PHYSICAL REVIEW VOLUME 106, NUMBER 4 MAY 15, 1957

The g Value in Conduction Electron Spin Resonance

Y. Yafet
Westinghouse Research Laboratories, Pittsburgh, Pennsylvania

(Received April 27, 1956; revised manuscript received January 14, 1957)

The departure of the g factor from the free-spin value due to spin-orbit interaction is calculated for conduction electrons in a nondegenerate band. The Kohn-Luttinger representation is used and the result is obtained to second order in the wave-vector of the electron at the Fermi surface. The result is expressed in two forms, one of these being a sum of volume and surface integrals over the unit cell. The orders of magnitude of these are discussed but no numerical calculations are made.

I. INTRODUCTION

THE purpose of this paper is to calculate the g value (spectroscopic splitting factor) of a conduction electron, more specifically to calculate the shift, due to spin-orbit interaction, from the free-spin value of the g factor in a spin-resonance experiment on electrons in a nondegenerate band. Only simple lattices possessing a center of space inversion will be considered; the alkali metals, which are the easiest to understand theoretically, and for which experimental data exist[1] belong to this class.

This problem had already been treated by the author,[2] but the result obtained there, although being of the right order of magnitude, is not quite correct. The source of the error lay in the improper treatment of the interaction of the electrons with the applied magnetic field. The lack of lattice periodicity of this interaction (due to the dependence of the vector potential on the particle coordinate) is a source of difficulty for problems involving the motion of electrons under the simultaneous effect of a periodic potential and a magnetic field; namely that since an exact solution for the energy levels is in general impossible, and since the magnetic fields used are small on an atomic scale, it is desirable to treat the effect of the field as a perturbation.[3] However, if the stationary states of the system (in the absence of the field) are extended in space, as the Bloch states are, then the effect of the field on these states cannot be viewed as a perturbation as the interaction term can be made arbitrarily large by going to large enough distances from the origin of the vector potential. The manner in which perturbation theory can be used in this case has been given by Peierls[3] for the limiting cases of free electrons and tightly bound electrons. Further progress in removing these restrictions has been made recently, in particular through the work of Adams[4] on magnetic susceptibilities, of Luttinger and Kohn[5] on the perturbed periodic lattice, and of Kjeldaas and Kohn[6] on magnetic susceptibilities.

In this paper, by using the Luttinger-Kohn representation (henceforth abbreviated as the L.-K. representation), it is found that the g shift is given by the average at the top of the Fermi distribution (or over the Boltzmann distribution if the band is almost empty) of the orbital magnetic moment induced by the spin-orbit interaction (abbreviated as the s. o. interaction). The expression for this is obtained as a trace which can be developed in a power series in the even powers of k_F^α, the components of the wave-vector at the top of the Fermi distribution. Only the first two terms, of orders zero and two in k_F^α, are evaluated. The result is expressed in two different forms, both being in terms of operations performed on the Bloch states of the band under consideration and averaged over the Fermi surface.

(a) In the first form, it is proportional to the sum of the components along the field (taken in the Z direction) of the periodic part of the magnetic moment as defined by Adams[7] and of the vector product of the periodic part[7] of the coordinate by the wave vector.

(b) In the second form, which is obtained by manipulation from the preceding one, the result is the sum of three terms: (1) a volume integral of the Z component of the magnetic moment, (2) a product involving the volume integral of the electron coordinate and the departure of the effective mass from the free-electron mass, and (3) a surface integral proportional to the normal component of the velocity evaluated over the wave function and certain combinations of its derivatives with respect to k^α. In the limit of infinite lattice constant, only the first of these terms survives and it reduces to the correct expression for free atoms. The motivation for expressing the result in the second form was to make a comparison with the result of reference 2 which is essentially given by the first term in (b). That result was used by Brooks[8] who, using the method of quantum defects, was able to obtain numerical answers without calculations involving wave functions and potentials. It is therefore interesting to see whether the second and third terms of (b) can be neglected. For the alkali metals with the exception of lithium, the second term is negligible; the third term is not neces-

---

[1] G. Feher and A. F. Kip, Phys. Rev. **98**, 337 (1955).

[2] Y. Yafet, Phys. Rev. **85**, 478 (1952).

[3] R. Peierls, Z. Physik **80**, 763 (1933).

[4] E. N. Adams, Phys. Rev. **89**, 633 (1953).

[5] J. M. Luttinger and W. Kohn, Phys. Rev. **97**, 869 (1955).

[6] T. Kjeldaas and W. Kohn, Phys. Rev. **105**, 806 (1957).

[7] E. N. Adams, J. Chem. Phys. **21**, 2013 (1953).

[8] H. Brooks, Phys. Rev. **94**, 1411(A) (1954) and unpublished work.

sarily so for sodium (numerical calculations of terms have not been made), but, as the atomic number increases, it is expected that, because of the localization of the s.o. interaction near the nucleus, the relative contribution of the surface integral will become less important. A rough estimate indicates that for sodium the third term may be of the order of 50% of the first when the boundary of the domain of integration is the sphere equivalent to the cellular polyhedron.

The details of the g-shift calculation are given in the next two sections.

II. THE g VALUE BY THE TRACE METHOD

The conduction electrons are treated in the one-electron approximation and the periodic potential is assumed, for simplicity, to contain no exchange term. The complete Hamiltonian of an electron under the influence of an external magnetic field H in the Z direction can be split into two parts: $\mathcal{H}_T=\mathcal{H}+\mathcal{H}_Z$. The first term $\mathcal{H}$ is the sum of the kinetic and potential energies, including the s.o. interaction given by:

$$\mathcal{H}_{\text{s.-o.}}=\frac{\hbar}{2m^2c^2}\mathbf{S}\times\nabla V\cdot\left(\mathbf{p}+\frac{e\mathbf{A}}{c}\right);\tag{1}$$

here $\mathbf{S}$ is the spin operator, V the periodic potential, and $\mathbf{A}$ the vector potential of the applied field. The second term $\mathcal{H}_Z$ is the Zeeman energy of the spin, $\mathcal{H}_Z=g_S\beta HS_Z$, where β is the Bohr magnetron and $g_S=2[1+(\alpha/2\pi)]=2.0023$.

Spin resonance is induced by a small alternating magnetic field at a right angle to H. The g factor as measured experimentally is given by the value of the energy quantum at the maximum of power absorption. The quantity calculated in this paper is the mean of the energy in the absorption spectrum. The difference between these two quantities should be negligible since exchange interactions[9] between conduction electrons and lattice scattering will tend to peak the line at the average absorption energy. The g factor is given therefore by the ratio of the first moment to the zeroth moment of the energy in the absorption spectrum. Since it is not practicable to obtain the eigenfunctions of the electron in the presence of the magnetic field, the moments will be expressed in the form of traces which can be evaluated in some convenient representation. The moments are given by[10]:

$$\begin{aligned}\mathfrak{M}_1&=\mathrm{Tr}\{\rho(\mathcal{H}_T)[S_x,[\mathcal{H}_T,S_x]]\},\\ \mathfrak{M}_0&=-\mathrm{Tr}\{\rho(\mathcal{H}_T)S_Z\};\end{aligned}\tag{2}$$

where ρ is the Fermi distribution function. Upon writing $\mathcal{H}_T=\mathcal{H}+\mathcal{H}_Z$ in the commutator of $\mathcal{H}_T$, the contributions of the two terms can be separated into $[S_x,[\mathcal{H}_Z,S_x]]$, which contributes $g_S\beta H$ to the ratio $\mathfrak{M}_1/\mathfrak{M}_0$, and $[S_x,[\mathcal{H},S_x]]$, which gives the shift in the g factor due to s.o. interaction:

$$\delta g\beta H=\frac{\mathrm{Tr}\{\rho(\mathcal{H}_T)[S_x,[\mathcal{H},S_x]]\}}{-\mathrm{Tr}\{\rho(\mathcal{H}_T)S_z\}}.\tag{3}$$

This expression, wanted only to first order in the s.o. interaction, will be computed in the L.-K. representation as developed in reference 6 (especially Sec. II) to which the reader is referred for an account of method and notation. That notation will be followed here except for a minor change: it is shown in reference 6 that the matrix element $\langle m\mathbf{k}|\mathcal{O}|n\mathbf{k}'\rangle$ of an operator $\mathcal{O}$ depending on the vector potential only through the combination $p^\alpha+eA^\alpha/c$ is given by a sum of terms, each of these being the product of two matrix elements: one of these involves only periodic operators and is to be taken between the Bloch states m and n at $\mathbf{k}=0$; the other depends only on powers of $p^\alpha+eA^\alpha/c$ and is to be taken between the plane waves $\mathbf{k}$ and $\mathbf{k}'$. In this paper, the matrix element with respect to the plane waves will not be taken and $p^\alpha+eA^\alpha/c$, left as an operator, will be labeled $\bar{k}^\alpha$. (From here on, we shall use atomic units for which $\hbar=m=e=1$.) Accordingly the notation $\langle m|\mathcal{O}(\bar{k}^\alpha)|n\rangle$ will replace $\langle m\mathbf{k}|\mathcal{O}|n\mathbf{k}'\rangle$.

The commutation properties of the $\bar{k}^\alpha$ are: $[\bar{k}^\alpha,\bar{k}^\beta]=-is\delta_{\alpha\beta Z}$, where the parameter $s=H/c$ and the symbol $\delta_{\alpha\beta Z}$ has the values: $+1$ for $\alpha=x$, $\beta=y$; -1 for $\alpha=y$, $\beta=x$; 0 otherwise.

Let n refer hence forth to the nondegenerate band under consideration. Then since the expectation value of the s.o. interaction over L.-K. functions determined with neglect of s.o. interaction vanishes it is possible to take for the states $|n,\mathbf{k}\rangle$ spinors having a large and a small component. The spin will be quantized along the applied field and the two spin states will be denoted by $|n,+,\mathbf{k}\rangle$ or $|n,-,\mathbf{k}\rangle$ depending on whether the spin is predominantly parallel or antiparallel to $\mathbf{H}$.

To evaluate (3), the interband matrix elements of $\rho(\mathcal{H}_T)$ will be eliminated to the desired order in $\bar{k}^\alpha$. As will be seen below, to obtain δg to order $k_F{}^2$ it is necessary to have $\mathcal{H}_T$ diagonal to order $(\bar{k}^\alpha)^4$. Since it is sufficient to have $\rho(\mathcal{H}_T)$ to zero order in s.o. interaction and as there are no interband matrix elements of $\mathcal{H}_Z$ to this order, it is sufficient to diagonalize $\mathcal{H}$ to order $(\bar{k}^\alpha)^4$. Let T be the transformation which accomplishes this and let $\tilde{S}_x=e^{-T}S_xe^T$. It can be shown by explicit calculation that the only part of $\tilde{S}_x$ which contributes to the trace is S_x. The expression for the g shift becomes:

$$\frac{s\delta g}{2}=\frac{\mathrm{Tr}_{k\alpha}\{[\rho(\tilde{H}+\mathcal{H}_z)_{n-}-\rho(\tilde{H}+\mathcal{H}_z)_{n+}](\tilde{H}_{n+}-\tilde{H}_{n-})\}}{\mathrm{Tr}_{k\alpha}\{\rho(\tilde{H}+\mathcal{H}_z)_{n-}-\rho(\tilde{H}+\mathcal{H}_z)_{n+}\}}.\tag{4}$$

Here in $\tilde{H}=e^{-T}\mathcal{H}e^T$, the notation $\tilde{H}_{n+}$ is short for $\langle n+|\tilde{H}(\bar{k}^\alpha)|n+\rangle$, and the subscript k^α on Tr indicates that the summation over the two states of spin has been performed and that the bands have been decoupled

---

[9] P. W. Anderson, J. Phys. Soc. Japan **9**, 316 (1954).

[10] K. Kambe and T. Usui, Progr. Theoret. Phys. Japan **8**, 302 (1952).

to the desired order in $\bar{k}^\alpha$. It remains to calculate $\tilde{H}_n(\bar{k}^\alpha)$ and $\tilde{H}_{n+}(\bar{k}^\alpha)-\tilde{H}_{n-}(\bar{k}^\alpha)$. The expression for the first of these has been given by Kjeldaas and Kohn under neglect of s.o. interaction. To include this, it is necessary[5] only to replace the matrix elements of the momentum $(p^\alpha)_{mn}$ by those of the velocity operator in the presence of s.o. interaction, $(\pi^\alpha)_{mn}$, with π^α given by:

$$\pi^\alpha = i[\mathcal{H}_0, x^\alpha] = p^\alpha + (1/2c^2)(\mathbf{S}\times\nabla V)^\alpha. \tag{5}$$

Here $\mathcal{H}_0$ is the Hamiltonian $\mathcal{H}$ for zero magnetic field. The parts of $\tilde{H}_n$ of order 2 and 4 in $\bar{k}^\alpha$ are:

$$\tilde{H}_n = \sum_{\alpha,\beta} E_n^{\alpha\beta}\bar{k}^\alpha\bar{k}^\beta + \sum_{\alpha,\beta,\gamma,\delta} E_n^{\alpha\beta\gamma\delta}\bar{k}^\alpha\bar{k}^\beta\bar{k}^\gamma\bar{k}^\delta, \tag{6}$$

with the coefficients given by[6]:

$$E_n^{\alpha\beta} = \tfrac{1}{2}\delta_{\alpha\beta} + \sum_i \frac{\pi^\alpha{}_{ni}\pi^\beta{}_{in}}{\omega_{ni}}, \tag{7}$$

$$\begin{aligned} E_n^{\alpha\beta\gamma\delta} = \Bigg[& \sum_{m\neq n}\sum_{j,l} \frac{\pi^\alpha{}_{nj}\pi^\beta{}_{jm}\pi^\gamma{}_{ml}\pi^\delta{}_{ln}}{\omega_{nj}\omega_{nm}\omega_{nl}} \\ & -\tfrac{1}{2}\sum_{j,l}\left(\frac{1}{\omega_{nj}{}^2\omega_{nl}}+\frac{1}{\omega_{nl}{}^2\omega_{nj}}\right)\pi^\alpha{}_{nj}\pi^\beta{}_{jn}\pi^\gamma{}_{nl}\pi^\delta{}_{ln} \\ & -\tfrac{1}{4}\sum_i \frac{\pi^\alpha{}_{ni}\pi^\beta{}_{in}\delta_{\gamma\delta} - 2\pi^\alpha{}_{ni}\pi^\delta{}_{in}\delta_{\beta\gamma} + \pi^\gamma{}_{ni}\pi^\delta{}_{in}\delta_{\alpha\beta}}{\omega_{ni}{}^2}\Bigg]. \end{aligned} \tag{8}$$

Here the ω_{ni} are interband energies at $\mathbf{k}=0$, and in order to avoid too many indices, the spin quantum number has been included in n, m, etc.$\cdots$; the notation $n+$, $n-$ will also be used below but no confusion should arise from the double usage of n.

The parts in the expressions that are odd in s.o. interaction will give $\frac{1}{2}(\tilde{H}_{n+}-\tilde{H}_{n-})$. This is found as follows:

By Kramers' theorem,[11] the Bloch states for each $\mathbf{k}$ in a nondegenerate band are spin-degenerate. In the expansion of the energy in powers of k^α (at zero field), the coefficients are even under spin reversal and real. In (8), the coefficient of a specific term $\bar{k}^\alpha\bar{k}^\beta\bar{k}^\gamma\bar{k}^\delta$ is not necessarily real; the sum of these coefficients over all the permutations of the given α, β, γ, δ must be real and even under spin reversal, since in the absence of a field the $\bar{k}^\alpha$ commute with one another. Therefore the part of $\tilde{H}_{n+}$ that is odd under s.o. interaction is due entirely to the imaginary part of each coefficient, and since $\mathcal{H}$ is Hermitian, this contributes only with the anti-Hermitian part of $\bar{k}^\alpha\bar{k}^\beta\bar{k}^\gamma\bar{k}^\delta$. From the commutation relations, this is found to be:

$$\begin{aligned} &\text{Anti-Hermitian part of } (\bar{k}^\alpha\bar{k}^\beta\bar{k}^\gamma\bar{k}^\delta) \\ &\quad = (s/4i)(\{\bar{k}^\alpha,\bar{k}^\beta\}\delta_{\gamma\delta z} + \{\bar{k}^\alpha,\bar{k}^\gamma\}\delta_{\beta\delta z} + \{\bar{k}^\alpha,\bar{k}^\delta\}\delta_{\beta\gamma z} \\ &\qquad + \{\bar{k}^\beta,\bar{k}^\gamma\}\delta_{\alpha\delta z} + \{\bar{k}^\beta,\bar{k}^\delta\}\delta_{\alpha\gamma z} + \{k^\gamma,k^\delta\}\delta_{\alpha\beta z}), \end{aligned} \tag{9}$$

where

$$\{\bar{k}^\alpha,\bar{k}^\beta\} = \bar{k}^\alpha\bar{k}^\beta + \bar{k}^\beta\bar{k}^\alpha.$$

Similarly the anti-Hermitian part of $\bar{k}^\alpha\bar{k}^\beta$ is $-is/2$. One obtains:

$$\begin{aligned} \tilde{H}_{n+}-\tilde{H}_{n-} = & \sum_{\alpha,\beta}[E_{n+}{}^{\alpha\beta} - (E_{n+}{}^{\alpha\beta})^*](s/2i) \\ & + \sum_{\alpha,\beta,\gamma,\delta}[E_{n+}{}^{\alpha\beta\gamma\delta} - (E_{n+}{}^{\alpha\beta\gamma\delta})^*](s/4i) \\ & \times(\{\bar{k}^\alpha,\bar{k}^\beta\}\delta_{\gamma\delta z} + \cdots + \{\bar{k}^\gamma,\bar{k}^\delta\}\delta_{\alpha\beta z}) + \cdots. \end{aligned} \tag{10}$$

In accordance with the van Leeuwen theorem, which states that a classical particle Hamiltonian can show no orbital magnetic effects, all of the contribution to the g shift arises from the noncommutativity of the $\bar{k}^\alpha$. After substituting (6) and (10) into (4), the trace can be taken by the method of Peierls, since the vector potential enters only through the $\bar{k}^\alpha$ which have the same properties as the corresponding components of the velocity of free electrons. Because $\tilde{H}_{n+}-\tilde{H}_{n-}$ is already of the first order in H, the trace of (4) is obtained by replacing everywhere $\bar{k}^\alpha$ with the numbers k^α. It is seen from (10) that if δg is needed to order k^2, the energy must be known to order $(\bar{k}^\alpha)^4$.

The physical interpretation of (4) is the following: the statistical factor $\rho_{n+}-\rho_{n-}$ gives the average at the top of the Fermi distribution; the quantity being averaged, $\tilde{H}_{n+}-\tilde{H}_{n-}$, is not, because of the dependence of $\bar{k}^\alpha$ on H, twice the orbital magnetic moment interaction, $2H(\partial\tilde{H}_{n+}/\partial H)_{H=0}$. It is easily seen, however, that the statistical averages of these two quantities are the same so that the g shift is given by the orbital magnetic moment. Finally it follows from reference 6 for instance, that the average of $(\partial\tilde{H}_{n+}/\partial H)_{H=0}$ in the absence of s.o. interaction is zero. This fact is the generalization for a nondegenerate band of the quenching of orbital momentum occurring in isolated atoms subjected to a crystalline field. (The fact that the expectation value of L_Z over a Bloch state can be made zero by choosing the shape of the unit cell to have inversion symmetry is not very useful since one cannot do perturbation theory on the Bloch states when $H\neq 0$.)

With $\bar{k}^\alpha$ replaced by k^α, the summation over the bands necessary for the evaluation of the coefficients $E_n^{\alpha\beta\gamma\delta}-(E_n^{\alpha\beta\gamma\delta})^*$, and the summation over the three components of $\mathbf{k}$ can be performed; let $u_n(\mathbf{k},\mathbf{r})$ be the periodic part of the Bloch function at $\mathbf{k}$ and let $\mathcal{H}(\mathbf{p}+\mathbf{k}) = e^{-i\mathbf{k}\cdot\mathbf{r}}\mathcal{H}e^{i\mathbf{k}\cdot\mathbf{r}}$. Then by considering $u_n(\mathbf{k},\mathbf{r})$ expanded to order k^3,[12] and after lengthy manipulation, it is found that to order k^2, (10) is equal to the real part of the following expression:

$$\begin{aligned} is\Bigg(\Bigg\langle n\mathbf{k}\Bigg|\frac{\partial\mathcal{H}(\mathbf{p}+\mathbf{k})}{\partial k^y}\frac{\partial}{\partial k^x} - \frac{\partial\mathcal{H}(\mathbf{p}+\mathbf{k})}{\partial k^x}\frac{\partial}{\partial k^y}\Bigg|n\mathbf{k}\Bigg\rangle \\ + \langle n\mathbf{k}|(\partial/\partial k^x)k^y - (\partial/\partial k^y)k^x|n\mathbf{k}\rangle\Bigg). \end{aligned} \tag{11}$$

---

[11] R. J. Elliott, Phys. Rev. **96**, 266 (1954).

[12] Actually it is sufficient to know u_{nk} to order k^2 but then the result is not expressible in the simple form (11).

Here the basis functions $|n\mathbf{k}\rangle$ are the periodic parts $u_n(\mathbf{k},\mathbf{r})$ of the Bloch functions for band n, spin up, and wave vector $\mathbf{k}$; in the following, matrix elements with subscripts n, m, etc., are to be taken between the Bloch states $\psi_{n\mathbf{k}}(\mathbf{r})$ for spin up. In the notation of Adams,[7] (11) can be rewritten as:

$$s[(X\pi^y-Y\pi^x)_{nn}+X_{nn}k^y-Y_{nn}k^x], \tag{12}$$

where π^α is the velocity operator defined above and the matrix elements of X (and similarly for Y) are given by:

$$X_{nm}=\int_\Omega u_n^*(\mathbf{k},\mathbf{r})i(\partial/\partial k^x)u_m(\mathbf{k},\mathbf{r})d\tau, \tag{13}$$

the integration being over the unit cell Ω with the $u_{m\mathbf{k}}$ normalized over it.

In the derivation of (11), the $\mathbf{k}$ dependence of the phases of the $u_{n\mathbf{k}}$ has been taken such that in the expansion of $u_{n\mathbf{k}}$ in terms of the complete set u_{m0} the coefficient of u_{n0} is real. This same choice is implied in (13) although it can be shown that an arbitrary change in the phase which adds to the X_{nn} and Y_{nn} the corresponding components of the gradient of a function of $\mathbf{k}$ does not change the trace of (4).

The g shift is given by the average of (12) at the Fermi surface so that (12) can be interpreted as the product by $2H$ of the expectation value of the orbital magnetic moment over the Bloch state $\psi_{n\mathbf{k}}$. Notice that this is different from the nn representative of the magnetic moment which is given by only the first two terms of (12). Notice also that the shift is due entirely to the departure of the Bloch function, s.o. interaction excluded, from a plane wave. This is because in (6) the $\pi_{nm}{}^\alpha$ for $n\neq m$ are zero for plane waves.

III. ALTERNATIVE FORM FOR THE g SHIFT

Although numerical calculations can be made with (12), this result will now be expressed in another form by writing $X_{nm}=x_{nm}+(X-x)_{nm}$ (here x is the coordinate measured from the nucleus) and substituting this into (12). The reason for making this transformation is that, among other terms, the average value over $\psi_{n\mathbf{k}}$ in the unit cell of the magnetic moment operator $(e/2c)\mathbf{r}\times\mathbf{v}$ will appear in the answer. This part is just the incorrect result of reference 2. Besides providing a more physical presentation for the answer obtained here, the new form makes possible a comparison of the new result with the former one and a comparison of the values that can be obtained from the two results in specific cases by the quantum defect method.[8]

Consider the first term of (12). By the use[13] of Green's theorem on the n, m matrix element of the commutator $[\mathcal{H},x]$ and of the relation[14] $\pi_{nm}=i\omega_{nm}X_{nm}$, $n\neq m$, one obtains:

$$\int_\Omega \psi_n^*x\psi_m d\tau =X_{nm}+\frac{i}{2\omega_{nm}}\int_S [x\psi_n^*\pi^\nu\psi_m+\psi_m(\pi^\nu x\psi_n)^*]dS,\qquad n\neq m. \tag{14}$$

Here ω_{nm} is the energy difference at $\mathbf{k}$ between bands n and m, the surface integral is taken over the cellular polyhedron (or the equivalent sphere), and ν is the outward direction normal to it. It follows that:

$$(X\pi^y)_{nn}=X_{nn}\pi^y{}_{nn}+\sum_{m\neq n}\left[\int_\Omega \psi_n^*x\psi_m d\tau\right]\pi^y{}_{mn} -\tfrac{1}{2}\sum_{m\neq n}\left\{\int_S [x\psi_n^*\pi^\nu\psi_m+\psi_m(\pi^\nu x\psi_n)^*]dS\right\}Y_{mn}. \tag{15}$$

Use of Green's theorem on the nn matrix element of $[\mathcal{H},x]$ gives:

$$\pi^x{}_{nn}=\tfrac{1}{2}\int_S [x\psi_n^*\pi^\nu\psi_n+\psi_n(\pi^\nu x\psi_n)^*]dS. \tag{16}$$

Adding and subtracting the term $m=n$ to the right-hand side of (15), and using (16) gives:

$$(X\pi^y)_{nn}=X_{nn}\pi^y{}_{nn}+Y_{nn}\pi^x{}_{nn}+\int_\Omega \psi_n^*x\pi^y\psi_n d\tau -\pi^y{}_{nn}\int_\Omega \psi_n^*x\psi_n d\tau-\tfrac{1}{2}\sum_m\left\{\int_S [x\psi_n^*\pi^\nu\psi_m +\psi_m(\pi^\nu x\psi_n)^*]dS\right\}Y_{mn}. \tag{17}$$

Finally by using the completeness property for periodic functions of the $u_{n\mathbf{k}}$, the last summation over m can be performed and gives a single surface integral. The first two terms on the right-hand side of (17) are cancelled by identical terms with opposite signs contributed by $-(Y\pi^x)_{nn}$. Leaving them out, one has $(X\pi^y)_{nn}$ in the desired form:

$$(X\pi^y)_{nn}=\int_\Omega \psi_n^*x\pi^y\psi_n d\tau-\pi^y{}_{nn}\int_\Omega \psi_n^*x\psi_n d\tau -\tfrac{1}{2}i\int_S\left[x\psi_n^*\pi^\nu\left(e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial u_n}{\partial k^y}\right) +(\pi^\nu x\psi_n)^*\left(e^{i\mathbf{k}\cdot\mathbf{r}}\frac{\partial u_n}{\partial k^y}\right)\right]dS. \tag{18}$$

A symmetrical expression with x and y interchanged is obtained for $(Y\pi^x)_{nn}$. In the spherical approximation

---

[13] See, for instance, E. Wigner and F. Seitz, Phys. Rev. **46**, 509 (1934), Eq. (14).

[14] This is a straightforward generalization for a Hamiltonian including s.o. interaction of Eq. (2.81.5) in A. H. Wilson, *Theory of Metals* (Cambridge University Press, London, 1953), second edition.

the part of π^{ν} depending on s.o. interaction, $(1/2c^2)\times(\mathbf{S}\times\nabla V)^{\nu}$ is zero and $\pi^{\nu}=-i\partial/\partial\nu$.

In order to transform the last two terms of (12), we use the identity:

$$X_{nn}=\int_{\Omega}\psi_n{}^*x\psi_n d\tau+i\int_{\Omega}\psi_n{}^*(\partial\psi_n/\partial k^x)d\tau. \tag{19}$$

The second term on the right can be transformed to a surface integral by considering the expression for $\int_{\Omega}\psi_{n\mathbf{k}}{}^*\mathcal{H}\psi_{n\mathbf{k}'}d\tau$, where $\mathbf{k}'=\mathbf{k}+\delta k_x\mathbf{i}$. Integration by parts of the differential operators in $\mathcal{H}$ and use of Green's theorem gives:

$$(E_{n\mathbf{k}'}-E_{n\mathbf{k}})\int_{\Omega}\psi_{n\mathbf{k}}{}^*\psi_{n\mathbf{k}'}d\tau$$

$$=\frac{1}{2i}\int_S[\psi_{n\mathbf{k}}{}^*\pi^{\nu}\psi_{n\mathbf{k}'}+(\pi^{\nu}\psi_{n\mathbf{k}})^*\psi_{n\mathbf{k}'}]dS. \tag{20}$$

Expansion of both sides in δk_x to the second order gives:

$$\int_{\Omega}\psi_n{}^*\left(\frac{\partial\psi_n}{\partial k^x}\right)d\tau=\frac{i}{4(\partial E_n/\partial k^x)}\int_S\left[\frac{\partial\psi_n{}^*}{\partial k^x}\pi^{\nu}\frac{\partial\psi_n}{\partial k^x}\right.$$

$$\left.+\left(\pi^{\nu}\frac{\partial\psi_n}{\partial k^x}\right)^*\frac{\partial\psi_n}{\partial k^x}\right]dS. \tag{21}$$

Upon substituting (21) and (18) into (12) and using again ordinary units, the complete expression for δg to order $k_F{}^2$ is given by the average at the Fermi surface of

$$2\left\{\int_{\Omega}\psi_n{}^*\left[x\left(\frac{1}{i}\frac{\partial}{\partial x}\right)-y\left(\frac{1}{i}\frac{\partial}{\partial x}\right)\right]\psi_n d\tau\right.$$

$$+\frac{1}{2mc^2}\int_{\Omega}\psi_n{}^*\left[\ \left(\frac{\partial V}{\partial x}\right)+y\left(\frac{\partial V}{\partial y}\right)\right]\psi_n d\tau$$

$$+\left[1-\frac{m}{m^*}\right]\int_{\Omega}\psi_n{}^*(xk^y-yk^x)\psi_n d\tau$$

$$-\tfrac{1}{2}\int_S\left[xu_n{}^*\left(\frac{\partial}{\partial\nu}\right)\left(\frac{\partial u_n}{\partial k^y}\right)-\left(\frac{\partial u_n}{\partial k^y}\right)\left(\frac{\partial}{\partial\nu}\right)xu_n{}^*\right.$$

$$\left.+2ik^{\nu}xu_n{}^*\left(\frac{\partial u_n}{\partial k^y}\right)\right]dS-\frac{m^*k^y}{4mk^x}\int\left[\frac{\partial\psi_n{}^*}{\partial k^x}\frac{\partial}{i\partial\nu}\frac{\partial\psi_n}{\partial k^x}\right.$$

$$\left.+\frac{\partial\psi_n}{\partial k^x}\left(\frac{\partial}{i\partial\nu}\frac{\partial\psi_n}{\partial k^x}\right)^*\right]dS+\text{terms obtained from}$$

$$\left.\text{the last two by interchanging } x \text{ and } y\right\}. \tag{22}$$

A discussion of the relative contributions of these terms in the alkali metals will now be given.

(*a*) *Volume terms.*—The first of these is given by the *z* component of orbital angular momentum and coincides with the result of reference 2. It contributes in orders k^2, k^4, etc., and to order k^2 is determined by the *p* part in the wave function. Its order of magnitude[8] is roughly the ratio of the lowest *p* doublet splitting in the free atom to an interband energy in the metal. The fact that the wave function is only partly of *p* character is counteracted by the increased (over the free atom) amplitude of the *p* part near the nucleus resulting from the necessity for the *p* part to vanish at the cell boundary. The value cited is thus reasonable.

The second term in (22) arises from the contribution to the velocity operator of s.o. interaction. In the limit of infinite lattice constant only this term survives and gives the correct, nonzero contribution for isolated atoms in an *s* state. The singularity of $r\partial V/\partial r$ (V is assumed spherically symmetric) is only of order r^{-1} as compared with the r^{-3} singularity of s.o. interaction so that the contribution of this term is expected to be much less than that of the preceding one. In fact one can express it through quantities determined for the metal under neglect of s.o. interaction. Thus, by partial integration, the contribution with the *s* part of the wave function ψ_0 can be shown to be given by

$$\int_{\Omega}\psi_0 r\left(\frac{\partial V}{\partial r}\right)\psi_0 d\tau=\psi_0{}^2(r_s)r_s{}^3[V(r_s)-E_0]+2\langle T\rangle_0, \tag{23}$$

where r_s is the radius of the unit cell and E_0 and $\langle T\rangle_0$ are the total and kinetic energies, respectively, at $\mathbf{k}=0$. The resulting shift is of order 10^{-5} and is completely negligible except possibly in lithium.

The third term is also negligible except in lithium because of the closeness[15] of the effective mass m^* to the free mass. Of the three volume integrals then only the first need be retained.

(*b*) *Surface terms.*—No clear-cut estimate can be made of these without numerical calculation. A rough argument depending on the rapidity with which s.o. interaction falls off away from the nucleus indicates that for a sufficiently steep rate of decrease the s.o. admixture to the wave function at the cell boundary may be small enough for these terms to be unimportant. To see whether this is so, a numerical calculation of one of the surface terms has been made for sodium using wave functions kindly supplied by Professor W. Kohn. The term $-\frac{1}{2}\int xu_n{}^*(\partial/\partial\nu)(\partial u_n/\partial k_y)dS$ contributes a shift of zero order in k through the *s* part in $u_n{}^*$ and the *p* part in $\partial u_n/\partial k_y$. This has been found to be of the order $\delta g\sim-0.5\times10^{-3}$, or 50% of the experimentally observed value. (No other term in the surface integral gives a contribution of zero order in k.) It is seen that

---

[15] H. Brooks, Phys. Rev. **91**, 1027 (1953); also F. S. Ham, *Solid State Physics* (Academic Press, Inc., New York, 1955), Vol. 1, p. 185.

this is not small. Although s.o. interaction falls off faster in the heavier alkalis, neglect of the surface terms cannot be justified for them without further examination.

It is to be noticed that the shift just found arises from the difference between the operators X, Y and x, y. Thus an electron at $\mathbf{k}=0$ in an s band can exhibit a g shift orders of magnitude larger than when in the same atom in the isolated state.

The estimate just given of the various terms of (22) summarizes the results of this calculation. In closing, it is perhaps worth while to remind oneself that there is no reason why the contributions of the higher orders in k should be insignificant. It is also important not to forget the limitations of the one-electron approximation. In the present problem it is the interaction with the core electrons (polarization, exchange) which is most likely to affect the result rather than the interaction between conduction electrons.

ACKNOWLEDGMENTS

The author is grateful to Professor H. Brooks for a prepublication copy of his quantum defects treatment of the g value. He is indebted to T. Kjeldaas and Professor W. Kohn for discussing their results prior to publication and to E. N. Adams and P. N. Argyres for helpful conversations. This field of research was first suggested by Professor C. Kittel.

PHYSICAL REVIEW VOLUME 106, NUMBER 4 MAY 15, 1957

Luminescence and Symmetry Properties of Color Centers*

JOHN LAMBE AND W. DALE COMPTON
United States Naval Research Laboratory, Washington, D. C.

(Received January 24, 1957)

A study has been made of the luminescent emission of F, M, and R centers in NaCl, KCl, and LiF. When such centers are excited by polarized light, the resulting emission can be analyzed for polarization. This yields information on the symmetry properties of the emitting center. In the case of M centers and of F centers made at 77°K the results obtained are consistent with the models widely used for these centers.

In the case of the R_1 and R_2 centers the situation is more complex and it appears that as far as optical properties are concerned some relationship exists between these centers. Excitation in either band yields the same emission band with very similar polarization properties. This has been interpreted in terms of an energy transfer process between R_1 and R_2 centers.

When crystals containing F, M, and R centers are investigated, the behavior of the F-band emission is markedly changed from the case where only F centers are present. The characteristic F-center emission disappears and instead F-band excitation gives the emissions characteristic of either the R_1 or M centers. Under these conditions the emission excited by polarized F-band light is polarized. Experiments were conducted to test whether these effects might be ascribable to the presence of "higher" excited states of the M and R centers in the region of the F band. This does not appear to be the case. It is therefore concluded that energy transfer processes can occur between the F center and the M and R centers. The observed dichrosim of the F band is ascribed to an interaction of F centers with nearby M and R_1 centers.

INTRODUCTION

SEVERAL experiments have been reported in recent years that deal with the symmetry properties of M centers in KCl. The work of Ueta[1] clearly demonstrated the anisotropic nature of the M center. This was done by bleaching in the M band with polarized light. This had the effect of removing M centers whose major absorption was along the direction of polarization while leaving behind M centers whose major absorption was in a different direction. Ueta was then able to observe a dichrosim in the M-band absorption. This anisotropy of the M center was also demonstrated in the work of van Doorn and Haven.[2] In their work a reorientation of M centers was induced by irradiation with polarized F-band light. They then found that both the M- and F-band absorptions were dichroic.

Another type of experiment which deals with the symmetry properties of color centers has been reported by Feofilov[3] on NaF and LiF. Feofilov utilized the emission of color centers to obtain information on their symmetry properties. This method is based upon the idea that an anisotropic absorber should be an anisotropic emitter. Thus excitation of such centers with polarized light leads to emission that is polarized. By studying the relation between polarization of the excitation and emission one can determine some of the symmetry properties of the emitter.

In the present work we have essentially utilized the technique of Feofilov and extended it to study two types of problems. The first part is a study of individual centers in KCl and NaCl; namely, the F, M, R_1, and R_2 centers. The second part is a study of interactions between these various centers.

In order to carry out the above program it was first necessary to study the M- and R-center luminescence, since no information was available on this aspect of

---

* This work was presented in part at the Color Center Symposium, Argonne National Laboratory (October, 1956).

[1] M. Ueta, J. Phys. Soc. Japan **7**, 107 (1952).

[2] C. Z. van Doorn and Y. Haven, Phys. Rev. **100**, 753 (1955).

[3] P. P. Feofilov, Doklady Akad. Nauk **92**, 743 (1953).