

Sublattice Magnetization and Resonance Frequency of Antiferromagnets with Large Uniaxial Anisotropy*

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The effect of large anisotropy on the thermal behavior of the sublattice magnetization and antiferromagnetic resonance frequency is discussed. It is shown that the curves for $M(T)/M(0)$ and $\omega(T)/\omega(0)$ vs T/T_c are shifted upward from those predicted by a Brillouin function magnetization curve. The shifts are due to a combination of the effect of the large anisotropy energy with that of electron exchange correlation. Corrections to the molecular field approximation arising from pair correlations are taken into account by an extension of the Oguchi method. These corrections are expected to be roughly $1/Z$ as large as the more accurate corrections which would arise from correlation with all Z neighbors. This expectation is supported by a comparison of the values of kT_c/J and $\bar{S}(0)$ for the Oguchi method with those obtained by the Bethe-Peierls-Weiss and spin-wave methods, respectively. The results are related to the experiments on FeF_2 where the anisotropy is comparable to the exchange energy.

1. INTRODUCTION

WE consider the effect of large uniaxial anisotropy on the temperature dependence of the sublattice magnetization and antiferromagnetic resonance frequency of an antiferromagnetic compound with nearest-neighbor exchange interactions. The simplified model treated gives an explanation for the peculiar behavior of these properties in FeF_2 where the anisotropy is comparable with the exchange energy. In FeF_2 , if the reduced sublattice magnetization, $M(T)/M(0)$, is plotted as a function of reduced temperature (T/T_c), the curve is shifted noticeably upward from that given by a Brillouin function.¹ Similarly, the reduced resonance frequency, $\omega(T)/\omega(0)$, curve is shifted upward from that expected for the case of Brillouin function sublattice magnetization dependence and small anisotropy field.²

In FeF_2 , $S=2$. Also a small part of the anisotropy energy is not uniaxial and second-neighbor exchange is important. We treat a simplified model for $S=1$ with nearest-neighbor exchange and large uniaxial anisotropy. This model suffices to explain the shifts in magnetization and resonance frequency. These are shown to be due to a combination of the effect of the large anisotropy energy with that of electron exchange correlation.

2. THE SUBLATTICE MAGNETIZATION

The Hamiltonian considered is

$$\mathcal{H} = 2|J| \sum_{\langle j,k \rangle} (\mathbf{S}_j \cdot \mathbf{S}_k) - D \sum_i S_{iz}^2 - D \sum_k S_{kz}^2. \quad (1)$$

As stated above, $S=1$. In the numerical calculations, Z_n , the number of nearest neighbors will be taken as 8. Body center sites are denoted j and corner sites, k . The first summation is over pairs of neighboring cations. The exchange constant is $|J|$, and D is the anisotropy

constant which may be estimated experimentally by paramagnetic resonance on ions of the type in question diluted in an identical compound of a nonmagnetic ion³ or by theoretical calculation.^{4,5} The fact that the z component of the individual spin is squared in the anisotropy energy means that the anisotropy energy is unchanged if a single spin changes sign. This would not be the case if the anisotropy energy were given by $-DS_{Az}^2 - DS_{Bz}^2$, the total sublattice spin squared.

The sublattice magnetization is found from the condition:

$$\bar{S} = \text{Tr} S_{iz} \exp(-\mathcal{H}/kT). \quad (2)$$

The crudest approximation yielding a value of \bar{S} is the molecular field approximation. This neglects all correlation between spins. From (2) we obtain

$$\bar{S} = \frac{\exp[(D+16|J|\bar{S})/kT] - \exp[(D-16|J|\bar{S})/kT]}{\exp[(D+16|J|\bar{S})/kT] + \exp[(D-16|J|\bar{S})/kT] + 1}. \quad (3)$$

This determines \bar{S} . The Curie temperature is the highest value of T for which the nonzero value of \bar{S} is stable.

The effect of correlation will be considered next. Several methods have been devised to take account of correlation at the high temperatures which are of greatest interest in connection with the experiments.^{6,7} Probably the most accurate such calculation is that of Brown and Luttinger⁸ giving the Curie temperature for nearest-neighbor exchange by the Bethe-Peierls-Weiss method. This method, however, has not been used in the present case both because of computational complexities and because of the presence of an anti-Curie tempera-

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⁴ K. Niira and T. Oguchi, Progr. Theoret. Phys. (Kyoto) **11**, 425 (1954).

⁵ T. Moriya, K. Motizuki, K. Kanamori, and T. Nagamiya, J. Phys. Soc. Japan **11**, 211 (1956).

⁶ P. R. Weiss, Phys. Rev. **74**, 1493 (1948).

⁷ P. W. Kastelijn and J. van Kranendonk, Physica **22**, 317, 367 (1956).

⁸ H. A. Brown and J. M. Luttinger, Phys. Rev. **100**, 685 (1955).

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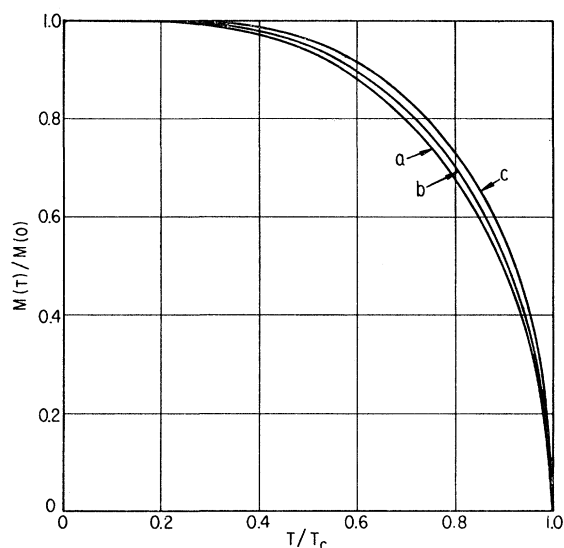


FIG. 1. (a) Brillouin function for $S=1$. (b) $M(T)/M(0)$ as a function of T/T_c for $D=2.5J$ including the effect of correlation of each spin with one neighbor. (c) $M(T)/M(0)$ as a function of T/T_c for $D=2.5J$, including the effect of correlation of each spin with all eight neighbors.

ture, which would make the values of magnetization unreliable for temperatures much removed from the Curie temperature. (The constant coupling method of Kastelajin and Van Kranendonk⁷ also has an anti-Curie temperature for the antiferromagnetic case.) Instead, we use an extension of a simpler method due to Oguchi.⁹ This method yields values for the sublattice magnetization at $T=0$ and for the Curie temperature which can be compared to the result of spin-wave theory and the Brown-Luttinger calculation to test its validity.

The Oguchi method consists of treating the interaction of an arbitrary pair of neighboring spins exactly while treating their interaction with their other neighbors by a molecular field approximation. In the region above the Curie temperature, the Oguchi method reduces to solving the Hamiltonian for a pair of spins (or a greater number of spins in higher approximations) exactly and neglecting all interactions with the rest of the lattice. This is the basis of calculations such as that of Smart¹⁰ finding the short-range order above the Curie temperature. The original calculation was for spin- $\frac{1}{2}$ particles with nearest neighbor exchange only. We extend this to the Hamiltonian (1).

The pair Hamiltonian is

$$\mathcal{H}_p = 2|J|\mathbf{S}_j \cdot \mathbf{S}_k + 2|J|(Z_n - 1)\bar{S}(-S_{jz} + S_{kz}) - D(S_{jz}^2 + S_{kz}^2). \quad (4)$$

It is to be noted that $S_{jz} + S_{kz}$ is a good quantum number for (4). However, $|\mathbf{S}_j + \mathbf{S}_k|^2$ is not a good quantum number even when $D=0$. Therein lies the difficulty in

⁹ T. Oguchi, Progr. Theoret. Phys. (Kyoto) **13**, 148 (1955).

¹⁰ J. S. Smart (to be published).

extending the Oguchi method to values of spin greater than 1.

We have solved for the eigenvalues and eigenfunctions of (4). This together with the use of (2) yields a transcendental equation for \bar{S} of the same type as (3), although more complex. From this equation we have found the condition determining the Curie temperature. This has been evaluated for $D=0$ and $D=2.5J$ (a value approximately equal that in FeF_2). At $T=0$, \bar{S} does not attain its saturation value of 1. The values of kT_c/J and $\bar{S}(0)$ are given in Table I for both the molecular field and pair correlation calculations. The graph of $\bar{S}(T)/\bar{S}(0)$ vs T/T_c has been found by both methods for $D=0$ and $D=2.5J$. Figure 1 compares curves obtained for $D=2.5J$ by the pair correlation method [Fig. 1(b)] and for $D=0$ by the molecular field method (Brillouin function) [Fig. 1(a)]. The upward shift due to anisotropy and spin correlation may be observed. For a given value of $\bar{S}(T)/\bar{S}(0)$, the value of T/T_c is shifted to the right. By calculation this shift has been found equal to the sum of the shifts for $D=2.5J$ in the molecular field calculation and $D=0$ in the pair correlation calculation. Thus the effects of anisotropy and spin correlation are additive. The shift due to correlation is about 15 to 20% of the total shift between Fig. 1(a) and Fig. 1(b) for temperatures up to about $0.90T_c$, while for higher temperatures correlation accounts for as much as 45% of this shift.

The values for T_c and $\bar{S}(0)$ with $D=0$ can be used to test the success of the pair correlation calculation in taking account of correlation. The molecular field calculation gives values for T_c and $\bar{S}(0)$, which take no account of correlation, while the Bethe-Peierls-Weiss type calculation of Brown and Luttinger and the spin-wave theory of Kubo give values of these quantities with the effect of correlation adequately included. The various values are shown in Table I.

We would expect the pair correlation method to underestimate the effects of correlation. This is borne out by the data of Table I. It is interesting to compare the shift in kT_c/J from the molecular field value for the Brown-Luttinger calculation with that for the pair correlation method.

The shift in kT_c/J comes about because the molecular field treatment completely neglects short-range order. In this picture, the Curie temperature, roughly speaking, corresponds to the thermal energy necessary to compensate for the energy in the ground state at $T=0^\circ$.

TABLE I. Values of kT_c/J and $\bar{S}(0)$ for the several methods.

	Molecular field		Pair correlation		Spin	Brown-
	$D=0$	$D=2.5J$	$D=0$	$D=2.5J$	wave	Luttinger
kT_c/J	10.67	11.42	10.48	11.24		9.03
$\bar{S}(0)$	1	1	0.9954	0.9965	0.925	

When correlation is included there is energy associated with short-range order still present at the Curie temperature. Therefore, the thermal energy necessary to destroy the long-range order is less than that given by the molecular field picture. Hence the value of kT_c/J is lower than in the molecular field treatment. The pair calculation would include the shift in kT_c due to one neighbor, which our calculation gives as $0.19J$. We expect the shift in kT_c caused by correlation effects to be approximately linear in the total number of neighbors. Then the shift for the Brown-Luttinger calculation should be about 8 times that for the pair. The shifts to be compared are $1.64J$ vs $1.52J$, which are about equal. $\bar{S}(0)$ is also shifted from the molecular field value when correlation is included. The similar comparison for $\bar{S}(0)$ would give a shift of 0.075 for spin waves as opposed to 0.037 for 8 times the pair shift. This difference is not surprising since the cluster calculation excludes the long-wavelength spin waves important at low temperatures. This exclusion would lead to a value for sublattice magnetization greater than the spin-wave value.¹¹ Also Fisher¹² has calculated the spin deviation in the antiferromagnetic ground state by a variational calculation. His result for the present case is 0.031. This would indicate that the spin-wave treatment may overestimate the spin deviation. The agreement between 0.037 and Fisher's value of 0.031 is good. In any case we are justified in considering that the pair method greatly underestimates the effect of correlation in shifting the reduced magnetization curve, probably by a factor equal to the number of interacting neighbors or more. This would indicate that the actual shift observed should be more than twice that between curves *a* and *b* of Fig. 1. Multiplying the shift due to the correlation with one neighbor by eight and adding this to the molecular field result for $D=2.5J$ gives the curve of Fig. 1(c).

We should point out that the numerical results quoted in Oguchi's paper⁹ would disagree with our statement that the correlation effect taking more neighbors into account is approximately linear. However, Oguchi's numbers are in error. In particular all the values for the first approximation of kT_c/J in Oguchi's Table I (the ferromagnetic case) are in error. For example, for $Z=8$, the correct result for the first approximation is 3.891, while that for the second approximation is 3.853. The zeroth approximation (molecular field) is 4. The correct values for kT_c/J for other values of Z are given in Table II. The first approximation is for a pair of spins and takes into account correlation with one neighbor for each spin. The second approximation is for three spins in a line. This includes correlation with two neighbors for the middle spin and with only one neighbor for the end spins. On the average then, the second approximation accounts for the correlation with one and a third neighbors of each spin. From our arguments above, the

TABLE II. Values of kT_c/J for the zeroth, first, and second Oguchi approximations, and for the Brown-Luttinger calculation for $S=\frac{1}{2}$ with ferromagnetic nearest-neighbor exchange.

Z	2	4	6	8	12
Zeroth approx.	1	2	3	4	6
First ^a approx.	0.656	1.80	2.86	3.891	5.92
Second approx.	0.518	1.73	2.81	3.853	5.88
Brown-Luttinger	...	no root	1.85	2.91	...

^a Professor Oguchi has kindly provided us with these corrected values of the first approximation for $Z=2, 4, 6, 12$. The values for the second approximation are those of the original paper for $Z=2, 4, 6, 12$. We have found the values of the first and second approximation for $Z=8$ using Oguchi's formulas.

difference between the first and second approximations should be about $\frac{1}{3}$ of that between the zeroth and first. This is satisfied very well. We have also done the calculation for four spins located on the corners of the square, so that the correlation of each spin with two neighbors is included. The value for kT_c/J for $Z=8$ is 3.777. The difference between this and the first approximation is 0.114 as compared to 0.109, the difference between the first and zeroth.^{12a} Now then, eight times the difference between the zeroth and first approximations should approximately equal the difference between the zeroth and the Brown-Luttinger result. This compares 0.872 to 1.09. We note that eight times the result for one neighbor gives somewhat less than the correct total effect of correlation. This is in agreement with the result above that the difference between the first and second is slightly greater than that between the first and zeroth approximation. Considering the existence of such a small increase between the differences of successive approximations, we would expect the Oguchi value to extrapolate to a value quite close to the Brown-Luttinger result when all neighbors are included. There are also errors in Oguchi's Table II. Thus the results of Oguchi as corrected, combined with our calculation for the square, agree with our statements that the corrections to the molecular field approximation arising from pair correlations are roughly $1/Z$ as large as the corrections if all neighbors were taken into account.^{12b}

3. ANTIFERROMAGNETIC RESONANCE FREQUENCY

The graph of $\omega(T)/\omega(0)$ vs T/T_c will be shifted in a way similar to that for $\bar{S}(T)/\bar{S}(0)$. The antiferromag-

^{12a} A calculation has been done of $\bar{S}(T)/\bar{S}(0)$ vs T/T_c for the four-spin case with ferromagnetic coupling. The shift from the Brillouin function is somewhat greater than twice that for the pair calculation of Oguchi. For the typical value $T/T_c=0.5$, the values of $\bar{S}(T)/\bar{S}(0)$ are: Brillouin, 0.9575; Oguchi pair, 0.9564; four spin, 0.9551.

^{12b} For four spins located on the corners of a square, $\bar{S}(0)$ with $S=\frac{1}{2}$ and antiferromagnetic coupling has been calculated. The spin deviation (the difference from $\frac{1}{2}$) is 0.0100 as compared to 0.0051 for the pair calculation.

¹¹ T. Oguchi and Y. Obata, Progr. Theoret. Phys. (Kyoto) **9**, 359 (1953).

¹² J. Fisher, J. Phys. Chem. Solids **10**, 44 (1959).

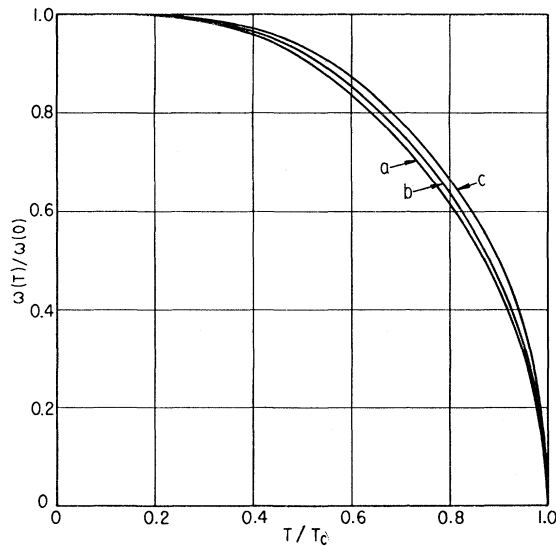


FIG. 2. (a) $\omega(T)/\omega(0)$ as a function of T/T_c for $D=2.5J$ calculated by the molecular field method using terms in D as a first-order perturbation on the energy with $D=0$. (b) $\omega(T)/\omega(0)$ as a function of T/T_c for $D=2.5J$, where full account has been taken of large anisotropy. (See text.) The effect of correlation of each spin with one neighbor is included. (c) $\omega(T)/\omega(0)$ as a function of T/T_c for $D=2.5J$, where full account has been taken of large anisotropy. The effect of correlation of each spin with all eight neighbors is included.

netic resonance frequency is¹³⁻¹⁵

$$\hbar\omega = g\beta[H_A(2H_E + H_A)]^{\frac{1}{2}}, \quad (5)$$

where

$$H_E = 2|J|Z_n\bar{S}/g\beta \quad (6)$$

is the exchange field and H_A is the anisotropy field. The temperature dependence of H_E follows directly from the information above. The principal problem in finding the temperature dependence of ω is in obtaining the thermal behavior of H_A . The method suggested by Yosida¹⁶ when the anisotropy is small leads to the following expression for $S=1$:

$$H_A(T)/H_A(0) = (3\langle S_z^2 \rangle - 2)/\bar{S}. \quad (7)$$

In deriving (7), the magnitudes of the plus and minus magnetization vectors are kept constant, though they can change their orientations.

We find an expression corresponding to (7) when the anisotropy energy is not negligible compared to the exchange energy. Let α, β, γ be the directional cosines of the z axis with respect to the axes defined by the direction of magnetization (X', Y', Z'). In the molecular field approximation, the Hamiltonian for a given spin is

$$\mathcal{H} = -2|J|Z_n\bar{S}S_{jz'} - D(\alpha S_{jx'} + \beta S_{jy'} + \gamma S_{jz'})^2. \quad (8)$$

The equation determining the eigenvalues can be found

in the usual way. The anisotropy field is given by

$$-\frac{N/2}{M(T)} \frac{d\langle \mathcal{H} \rangle}{d\gamma} \bigg|_{\gamma=1} = H_A. \quad (9)$$

To find H_A , it is necessary only to know the eigenvalues and their derivatives with respect to γ at $\gamma=1$. H_A is given by

$$H_A(T) = -\frac{1}{g\beta} \left\{ \frac{2Z_n|J|D}{2Z_n|J|\bar{S} + D} \exp[(D + 2Z_n|J|\bar{S})/kT] - \frac{8|J|^2Z_n^2\bar{S}}{4|J|^2Z_n^2\bar{S}^2 - D^2} + \frac{2Z_n|J|D}{2Z_n|J|\bar{S} - D} \exp[(D - 2Z_n|J|\bar{S})/kT] \right\} \{ \exp[(D + 2Z_n|J|\bar{S})/kT] + 1 + \exp[(D - 2Z_n|J|\bar{S})/kT] \}. \quad (10)$$

In deriving this we have assumed that the magnitude of the sublattice magnetization is constant for small variations in γ . For $\bar{S}=0$, $H_A=0$. The resonance frequency goes to 0 at the Curie temperature in this model.

Equations (5), (6), and (10) can be combined to find $\omega(T)$. At $T=0$,

$$\hbar\omega(0) = \left[\frac{2Z_n|J|D}{2Z_n|J| + D} \left(4Z_n|J| + \frac{2Z_n|J|D}{2Z_n|J| + D} \right) \right]^{\frac{1}{2}}. \quad (11)$$

Correlation effects have also been considered. This may be done for D considered negligible compared to exchange by regarding the term in D of Eq. (8) as a perturbation on the pair spin functions for $D=0$ found by the Oguchi method. This leads to an expression for the anisotropy field:

$$H_A(T) = 2D\langle S_{ja}^2 \rangle / g\beta\bar{S}, \quad (12)$$

where

$$S_{ja}^2 \equiv S_{jz}^2 - \frac{1}{4}(S_j^+S_j^- + S_j^-S_j^+). \quad (13)$$

The result would be the same as (7) if correlation were neglected.

Equations (5), (6), and (12) can be used to find $\omega(T)$. At $T=0$, for $Z_n=8$,

$$\hbar\omega(0) = [0.9915D(31.8528|J| + 0.9915D)]^{\frac{1}{2}}. \quad (14)$$

We have found $\omega(T)/\omega(0)$ as a function of T/T_c for both the above cases (molecular field considering D not negligible; pair correlation treating D as negligible) and compared the results to that obtained from Eq. (7). If the effects of anisotropy and correlation are assumed to be additive as they were found to be for the sublattice magnetization, we obtain values of $\omega(T)/\omega(0)$ vs T/T_c including both effects [Fig. 2(b)]. [$\omega(T)/\omega(0)$ goes to zero at the Curie temperature.] These can be compared to the values obtained in the molecular field picture

¹³ C. Kittel, Phys. Rev. **82**, 565 (1951).

¹⁴ T. Nagamiya, Progr. Theoret. Phys. (Kyoto) **6**, 342 (1951).

¹⁵ F. Keffer and C. Kittel, Phys. Rev. **85**, 329 (1952).

¹⁶ K. Yosida, Progr. Theoret. Phys. (Kyoto) **6**, 691 (1952).

considering D as negligible [Fig. 2(a)]. Correlation effects account for approximately 15 to 20% of the total shift between curves a and b in Fig. 2 for temperatures up to about $0.85T_c$ (the range of experimental interest), while for higher temperatures correlation effects account for as much as 40% of this shift. As in the case of sublattice magnetization, the pair correlation calculation probably underestimates the effect of correlation on the shift by a factor equal to the number of neighbors. If this expected further shift from curve b is added in, curve c is obtained.

4. DISCUSSION

We have shown that the combined effects of large uniaxial anisotropy and exchange correlation can account for a shift in the thermal dependence of both the sublattice magnetization and the antiferromagnetic resonance frequency from that predicted by a Brillouin function magnetization curve. Such a departure has been noted experimentally for FeF_2 .^{1,2} In FeF_2 the situation is more complicated than that described above

because $S=2$, there is second-neighbor exchange, and the anisotropy is given by $-DS_{jz}^2 - E(S_{jx}^2 - S_{jy}^2)$. However,³ E is only about 10% of D , so that the terms in E can be neglected to a good approximation. A calculation of the thermal dependence of the resonance frequency of the molecular field type discussed above has been carried out by Cooper and Ohlmann.² This accounts for perhaps 50% of the observed shift from behavior corresponding to Brillouin-function magnetization dependence. The previous discussion would indicate that the remaining shift can be accounted for by correlation effects.

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Electron Levels in a One-Dimensional Random Lattice

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Let the potential of a one-dimensional scalar particle be $V(x) = V_0 \sum_{-\infty}^{\infty} \delta(x - x_j)$, $-\infty < x < \infty$, where $V_0 < 0$, and where the sequence (x_j) is random, with a Poisson distribution. The quantity of interest is a certain limiting level distribution, equal numerically to the node density of real solutions $\psi(x)$ of the Schrödinger equation. The random variables $z_j = \psi'(x_j - 0)/\psi(x_j)$, $-\infty < j < \infty$, constitute an ergodic stationary Markov process. The stationary density $T(z)$ of the (z_j) satisfies a first-order linear differential-difference equation, and the node density is given (with probability 1) by $\lim_{z \rightarrow \infty} z^2 T(z)$ (Rice's formula). Numerical results are obtained by integrating the second-order linear differential equation satisfied by the Fourier transform of $T(z)$.

1. INTRODUCTION

WE are concerned with the distribution of energy levels of a one-dimensional electron (scalar particle) moving in a one-dimensional random array of atoms. The atoms, all of one kind, have (randomly) fixed positions, and the electron-atom potentials are assumed to be δ functions. The Schrödinger equation for an electron of mass m and energy E is then

$$-\frac{\hbar^2}{2m} \frac{d^2\psi(x)}{dx^2} + V_0 \sum_{j=-\infty}^{\infty} \delta(x - x_j) \psi(x) = E\psi(x), \quad (1)$$

where $V_0 < 0$ is the strength of each electron-atom interaction (attractive) and $\dots \leq x_{-1} \leq x_0 \leq x_1 \leq \dots$ are the positions of the atoms, randomly distributed on the infinite line. We consider in detail only the case where the x_j 's have a Poisson distribution, although our methods are applicable to certain more general

distributions (described in Sec. 6). Boundary conditions for (1) are discussed presently.

One model which gives rise to (1) (and the one which led to the present investigation) is the impurity band model of Lax and Phillips.¹ The "atoms" represent impurity atoms in a one-dimensional crystal; the periodic potential of the pure crystal is replaced by a constant (included in E). Another model to which (1) might be applied is a one-dimensional liquid metal. We do not discuss such applications, confining ourselves to a mathematical study of (1). A detailed discussion of the impurity band model, with references to the literature, is given in the Lax and Phillips article.

2. LEVEL DISTRIBUTION

The quantity we seek is the limiting distribution-in-energy of the eigenvalues of (1), defined as follows. Let

¹ M. Lax and J. C. Phillips, Phys. Rev. **110**, 41 (1958).