

Knight Shift in Potassium

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The K^{39} nuclear magnetic resonance has been observed in metallic potassium and in aqueous solutions of KNO_3 and $K_3Co(CN)_6$. From these observations a Knight shift of $(0.248 \pm 0.005)\%$ has been obtained. Using Pines' value 0.60×10^{-6} for the spin susceptibility gives $P_f = 0.95 a_0^{-3}$. This is compared with the theoretical values $0.786 a_0^{-3}$ obtained by Callaway and $0.909 a_0^{-3}$ obtained by a quantum defect calculation in this paper.

INTRODUCTION

EARLY in the evolution of nuclear magnetic resonance it was discovered, by Knight,¹ that the nuclear magnetic resonance of a metallic nucleus occurs at a higher frequency in the metal than in a compound containing the same nucleus. This relative shift between the resonance frequency in the metal and the resonance frequency in a compound subsequently received the name Knight shift. One of the most interesting classes of metals in which the Knight shift can be investigated is the alkali metals. Knight's original work¹ reported the measurement of the Knight shift in lithium and sodium; shortly thereafter Gutowsky and McGarvey^{2,3} reported the measurement of the Knight shift in cesium and rubidium. More recently Benedek and Kushida⁴ have investigated lithium, sodium, rubidium, and cesium, measuring, not only the Knight shift, but also its pressure dependence to approximately 10 000 atmospheres. It is perhaps worth noting that Benedek and Kushida comment that they did not investigate potassium because of the very poor signal-to-noise ratio. In fact, no value for the Knight shift in potassium has been published.⁵

The first theoretical work was that of Townes, Herring, and Knight.⁶ In this work an explanation of the Knight shift based on the Pauli paramagnetism of the conduction of electrons in metals was developed. Korringa⁷ has examined the question more precisely and obtained the same result as the earlier workers and, in addition, a relationship between the spin-lattice relaxation time and the Knight shift. The expression for the Knight shift contains two quantities which are characteristic of the metal being investigated; namely, the Pauli susceptibility and the probability density of a conduction electron at the nucleus,

averaged over states at the Fermi surface. If one of these is known, then the other is implied through a measurement of the Knight shift. The most directly accessible of the two quantities is the Pauli susceptibility. This has, in fact, been measured for two of the alkali metals and a relatively good theory, namely that of Pines,⁸ is available for the other alkali metals. As a result, the recent emphasis in the theoretical work has been on the prediction of the probability density of a conduction electron at the nucleus, averaged over states at the Fermi surface. The principal values are those obtained by Brooks, by Kohn, by Kohn and Kjeldaa, and by Callaway⁹ and his co-workers. At least two of these groups have attacked each of the alkali metals except possibly potassium. For lithium and sodium relatively good agreement has been obtained. However, for rubidium and cesium the agreement is somewhat less satisfactory.

In this paper we wish to report the measurement of the Knight shift and a calculation of the probability density of a conduction electron at the nucleus, averaged over states at the Fermi surface. The calculation uses the variational method of Kohn¹⁰ together with quantum defect wave functions as discussed by Brooks and Ham.¹¹

EXPERIMENTS

Metallic potassium samples were prepared by using high-intensity ultrasonics to disperse molten potassium in molten paraffin. The paraffin was allowed to solidify before removing the source of ultrasonic energy in order to prevent coagulation of the potassium dispersion. It is estimated that a dispersion consisting primarily of potassium particles of less than fifty microns in diameter was produced in this way. The nuclear magnetic resonance of K^{39} was observed in this metallic dispersion as well as in aqueous solutions of KNO_3 and $K_3Co(CN)_6$. The observations were made using a standard Varian model V4200 broad-line nuclear magnetic resonance spectrometer operating at approxi-

¹ W. D. Knight, *Phys. Rev.* **76**, 1259 (1949).

² H. S. Gutowsky, *Phys. Rev.* **83**, 1073 (1951).

³ H. S. Gutowsky and B. R. McGarvey, *J. Chem. Phys.* **20**, 1472 (1952).

⁴ G. B. Benedek and T. Kushida, *J. Phys. Chem. Solids* **5**, 241 (1958).

⁵ Subsequent to the completion of our experimental work we learned that the Knight shift in potassium has also been measured by R. G. Barnes and co-workers [R. G. Barnes, W. J. Jones, Jr., and T. P. Graham (to be published)].

⁶ C. H. Townes, C. Herring, and W. D. Knight, *Phys. Rev.* **77**, 852 (1950).

⁷ J. Korringa, *Physica* **16**, 601 (1950).

⁸ D. Pines, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 367.

⁹ A useful tabulation of experimental and theoretical results for the alkali metals is given by J. Callaway, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1958), Vol. 7, p. 144.

¹⁰ W. Kohn, *Phys. Rev.* **87**, 472 (1952).

¹¹ H. Brooks and F. S. Ham, *Phys. Rev.* **112**, 344 (1958).

mately two megacycles. The external field was supplied by a twelve-inch magnet and was about ten thousand gauss. Field sweep was used for all observations and the magnetic field measured using a Harvey Wells gaussmeter together with a specially calibrated BC 221 frequency meter. The details of the observations are given in Table I. No chemical shift between the compounds KNO_3 and $\text{K}_3\text{Co}(\text{CN})_6$ was observed, although it is estimated that a shift of about 0.02% could have been seen easily. The Knight shift was found to be $(0.248 \pm 0.005)\%$.

The Varian spectrometer is a crossed-coil type instrument and consequently the rf head must be adjusted to observe either the dispersion or the absorption mode. It is interesting to note that with the large metallic potassium sample that was used it was not possible to balance the rf head for the absorption mode. For the nonmetallic samples the head could be balanced for either mode of operation.

Comparison with Theory

The relationship of the Knight shift to the Pauli susceptibility and the probability density of a conduction electron at the nucleus, averaged over states at the Fermi surface, is given by^{6,7}

$$\frac{\Delta H}{H} = \frac{8\pi}{3} \chi_p V \langle |\psi(\mathbf{k}, 0)|^2 \rangle_{\text{av}}, \quad (1)$$

where χ_p is the spin or Pauli susceptibility in volume units (χ_p is dimensionless), V is the volume in which $\psi(\mathbf{k}, \mathbf{r})$ is normalized, and

$$\langle |\psi(\mathbf{k}, 0)|^2 \rangle_{\text{av}} = [4\pi^3 \rho(W_F)]^{-1} \times \int_{S_F} |\psi(\mathbf{k}, 0)|^2 \frac{dS_F}{|\text{grad}_k E|} \equiv P_f. \quad (2)$$

In (2), S_F is the Fermi surface in k space and $\rho(W_F)$ the density of states per unit energy at the Fermi surface. It is convenient to use the atomic volume for the normalization of the wave function.

Since the spin susceptibility of potassium has not been measured, the theoretical value given by Pines,⁸ $\chi_p = 0.60 \times 10^{-6}$ (cgs volume units), seems to be the best that is available. If the trend shown in the comparison of Pines' values with experiments for lithium and sodium persists for potassium, then the susceptibility quoted above might be 10% too low. Using Pines' value for χ_p and $520a_0^3$ for the atomic volume, our measured Knight shift implies

$$P_f = 0.95a_0^{-3}.$$

This value may be as much as 10% too large due to the use of Pines' χ_p in obtaining it.

Callaway⁹ has calculated P_f using a perturbation

TABLE I. K^{39} nuclear magnetic resonance observations.

Compound	Nucleus studied	Frequency in Mc/sec	Magnetic field in gauss	Shift
Metal	K^{39}	1.9745 ± 0.0001	9915.6 ± 0.5	$(0.248 \pm 0.005)\%$
$\text{K}_3\text{Co}(\text{CN})_6$	K^{39}	1.9745 ± 0.0001	9940.5 ± 0.5	
KNO_3	K^{39}	1.9745 ± 0.0001	9939.9 ± 0.5	

approach and obtained the value

$$P_f = 0.786a_0^{-3}.$$

This value is barely consistent with the limits placed on our experimental Knight shift and the estimated uncertainty in Pines' χ_p . Another approach, which has been suggested by Kohn¹⁰ and by Brooks and Ham,¹¹ involves the use of quantum defect wave functions together with a matching formula developed from a WKB approximation to evaluate the conduction electron wave functions at the nuclear site. The result of a calculation of P_f based on such wave functions and Kohn's variational method gives

$$P_f = 0.91a_0^{-3},$$

which is in good agreement with the experimental value. There are, however, some difficulties with the calculation which will be discussed in more detail in the next section.

Quantum Defect Calculation

The quantum defect method (QDM) was initially applied to solids by Kuhn and Van Vleck¹²⁻¹⁴ and subsequently applied and extended by Brooks,¹⁵ Kambe,¹⁶ and Brooks and Ham.¹¹ Excellent discussions of the present state of the QDM and reviews of most of the applications to date may be found in the review articles by Ham¹⁷ and by Brooks.¹⁸

We have used quantum defect (QD) wave functions in Kohn's variational principle. The procedure for applying this variational principle in a form appropriate for use with QD wave functions is as follows.¹⁹ Inside the equivalent sphere the electronic wave function is a solution of

$$\left(-\frac{\hbar^2}{2m} \nabla^2 + V(\mathbf{r}) - E \right) \psi(\mathbf{r}) = 0, \quad (4)$$

¹² T. S. Kuhn and D. H. Van Vleck, Phys. Rev. **79**, 382 (1950).

¹³ T. S. Kuhn, Phys. Rev. **79**, 515 (1950).

¹⁴ J. H. Van Vleck, Proceedings of the 1953 International Conference on Theoretical Physics, Tokyo, 1954 (unpublished).

¹⁵ H. Brooks, Phys. Rev. **91**, 1027 (1953).

¹⁶ K. Kambe, Phys. Rev. **99**, 419 (1955).

¹⁷ F. S. Ham, in *Solid-State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1955), Vol. 1, p. 127.

¹⁸ H. Brooks, Suppl. Nuovo cimento **7**, 165 (1958).

¹⁹ The following discussion is very similar to that given by Kohn in connection with the calculation of the Knight shift in Li, W. Kohn, Phys. Rev. **96**, 590 (1954).

subject to boundary conditions

$$\psi(\mathbf{r}) = e^{2ikr \cos\theta} \psi(-\mathbf{r}), \quad r = r_s \quad (5)$$

$$\frac{\partial \psi(\mathbf{r})}{\partial r} = -e^{2ikr \cos\theta} \frac{\partial \psi(-\mathbf{r})}{\partial r}, \quad r = r_s \quad (6)$$

where k is the magnitude of the wave vector (radius of the Fermi surface), $kr_s = 1.9192$, and θ is the angle between \mathbf{k} and \mathbf{r} . Assume that $\psi(\mathbf{r})$ can be expanded in terms of solutions of (4) characterized by a definite angular momentum, we have

$$\psi(\mathbf{r}) = C_0 R_0(r) + i c_1 R_1(r) P_1(\cos\theta) + C_2 R_2(r) P_2(\cos\theta) + \dots \quad (7)$$

Kohn's variational principle determines the c_i 's by making the integral

$$K = \int_s \frac{\partial \psi(\mathbf{r})}{\partial r} \psi^*(-\mathbf{r}) e^{-2ikr_s \cos\theta} \sin\theta d\theta \quad (8)$$

stationary. This is accomplished if the c_i 's satisfy

$$\begin{aligned} 2L_0 I_{00} c_0 + (L_0 + L_1) i I_{01} c_1 + (L_0 + L_2) I_{02} c_2 \\ + (L_0 + L_3) i I_{03} c_3 + \dots = 0, \\ (L_0 + L_1) i I_{01} c_0 - 2L_1 I_{11} c_1 + (L_1 + L_2) i I_{12} c_2 \\ - (L_1 + L_3) I_{13} c_3 + \dots = 0, \end{aligned} \quad (9)$$

where

$$L_i = \left[\frac{dR_i}{dr} / R_i \right], \quad r = r_s \quad (10)$$

$$I_{ij} = \int_0^\pi e^{-2ikr_s \cos\theta} P_i(\cos\theta) P_j(\cos\theta) \sin\theta d\theta. \quad (11)$$

Practically, one must terminate the series (7) at some finite l , say \bar{l} , determine a value of the energy such that Eqs. (9) are consistent, and solve for the c_i 's. The average square of the conduction electron wave function which enters into (1) is then

$$P_f = C_0^2 [R_0(0)]^2 / \sum_{l=0}^{\bar{l}} C_l^2 N_l, \quad (12)$$

with

$$N_l = \frac{4\pi}{2l+1} \int_0^{r_s} [R_l(r)]^2 r^2 dr. \quad (13)$$

The QDM provides a method for evaluating $R_l(r_s)$ by extrapolating the experimental quantum defect to the energy value appropriate to the solid. This is accomplished by writing²⁰

$$R_l(r) = \frac{1}{r} U^l(r) = \frac{1}{r} [{}^0U^l(r) - (\tan\pi\eta_l) {}^2U^l(r)]. \quad (14)$$

²⁰ R_l so defined is not normalized to unity at $r=r_s$. However, since the normalization is not important until P_f is actually evaluated, the form (14) can be used for most of the calculation.

The functions ${}^0U^l$ and ${}^2U^l$ are the two independent solutions of the radial Coulomb equation originally introduced by Wannier.²¹ The quantity η_l is called the η defect. Brooks and Ham¹⁰ have investigated the relationship of the η defect to the conventional atomic quantum defect δ_m defined by $\epsilon_m = -(m - \delta_m)^{-2}$. Here ϵ_m is an atomic energy eigenvalue, and m is an integer which increases by one between successive terms of a given spectral series. As a result of their work, the experimental η defect can be determined from the atomic energy levels of a specified angular momentum. Because of the nature of the η defect, it can be extrapolated smoothly to energy values appropriate to solids. Appropriate extrapolations are given by Brooks and Ham¹¹ for $l=0, 1, 2$, together with corrections for the polarization of the core by the valence electrons. Having this extrapolated defect, R_l and its derivative can be evaluated at r_s and the L_l 's obtained for various energies. Eqs. (9) can then be set up and the value of the energy found for which they are consistent. This value of the energy is, of course, the Fermi energy. The consistent set is then solved for the c_i 's.

Brooks and Ham¹¹ have shown also that the value of R_0 at $r=0$ is related to the value at $r=r_s$ by

$$\frac{R_0(0)}{R_0(r_s)} = \frac{2z^{\frac{1}{2}} r_s}{\cos\pi\eta_0 [{}^0U^0(r_s) - (\tan\pi\eta_0) {}^2U^0(r_s)]}. \quad (15)$$

Since the c_l obtained from the variational calculation are appropriate to $R_l(r_s)=1$, the left-hand side of (15) is just $R_0(0)$.

The final ingredient in the calculation of P_f is N_l . Once again Brooks and Ham¹¹ provide the appropriate formula

$$\begin{aligned} K_l = \int_0^{r_s} [{}^0U^l - (\tan\pi\eta_l) {}^2U^l]^2 dr \\ = -2 \frac{d\eta_l}{d\epsilon'} \sec^2\pi\eta_l + \left[{}^0U^l, \frac{d}{d\epsilon'} ({}^0U^l) \right]_{r=r_s} \\ - 2 \tan\pi\eta_l \left[{}^0U^l, \frac{d}{d\epsilon'} ({}^2U^l) \right]_{r=r_s} \\ + \tan^2\pi\eta_l \left[{}^2U^l, \frac{d}{d\epsilon'} ({}^2U^l) \right]_{r=r_s}, \end{aligned} \quad (16)$$

where the square brackets of the form $[A, B]$ is defined by

$$[A, B] = A \frac{dB}{dr} - \frac{dA}{dr} B, \quad (17)$$

and $\epsilon' = -\epsilon$ (a positive number). The normalization

²¹ G. Wannier, Phys. Rev. **64**, 358 (1943). These functions can be computed conveniently with the help of tables prepared by F. S. Ham, Technical Report No. 204, Cruft Laboratory, Harvard University, Cambridge, Massachusetts, 1955 (unpublished).

TABLE II. Fermi energies and P_f for various l 's.

l	ϵ_f' (rydbergs)	P_f
2	0.3172	$1.107 a_0^{-3}$
3	0.3208	$0.927 a_0^{-3}$
4	0.3227	$0.946 a_0^{-3}$
5	0.3241	$0.802 a_0^{-3}$
6	0.3235	$0.909 a_0^{-3}$

integrals N_l are given by

$$N_l = \frac{4\pi r_s^2}{2l+1} \frac{K_l}{[{}^0U^l(r_s) - (\tan\pi\eta_l) {}^2U^l(r_s)]^2}. \quad (18)$$

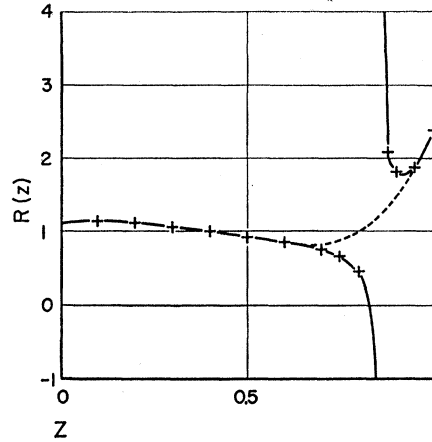
The procedure outlined above has been applied to potassium as follows. Ham's²¹ tables were used to supply inputs to an IBM 650 program which evaluated the functions ${}^0U^l$ and ${}^0D^l = rd({}^0U^l)/dr$ for $0 \leq l \leq 8$ and the functions ${}^2U^l$ and ${}^2D^l = rd({}^2U^l)/dr$ for $0 \leq l \leq 2$. This was done for $\epsilon' = 0.30(0.01)0.35$ and the determinants of the coefficients in (10) set up. These determinants were truncated at $l=2, 3, 4, 5, 6$ and evaluated. For each l the values of the determinants were plotted against energy to determine the value of the energy at which the equations were consistent. The Fermi energies obtained in this way are tabulated in Table II.

The function evaluating program was next used to obtain the U 's and D 's for each ϵ_f' and $\epsilon_f' \mp 0.005$. From these U 's and D 's the L 's and the energy derivatives appearing in the normalization equation were computed. Equations (12) were set up for the appropriate values of ϵ_f' and solved for the c_l 's with $c_0=1$. The normalization integrals were evaluated using (16) and (18) and finally P_f was evaluated. These results are also given in Table II.

Both P_f and ϵ_f' as given in Table II behave much like the corresponding quantities in Kohn's calculation of Li. P_f seems to vary more drastically with l in our calculation than in Kohn's but nonetheless seems to be converging. We have tested the fit of the $l=6$ calculation to the boundary condition (5) by calculating $R(z)$:

$$R(z) = \frac{1}{\tan(kr_s z)} \left\{ \frac{c_1 P_1(z) + c_3 P_3(z) + \dots}{c_0 P_0(z) + c_2 P_2(z) + \dots} \right\}. \quad (19)$$

If the boundary condition were exactly satisfied, the $R(z)$ would be identically one. Figure 1 shows $R(z)$ as a function of z for the $l=6$ calculation. From $z=0$ to $z=0.75$ the ratio is reasonably close to unity; however, between $z=0.8$ and $z=0.9$ it deviates radically from one. This deviation is caused by failure to match exactly the position of the zero of $c_0 P_0 + c_2 P_2 + c_4 P_4 + c_6 P_6$, at $z=0.84$, with the position of the singularity of $\tan(kr_s z)$, at $z=0.81$. If the match were perfect, then $R(z)$ would presumably behave much like the broken curve in Fig. 1. Although even the broken curve can hardly be called an excellent fit, we feel that it is

FIG. 1. The function $R(z)$ for $l=6$.

satisfactory. Further tests could be made; however, we do not feel that this is warranted at this time.

DISCUSSION

The excellent agreement between the theoretical and experimental values of P_f is reassuring but could be destroyed by further refinements. The QDM takes approximate account of the effects of correlation and exchange between the conduction electrons and the core electrons on the wave functions of the conduction electrons. The calculation as carried through above does not, however, take into account the contribution of the core polarization to the spin density at the nucleus. Cohen *et al.*²² have considered this contribution in the metallic Li and Na and found that it results in an additional contribution to the effective theoretical values of P_f of approximately 25% in the case of Li and approximately 5% in the case of Na. Such calculations have not been carried out for K, however, since the Fermi surface for K is only slightly less spherical than for Na and since the 1s and 2s contributions can be expected to partly cancel a correction of the order of 10% might be reasonably expected for K. A correction of this magnitude would increase the effective theoretical value of P_f to $1.00 a_0^{-3}$ which is still in good agreement with the experimental result. A smaller correction would improve the agreement. It may be noted that the correction does not improve the Brooks and Ham results for the atomic hyperfine interaction but actually makes them worse. In the case of Brooks²³ calculations of the Knight shift in Li and Na by the QDM, one finds that the agreement with experiment deteriorates when the core polarization correction is included. Extrapolating the results of Cohen *et al.* to the cases of Rb and Cs is tenuous at best; however, if the correction is only of the same sign for these elements as for Li and Na it would improve the agreement between Brooks' calculations and experiment. We may

²² M. H. Cohen, D. A. Goodings, and V. A. Heine, Proc. Phys. Soc. (London) **73**, 811 (1959).

²³ H. Brooks, unpublished quoted by Callaway.⁹

summarize by saying that the core polarization effect does not seem to affect significantly the agreement between our theoretical and experimental values of P_f ; however, this conclusion cannot be extended to other quantum defect calculations. Further investigation of this point would appear to be very desirable.

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Theory of Electron-Phonon Interactions

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The theory of the interaction of electrons and acoustic phonons in nonpolar crystals has been formulated in terms of a new set of basis states, whose wave functions are essentially Bloch functions that deform with the lattice. The major part of the interaction may then be calculated in terms of the strain tensor rather than the displacement of the lattice. A result of the theory is a generalization of the deformation potential theorem.

I. INTRODUCTION

IN considering the mobility of electrons in nonpolar semiconductors, Bardeen and Shockley¹ introduced a new approach to electron-phonon coupling. They showed that in certain simple semiconductors the electron-phonon interaction can be accounted for by replacing the interaction term in the Hamiltonian by $D\nabla \cdot \mathbf{u}$, where \mathbf{u} is the displacement of the lattice due to the thermal vibrations. The constant D is the deformation potential. It is defined by setting the change in the electron energies in a homogeneously strained crystal equal to $D\nabla \cdot \mathbf{u}$; hence D can be determined from experiments independent of the electron-phonon interaction.²⁻⁵ This idea has already proved very fruitful and has been extended to include arbitrary strains and more complicated semiconductors.⁵

It was the feeling that the deformation potential approach affords a basis for a much more comprehensive theory of electron-phonon interactions (within the framework of the one-electron model) that motivated the present research. Moreover, it was felt that if one could find a means of expanding the Hamiltonian in a power series in the strains, instead of the lattice displacements (as is done in the standard theory⁴), the deformation potential theorem in its most general form would follow immediately.

We find that we are able to carry through this

program when we express the Hamiltonian in terms of a new representation.⁶ The basis states of this new representation [orthogonalized deformed Bloch (ODB) functions] are essentially Bloch functions that deform with the lattice. These states have the convenient property that the matrix elements of the pertinent operators with respect to the ODB states can be expressed as matrix elements of closely related operators with respect to the Bloch states (Sec. III). In Sec. IV we show that the Hamiltonian in the ODB representation can be expanded in a power series in the strains and the lattice velocity, and that the resulting first-order coupling terms, $E^I + E^{II}$, admit of a simple physical interpretation. E^I is the dominant term and can be written as a deformation potential operator (whose diagonal matrix elements are shown in Sec. V to be just the deformation potentials) times the strain. It leads directly to a generalized deformation potential theorem (Sec. VII) which refers to the coupling between the ODB rather than the Bloch states. However, in Sec. VI we show that, to the first approximation, the transition rates between the Bloch or between the ODB states may be used interchangeably in the Boltzmann equation.

E^{II} is shown in Sec. VII to be a small term associated with the fact that a moving lattice tends to drag the electrons with it.

II. THE BLOCH REPRESENTATION

The Hamiltonian for a nonpolar crystal with one electron in the conduction band, in the one-electron

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¹ J. Bardeen and W. Shockley, *Phys. Rev.* **80**, 72 (1950).

² G. Weinrich, T. M. Sanders, and H. G. White, *Phys. Rev.* **114**, 33 (1959).

³ J. R. Drabble, *J. Electronics and Control* **5**, 362 (1958).

⁴ F. J. Blatt, in *Solid State Physics*, edited by F. Seitz and D. Turnbull (Academic Press, Inc., New York, 1957), Vol. 4.

⁵ W. P. Dumke, *Phys. Rev.* **101**, 531 (1956); and C. Herring and E. Vogt, *Phys. Rev.* **101**, 944 (1956).

⁶ George Whitfield, *Phys. Rev. Letters* **2**, 204 (1959). Equations (7) and (8) of this reference are incorrect; see Sec. VII A-1 of this paper.