-1/2}, \qquad (39)$$

with x approaching unity. A rapidly convergent series of $\varphi(x)$ for $0\leqq x\leqq 1$, whence $\varphi(x)$ and $\varphi'(x)$ have been computed, is given in the Appendix.

We shall now discuss the temperature dependence of $\chi_{\parallel}-\chi_{\perp}$. $x^{1/2}$ can be approximated by T_N/T within an error of 1%. At high temperatures, the last two terms in the braces in (36) are canceled by each other; hence $\chi_{\parallel}-\chi_{\perp}$ becomes positive. However, with decreasing temperature, the last term increases until it dominates the first two terms, causing $\chi_{\parallel}-\chi_{\perp}$ to become negative very near T_N. In Fig. 1 the theoretical curve for $\chi_{\parallel}-\chi_{\perp}$ vs T is shown, together with the experimental curve for MnF_2. As apparent from the curve, our theory satisfactorily reproduces the experimental behavior of the magnetic anisotropy in the vicinity of the Néel point.

If the temperature approaches T_N, the magnetic anisotropy $\chi_{\parallel}-\chi_{\perp}$ has a very large value, with the negative sign due to the divergent character of $g(0)$. Actually, the Néel point should appear at the temperature determined by (35). Thus $\chi_{\parallel}-\chi_{\perp}$ remains finite at T_N. The value of this limit is easily obtained when D is very small. Equation (35) gives

$$T_N{}^*=T_N+T_A/\varphi(1), \qquad (40)$$

where $T_N{}^*$ is the actual Néel point and $T_A=2D/5k_B$. If we retain only the singular term, being dominant very near T_N, $\chi_{\parallel}-\chi_{\perp}$ is written asymptotically

$$(\chi_{\parallel}-\chi_{\perp})_{T_N{}^*}\cong-\frac{3}{\pi}\left(\frac{2}{\varphi(1)}\frac{T_A}{T_N}\right)^{1/2}\chi_c(T_N), \qquad (41)$$

for $T_A/T_N\ll 1$, using (37) and (39). Here $\chi_c(T_N)$ denotes the powder susceptibility at T_N.

By making $(\chi_{\parallel}-\chi_{\perp})_{\text{theor}}$ fit its experimental value at $T/T_N=4.0$, we estimate T_A/T_N to be 3.9×10^{-3} and get $-0.07\chi_c(T_N)$ for $(\chi_{\parallel}-\chi_{\perp})_{T_N{}^*}$; a result in

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[14] The Weiss approximation for $\chi_{\parallel}$ gives

$$\chi_{\parallel}=(N\mu^2/3k_BT)[1+\tfrac{2}{5}(D/k_BT)]/\{1+(A/3k_BT)+(2/15)\times[AD/(k_BT)^2]\}.$$

Expanding and retaining the term linear in D, we approximate the above by

$$\chi_{\parallel}=(N\mu^2/3k_BT)[(1+A/3k_BT)^{-1}+\tfrac{2}{5}(D/k_BT)(1+A/3k_BT)^{-2}].$$

The corresponding expressions given in reference 18, (11.16) to (11.18), are different from the present result. This discrepancy comes from the neglect of a relevant higher-order term in the high-temperature expansion in reference 18.

[15] G. N. Watson, Quart. J. Math. **9–10**, 269 (1938).

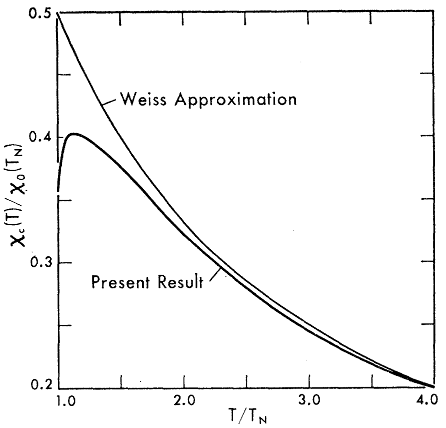

FIG. 3. The theoretical temperature dependence of the powder susceptibility $\chi_c(T)$ reduced in units of $\chi_0(T_N) \equiv N\mu^2/3k_BT_N$ (bcc).

rather good agreement with its experimental value $-0.03\chi_c(T_N)$. Actually, the anisotropy energy for MnF_2 comes from the magnetic dipole interaction; the predictions given will be more or less different from those to be obtained on the basis of the magnetic dipole interaction. It appears that $(\chi_{\parallel}-\chi_{\perp})_{T_N^*}$ is three times larger than the observed value if we estimate D from the antiferromagnetic data.

As D increases, T_N^* shifts toward the higher temperature until it crosses the temperature of sign-change of $\chi_{\parallel}-\chi_{\perp}$. This should be the case for FeF_2; however, in order to achieve this crossing, we need $T_A/T_N > 0.2$ which is too large for FeF_2.

V. ALTERNATE SHORT-RANGE ORDER EFFECTS

In this section, we shall discuss the approximate nature of the present theory and the other short-range order effect to be predicted from our theory. The anisotropy term will be omitted throughout this section.

The Sum Rule and the Normalization Constant

Our $\chi(\mathbf{j}-\mathbf{l})$ is very similar to the expression given by de Gennes and Villain[16] except for an important factor, $f(0)$. This factor has been introduced in the present theory in order to satisfy (16), namely, $\chi(0)=\mu^2/3k_BT$. We note that (16) gives a sum rule for the Fourier transform of $\chi(\mathbf{j})$, $\bar{\chi}(\mathbf{k})$. The sum rule can be obtained easily as

$$\sum\nolimits_{\mathbf{k}} \bar{\chi}(\mathbf{k}) = N\mu^2/3k_BT, \tag{42}$$

if we remember that

$$\bar{\chi}(\mathbf{k}) = \sum\nolimits_{\mathbf{j}} \chi(\mathbf{j}) \exp(i\mathbf{k}\cdot\mathbf{j}). \tag{43}$$

It is this Fourier-transformed susceptibility $\bar{\chi}(\mathbf{k})$ that plays a central part in the diffuse magnetic scattering of neutrons. The sum rule (42) is correct as far as the system is assumed to be classical and paramagnetic.[17] If we neglect the normalization constant $f(0)$, $\bar{\chi}(\mathbf{k})$ will be overestimated by $\sim 40\%$ very near the transition point.

Temperature Dependence of χ

The introduction of the normalization constant gives rise to a deviation of the susceptibility from the simple Curie-Weiss law. It appears that the peak of χ shifts toward a temperature higher than the Néel point (Fig. 3). This feature has been observed commonly in the temperature dependence of χ. For MnF_2 the observed peak appears near 73°K which is higher than the temperature of the specific-heat anomaly, 67°K. See Nagamiya, Yosida, and Kubo[18] for the other observed data. The Weiss temperature is estimated to be $-1.5T_N$ from the slope of $1/\chi$ vs T in the temperature range $1.5 \leqq T/T_N \leqq 2.5$, and $-1.2T_N$ from the slope in the range $2 \leqq T/T_N \leqq 3$.

The Short-Range Order

The degree of the short-range order is defined by

$$\sigma = |\langle \cos\theta_j \cos\theta_l \rangle| / \langle \cos^2\theta_j \rangle = |\tilde{f}(\mathbf{j}-\mathbf{l})|, \tag{44}$$

where $\mathbf{j}$, $\mathbf{l}$ are a nearest-neighbor pair. Using (27), (25), and (37),

$$\sigma = (1/\alpha)[1-1/\varphi(\alpha^2)]. \tag{45}$$

At the transition point σ is estimated to be 0.283 by using $\varphi(1)=1.3932$. Li[19] and Kastelijn and Kranendonk[20] estimated the corresponding value to be 0.242 and 0.295

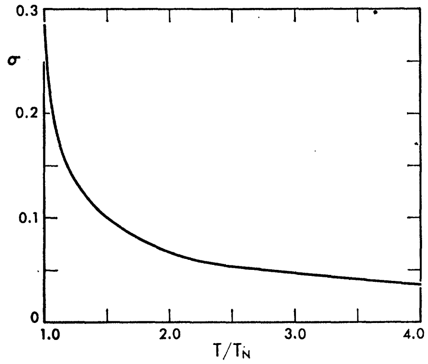

FIG. 4. Theoretical curve for σ vs T/T_N. (bcc) The degree of the short-range order σ is defined by Eq. (44).

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[16] P. G. de Gennes and J. Villain, J. Phys. Chem. Solids **13**, 10 (1960).

[17] Including the quantum correction to the sum rule, we have

$$\sum\nolimits_{\mathbf{k}} \bar{\chi}(\mathbf{k}) = [N(g\mu_B)^2/3k_BT]S(S+1)[1+\gamma_0(2J/3k_BT)^2S(S+1)+\cdots],$$

where the exchange interaction is assumed to be given by $2J\sum \mathbf{S}_j\cdot\mathbf{S}_l$

[18] T. Nagamiya, K. Yosida, and R. Kubo, in *Advances in Physics*, edited by N. F. Mott (Taylor and Francis, Ltd., London, 1955), Vol. 4, p. 1.

[19] Y. Y. Li, Phys. Rev. **84**, 721 (1951).

[20] P. W. Kastelijn and J. Van Kranendonk, Physica **22**, 317, 367 (1956); the same method has been given in T. Nakamura, Busseiron-Kenkyu **63**, 12 (1952).

respectively, for an antiferromagnet with spin $\frac{1}{2}$, using the quantum-statistical treatment. It may be interesting to note that the Kastelijn-Kranendonk theory predicts that the peak of χ shifts toward a higher temperature than T_N, but Li's theory does not, both for spin $\frac{1}{2}$. It is also noted that the short-range order to be obtained by their methods decreases with increasing spin quantum number, namely, with decreasing quantum nature.

The general characteristic of our σ is a sharp rise near the transition point, as can be seen in Fig. 4. Because of this, the specific heat shows an infinite peak of $1/(T-T_N)^{1/2}$ at the transition point. This singularity at the transition point has been predicted also by Brout's theory of the Ising ferromagnet,[21] but his theory erroneously predicts a different temperature for the singularity of specific heat and ferromagnetic susceptibility. However, our theory treats these two effects consistently.

Comparison with the High-Temperature Expansion Formula

We examine further the accuracy of our theory by comparing it with the exact high-temperature expansion. If we expand $\varphi(\alpha^2)$ in a power series of α^2 and substitute the resulting series into (45), σ is written

$$\sigma=(\lambda_1/\lambda_0)+19(\lambda_1/\lambda_0)^3+\cdots. \tag{46}$$

The exact coefficients are 1 and 12 for the respective powers of λ_1/λ_0. A similar expression for χ is obtained from (31):

$$\chi=(N\mu^2/3k_BT)[1-8(\lambda_1/\lambda_0)+56(\lambda_1/\lambda_0)^2 \\ -448(\lambda_1/\lambda_0)^3+-\cdots]. \tag{47}$$

The exact coefficients are 1, -8, 56, and -392 for the respective powers of λ_1/λ_0.

If we assume the normalization constant $f(0)$ to be unity, σ becomes identically zero in the paramagnetic region, corresponding to the Weiss approximation. The power series of χ to be obtained from the Weiss approximation does not reproduce correctly the third term in the brackets in (47). Thus the introduction of the normalization constant serves to improve the Weiss approximation.

VI. CONCLUSIONS

The molecular field approximation fails to predict the temperature dependence of the magnetic anisotropy in antiferromagnets near T_N, even if we use the ordinary local-field method with a higher approximation, e.g., the Bethe-Peierls approximation. This is because these approximate methods do not take into account the cluster formation of spins, which develops with decreasing temperature and covers the whole lattice at T_N. An elementary theory has been presented in which the spin correlations are taken into account.

The effect of the anisotropy energy on the susceptibility is to bring about two kinds of important singularisies at T_N. One of these has the character $1/(T-T_N)^2$ which appears in the susceptibility for the staggered field χ', making the transition point shift by T_A. The shift T_A is linear with respect to the anisotropy conttant. This effect can be predicted from the local-field approximation. The other singularity has the character $1/(T-T_N)^{1/2}$, which appears in the uniform susceptibility χ, giving χ an antiferromagnetic tendency. This effect cannot be predicted from the local-field approximation. Due to the shift of the Néel point, the term with the singularity $1/(T-T_N)^{1/2}$ remains essentially finite only at the actual Néel point. The finite value has proved to be of the order of $(T_A/T_N)^{1/2}$ times the powder susceptibility at T_N, in agreement with experiment.

Although the present statistical theory gives nearly the same Néel point as that obtained from the Weiss approximation, correlations are taken into account. This is accomplished by introducing a normalization constant into the expression for the local susceptibility. The local susceptibility thus obtained will be satisfied by a sum rule. The resultant improvement of the statistical approximation causes the peak of the powder susceptibility to shift toward a temperature higher than T_N, in agreement with experiment. The degree of the short-range order predicted amounts to 28% at T_N, accompanying a singular behavior of the specific heat as $1/(T-T_N)^{1/2}$. However, the present method fails in a two-dimensional lattice, because the normalization constant diverges logarithmically at the transition point in this case. This failure may be attributed to the transition that occurs at lower temperatures.

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APPENDIX

A rapidly convergent series for $\varphi(x)$,

$$\varphi(x)=\frac{2}{(2\pi)^3}\iiint_{-\pi}^{\pi} \times\frac{dk_1dk_2dk_3}{1-x\cos^2(k_1/2)\cos^2(k_2/2)\cos^2(k_3/2)}, \tag{A1}$$

for $0\leqq x\leqq 1$, will be given below. Integrating (A1) twice, we get[15,22]

$$\varphi(x)=(1/\pi^2)\int_{-\pi}^{\pi} F[\pi/2, x^{1/2}\cos(k_3/2)]dk_3. \tag{A2}$$

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[21] R. Brout, Phys. Rev. **118**, 1009 (1960).

[22] R. Kubo, Revs. Modern Phys. **25**, 344 (1953).

$F(\pi/2,\kappa)$ represents a complete elliptic integral of the first kind defined by

$$F(\pi/2,\kappa)=\int_0^{\pi/2}(1-\kappa^2\sin^2 u)^{-1/2}du, \tag{A3}$$

which has a logarithmic singularity at $\kappa=1$. The principal part of $F(\pi/2,\kappa)$ at the singular point proves to be given by

$$-\tfrac{1}{2}\ln(1-\kappa^2), \tag{A4}$$

as can be seen easily by replacing $\sin^2 u$ in the denominator of (A3) by $1-u^2$. Now (A3) is expanded in a power series by κ^2, followed by integration over u. The series thus obtained is subtracted by the series of $-\frac{1}{2}\ln\times(1-\kappa^2)$, assuming uniform convergence. The result becomes

$$F(\pi/2,\kappa)=-\tfrac{1}{2}\ln(1-\kappa^2)+(\pi/2)\{1+\tfrac{1}{2}(\tfrac{1}{2}-2/\pi)\kappa^2 +\tfrac{1}{2}[2(\tfrac{3}{8})^2-1/\pi]\kappa^4+\tfrac{1}{2}[2(\tfrac{5}{16})^2-2/(3\pi)]\kappa^6+\cdots\}. \tag{A5}$$

The above series is now convergent at $\kappa=1$ because the singular part which causes a divergence at $\kappa=1$ has been picked up in the first term.

Substituting (A5) into (A2), we have, after integration,

$$\varphi(x)=(2/\pi)\ln 2-(2/\pi)\ln[1+(1-x)^{1/2}]+1 +\tfrac{1}{4}(\tfrac{1}{2}-2/\pi)x+\tfrac{3}{16}[2(\tfrac{3}{8})^2-1/\pi]x^2 +\tfrac{5}{32}[2(\tfrac{5}{16})^2-2/(3\pi)]x^3+\cdots, \tag{A6}$$

using

$$\int_0^{2\pi}\ln[1-x\cos^2(k/2)]dk=4\pi\ln\{[1+(1-x)^{1/2}]/2\}.$$

The series given above reproduces the first three figures correctly for $\varphi(1)$.

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Distribution Functions and Ionization Rates for Hot Electrons in Semiconductors

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The distribution of electrons in a semiconductor at high electric field is governed by a Boltzmann equation which describes the effects of the field, the phonons, and the ionization processes on the electrons. This equation can be converted to an integral equation for the space and energy dependent collision density by performing the angular integrations. The integral equation is solved numerically to obtain alpha, the ionization rate per unit path length. The resulting alpha shows a dependence on field strength $\mathcal{E}$ which is roughly $\exp(-b/\mathcal{E})$ at low fields and $\exp(-c/\mathcal{E}^2)$ at high fields, but there are significant differences from the earlier calculations of Wolff and Shockley. These differences result from the approximations used by the earlier workers to treat the angular dependence. We present graphs of $\log\alpha$ vs $(1/\mathcal{E})$ for a wide range of material parameters. These graphs are useful in interpreting measurements of charge multiplication in terms of the properties of the material supporting the transport process.

I. INTRODUCTION

MEASUREMENTS of the charge multiplication at high electric fields in semiconducting materials can be used to supply basic information about the interaction of hot electrons with the material, provided that one has an adequate model for interpreting the data. A reasonably satisfactory two-part model exists, based on the analogy between the processes taking place in the semiconductor and those taking place in a gas discharge. The first part relates the charge multiplication to the ionization rate per unit path length, α_i,[1,2] and the second part relates this quantity, Townsend's alpha coefficient, to the distribution function for the hot electrons in the material.[3,4]

Calculating the distribution function for the hot electrons is not a particularly simple task, however, and different approximations made at this stage result in different predictions about the field dependence of Townsend's alpha. Wolff,[3] for example, neglects the band structure of the silicon, which was unknown at the time of his calculations, and expands the distribution function in spherical harmonics, retaining only the P_0 and P_1 terms. This procedure is justified at high fields, as Wannier has shown,[5] where the energy loss per collision is so much smaller than the energy gain that the collisions serve to keep the distribution nearly isotropic. The result of retaining only the P_0 and P_1 is a diffusion theory approximation, in which the electrons undergo many collisions in transport from one energy to another. It results in a distribution which, below ionization threshold, is quasi-Maxwellian with a temperature re-

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[1] K. G. McKay, Phys. Rev. **94**, 877 (1954).
[2] S. L. Miller, Phys. Rev. **105**, 1246 (1957).
[3] P. A. Wolff, Phys. Rev. **95**, 1415 (1954).
[4] W. Shockley, Czech. J. Phys. **B11**, 81 (1961) and Solid-State Electron. **2**, 35 (1961).
[5] G. H. Wannier, Bell System Tech. J. **32**, 170 (1953).