The Temperature Dependence of the g-Shifts of Conduction Electrons in Pure and Impure Alkali Metals (*).

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Summary. — The g-shifts of conduction electrons in pure and impure alkali metals have been calculated by taking the average over the Fermi surface along the [100], [110] and [111] directions. The conduction-electron wave functions are approximated by taking orthogonalized plane waves orthogonal to the core states and are the irreducible representations in the double group. The calculated g-shift for Li is $-6.7 \cdot 10^{-5}$ which is in satisfactory agreement with the experimental result $(-6.1 \pm 0.2) \cdot 10^{-5}$. The temperature dependence of the g-shift is obtained when the integration over the K-vector involves the Fermi-Dirac distribution. The g value for Li shifts only about 0.3% from a temperature of 4 °K to 500 °K. The wave functions for the impure alkali metals are obtained by Bardeen expansion to second order around the center of the Brillouin zone.

1. – Introduction.

In the observation of ESR the energies of the paramagnetic species are discrete, and the external magnetic field splits the Kramers degeneracies to give discrete Zeeman levels. By a study of the transitions induced by r.f. fields between these Zeeman levels, one can obtain information about the crystal

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field, hyperfine interactions, spin-orbit interaction and various other quantities of the substance. For the magnetic resonance of conduction electrons, the situation becomes more complicated. The energy levels of conduction electrons are quasi-continuous, and the wave functions are not localized but extend through the crystal. In magnetic field, the Zeeman states are not well defined, the phase factors of the wave functions depend on the particular gauge which can give the physically sensible Aharnov-Bohm effect [1]. Also, the orbital motions through the crystals are quantized. In contrast, the orbital momentum in paramagnetic salts are usually quenched.

YAFET [2] gave the first theoretical treatment of g-shifts of metals and semi-conductors. He used the Bardeen method to find the wave function including spin-orbit effects. The Bardeen-expansion method is valid only for small wave vectors and inapplicable to alkali metals where the radius of Fermi surfaces is large. The most complete calculation has been reported by BIENENSTOCK and BROOKS [3], who used the quantum defect method. Their results are in satisfactory agreement with experiment, but their theory is extremely complex, and its real physical meaning is difficult to comprehend. There is no apparent reason why, for good agreement with experiment, the « polarized correction » should be neglected and the « Hatree term » should be included. Recently OVERHAUSER and DE GRAFF [4] proposed a single procedure for estimating the g-shift in alkali metals. The wave functions are approximated by single orthogonalized plane waves (SOPW), and the g-shifts are integrated over the Fermi surface which is assumed to be spherical.

In our theory the Fermi surface is not necessarily spherical. The different wave functions at different symmetry points in the Brillouin zone are derived. The wave functions are the irreducible representations in the double group when spin-orbit interaction is presented. The corresponding g-shift is the Fermi-surface average along the [100], [110] and [111] directions. The temperature dependence of the g-shift is obtained when the integration over the k-vector involves the Fermi-Dirac distribution.

2. – Theory of the g-factor.

2`1. *The matrix element of the g-shift.* – In paramagnetic salts the g-factor may be defined as

$$(1) \qquad g = 2 \langle \varphi_n(r) \chi_i(s) | L_z + 2S_z | \varphi_n(r) \chi_i(s) \rangle \,,$$

[1]   J. J. SAKURAI: *Advanced Quantum Mechanics* (Cambridge, Mass., 1967), p. 16.
[2]   Y. YAFET: *Phys. Rev.*, **85**, 478 (1952); *Solid State Phys.*, **14**, 1 (1963).
[3]   A. BIENENSTOCK and H. BROOKS: *Phys. Rev.*, **136**, A 784 (1964).
[4]   A. W. OVERHAUSER and A. M. DE GRAFF: *Phys. Rev. Lett.*, **22**, 127 (1969); *Phys. Rev.*, **180**, 701 (1969); *Phys. Rev. B*, **2**, 1437 (1970).

where $\varphi_n(r)$ and $\chi_i(s)$ are the orbital and spin wave functions, respectively. For conduction electrons the calculation of the g value is not so straightforward, since there are no well-defined wave functions $\varphi_n(r)$ and the levels that participate in the resonance are a quasi-continuous series of levels [5]. The energies of the levels split by an external magnetic field need not all be the same, particularly when a large fraction of the Brillouin zone is occupied.

The g-factor as measured experimentally is determined by the position of the static magnetic field H_0 at which the maximum of power absorption of the r.f. field (perpendicular to H_0) occurs. Theoretically, the quantity calculated is the mean of the energy in the absorption spectrum. The difference between these two quantities can be negligible since the exchange interaction between conduction electrons and lattice scattering will tend to peak the line at the average absorption energy [6].

The g-factor therefore can be determined by the ratio of the first moment to the zeroth moment of the Hamiltonian in the absorption spectrum [7]. Utilizing the trace method [8], YAFET [9] has shown that the g-shift is given by the average of the orbital momentum induced by the spin-orbit interaction at the top of the Fermi distribution, or

$$(2) \qquad \Delta g = 2[(X\pi_y - Y\pi_x)_{nn} + X_{nn}(\pi_y)_{nn} - Y_{nn}(\pi_x)_{nn}] \,,$$

where the subscript nn indicates that these are expectation values for n-th conduction band state, π is the velocity operator $\hat{p} + (1/2c^2)\hat{\sigma}\times\nabla\hat{V}$, and X is the co-ordinate operator, and the matrix elements are

$$(3) \qquad X_{nn} = \int\limits_{\substack{\text{unit}\\ \text{cell}}} u_n^*(k, r)\, i\, \frac{\partial u_n}{\partial k_x}(k, r)\, \mathrm{d}^3 r \,.$$

Equation (2) can be evaluated to second order in the Bloch vectors; it gives

$$(4) \qquad \Delta g(k) = \frac{1}{2}\int \Psi^*(\hat{r}\times\hat{\nabla})_z\Psi\,\mathrm{d}^3 r + \frac{1}{2mc^2}\int \Psi^*\left[X\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y}\right]\Psi\,\mathrm{d}^3 r - S \,,$$

where S is the surface term and is equal to

$$-\int\left[u^*(\hat{r}\times\hat{\nabla}_k)\frac{\partial u}{z\,\partial\nu} + 2ik_\nu u^*(r\times\nabla_k)_z u - \frac{\partial u}{\partial k_y}\frac{\partial}{\partial\nu}xu^* + \frac{\partial u}{\partial k_x}\frac{\partial}{\partial\nu}yu^*\right]\mathrm{d}S -$$

$$-IM\int\left[\frac{k_y}{k_x}\frac{\partial\Psi^*}{\partial k_x}\frac{\partial}{\partial\nu}\frac{\partial\Psi}{\partial k_x} - \frac{k_x}{k_y}\frac{\partial\Psi^*}{\partial k_y}\frac{\partial}{\partial\nu}\frac{\partial\Psi}{\partial k_y}\right]\mathrm{d}S \,.$$

[5]   J. M. ZIMAN: *Electrons and Phonons* (London, 1968), p. 521.
[6]   P. W. ANDERSON: *Journ. Phys. Soc. Japan*, **9**, 316 (1954).
[7]   K. KAMBE and T. USUI: *Progr. Theor. Phys. Japan*, **8**, 302 (1952).
[8]   G. E. PAKE: *Paramagnetic Resonance* (New York, N. Y., 1962), p. 85.
[9]   Y. YAFET: *Phys. Rev.*, **106**, 679 (1957).

The integral is over the cellular polyhedron (or the equivalent sphere), and ν is the outward direction normal to it.

The meanings of the terms of eq. (4) are: the first is a volume integral of the Z-component (parallel to H_0) of the orbit magnetic moment; the second term arises from the spin-orbit interaction; and in the third, the surface integral term is proportional to the normal component of the velocity evaluated over the wave function and certain combinations of its first derivatives with respect to k_α.

In addition to Yafet's term in eq. (4) there is another contribution to the g-shift which arises from the fact that the spin precession frequency of a moving electron is smaller than that of one at rest by the relativistic factor $(1 - v^2/c^2)^{\frac{1}{2}} \approx 1 - v^2/2c^2$, as discussed by OVERHOUSER [4]. This leads to a negative shift

$$(5) \qquad (\Delta g)'' = - (m^2 c^2)^{-1} \int_\Omega \Psi^\dagger p^2 \Psi \, \mathrm{d}^3 r \,.$$

2'2. *Pure alkali metals.* – The alkali metals have just one electron outside the completely closed shells. At ordinary temperatures they are all crystallized in body-centered cubic structures. The form of the Brillouin zone together with the symbols showing the symmetry points and the Fermi surface is given in Fig. 1. There is no direct experimental measure of the anisotropy of the Fermi surface in any of the alkali metals. However, the Fermi radii at the
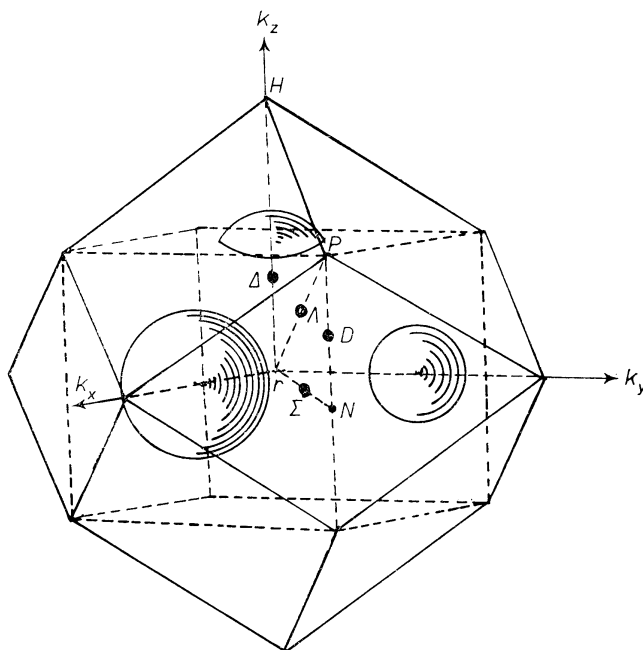

Fig. 1. – The Brillouin zone together with the symbols showing the symmetry points and the Fermi surface of the body-centered cubic structure.

[100], [110] and [111] directions are available in the literature ([10,11]). The Fermi surface seems to be pulled out in the direction Γ_N and pushed in along the cubic axes Γ_H. An indirect evidence suggests that only in Na the Fermi surface is nearly spherical; in K it probably bulges about half-way towards the zone boundary; in Rb and Cs even further; and in Li it is quite contrary to a sphere. The previous calculation ([4]) of the g-shift with the Fermi surface assumed to be spherical is not quite acceptable. We shall calculate the g-shift along the [100], [110] and [111] directions, respectively, and then take the average value over the Fermi surface.

The k-vectors can be anywhere along the [100], [110] and [111] directions. The symmetry types of the wave vectors are Δ, Σ and Λ. The classification of the atomic states and the basic functions are given in Table I ([12]).

TABLE I. – *Atomic states and basic functions at the degenerate points of the Brillouin zone.*

Symmetry points	Δ_1	Δ_5	Σ_1	Σ_3	Σ_4	Λ_1	Λ_3
Atomic states	s	p	s	p	p	s	p
Basis functions	1	$\{x, y\}$	1	z	$\{x - y\}$	1	$\{x - z, y - z\}$

The free-electron wave functions at the degenerate points can be found by use of the method given by JONES ([13]). They are given in eq. (6). Since the free-electron wave-function cannot give the correct g-shift, it is convenient to use the othogonalized plane waves (OPW). These are

$$
(6)
\begin{cases}
\Phi_{\Delta_1} = N_1 \left\{ \exp\left[ik_\zeta z\right]\left(\cos\frac{2\pi}{a}x + \cos\frac{2\pi}{a}y\right) - \sum_n B_{n1} R_{n0} Y_0^0 \right\}, \\[2ex]
\Phi_{\Delta_5}^x = N_{11} \left\{ \exp\left[ik_\zeta z\right]\sin\frac{2\pi}{a}x - \sum_n A_{n11} R_{n1}\left(\frac{Y_1^{-1} - Y_1^1}{\sqrt{2}}\right) \right\}, \\[2ex]
\Phi_{\Delta_5}^v = N_{12} \left\{ \exp\left[ik_\zeta z\right]\sin\frac{2\pi}{a}y - \sum_n A_{n12} R_{n1}\frac{i(Y_1^{-1} + Y_1^1)}{\sqrt{2}} \right\}, \\[2ex]
\Phi_{\Sigma_1} = N_2 \left\{ \exp\left[ik_\eta(x + y)\right]\cos\frac{2\pi}{a}z \cos\frac{2\pi}{a}(x - y) - \sum_n B_{n2} R_{n0} Y_0^0 \right\}, \\[2ex]
\Phi_{\Sigma_3} = N_{21} \left\{ \exp\left[ik_\eta(x + y)\right]\sin\frac{2\pi}{a}z \cos\frac{2\pi}{a}(x - y) - \sum_n A_{n21} R_{n1} Y_1^0 \right\},
\end{cases}
$$

([10]) J. M. ZIMAN: *Electrons and Phonons* (London, 1968), p. 111.

([11]) F. S. HAM: *Phys. Rev.*, **128**, 82 (1962).

([12]) H. JONES: *The Theory of Brillouin Zones and Electronic States in Crystals* (Amsterdam, 1960), p. 106.

([13]) H. JONES: *The Theory of Brillouin Zones and Electronic States in Crystals* Amsterdam, 1960), Sect. **30**.

(6)

$$\Phi_{\Sigma_4} = N_{22}\left\{\exp\left[ik_\eta(x+y)\right]\cos\frac{2\pi}{a}z\sin\frac{2\pi}{a}(x-y) -\right.$$

$$\left. -\sum_n A_{n22}R_{n1}\frac{[(1+i)Y_1^{-1}+(1-i)Y_1^1]}{\sqrt{2}i}\right\},$$

$$\Phi_{A_1^{'}} = N_3\left\{\exp\left[ik_\xi(x+y+z)\right]\left[\cos\frac{2\pi}{a}(x-y)+\cos\frac{2\pi}{a}(y-z)+\right.\right.$$

$$\left.\left. +\cos\frac{2\pi}{a}(z-x)\right]-\sum_n B_{n3}R_{n0}Y_0^0\right\},$$

$$\Phi_{A_3}^{x-z} = N_{31}\left\{\exp\left[ik_\xi(x+y+z)\right]\sin\frac{2\pi}{a}(x-z) -\right.$$

$$\left. -\sum_n A_{n31}R_{n1}\left[\frac{1}{\sqrt{2}}(Y_1^{-1}-Y_1^1)-Y_1^0\right]\right\},$$

$$\Phi_{A_3}^{y-z} = N_{32}\left\{\exp\left[ik_\xi(x+y+z)\right]\sin\frac{2\pi}{a}(y-z) -\right.$$

$$\left. -\sum_n A_{n32}R_{n1}\left[\frac{i}{\sqrt{2}}(Y_1^{-1}+Y_1^1)-Y_1^0\right]\right\}.$$

In the absence of spin the representation at a general point of the Brillouin zone is singly degenerate. It becomes Kramers degenerate when we introduce the spin. The energy change in the band due to the spin is small compared to the band energy if the spin-orbit interaction is small. The wave functions at points of high symmetry in the zone will be split because of the spin. The direct product of the above irreducible representations in the space group with the spin wave function (S^{-1}) can be found with the method given by TINKHAM ([14]). The results are shown in Table II.

TABLE II. – *Direct products of the irreducible representation in the space group and the spin wave function.*

s-state	$S^{-1}\times\Delta_1=\Delta_5$	$S^{-1}\times\Delta_1=\Delta_6$	$S^{-1}\times\Sigma_1=\Sigma_3+\Sigma_4$
p-state	$S^{-1}\times\Delta_5=2\Delta_5$	$S^{-1}\times\Delta_3=\Delta_4+\Delta_5+\Delta_6$	$S^{-1}\times\Sigma_3=\Sigma_3+\Sigma_4$
			$S^{-1}\times\Sigma_4=\Sigma_3+\Sigma_4$

The s-state wave function in the double group can be readily obtained by multiplication of the wave function in the space group by the spin states. The basis functions, or symmetry types, of the p-state are a bit more difficult

([14]) M. TINKHAM: *Group Theory and Quantum Mechanics*, Sect. 3'10, 4'7 (New York, N. Y., 1964).

to find. These can be obtained by following the method given by JONES [15]. For example, the symmetry type of Λ_4 will be of the form

$$(7) \qquad \Psi = \begin{pmatrix} aP_{x-z} + bP_{y-z} \\ cP_{x-z} + dP_{y-z} \end{pmatrix}.$$

The constants a, b, c, d are determined by applying the operations of the O_h group and making the results agree with the characteristic table of Λ_4. To illustrate this process one operation will be given in detail. Consider the operator which belongs to the class C_3 which transforms $(x, y, z) \rightarrow (y, z, x)$. In matrix form this can be written as

$$(8) \qquad Q = \begin{pmatrix} 010 \\ 001 \\ 100 \end{pmatrix}.$$

Compare eq. (8) with the matrix of a proper rotation

$$(9) \qquad Q =$$

$$= \begin{pmatrix} \cos\alpha\cos\beta\cos\gamma - \sin\alpha\sin\gamma & \sin\alpha\cos\beta\cos\gamma + \cos\alpha\sin\gamma & -\sin\beta\cos\gamma \\ -\cos\alpha\cos\beta\sin\gamma - \sin\alpha\cos\gamma & -\sin\alpha\cos\beta\sin\gamma + \cos\alpha\cos\gamma & \sin\beta\sin\gamma \\ \cos\alpha\sin\beta & \sin\alpha\sin\beta & \cos\beta \end{pmatrix},$$

We find that $\alpha = 0$, $\beta = \gamma = \pi/2$. The spin operator

$$(10) \qquad S = \begin{pmatrix} \cos(\beta/2)\exp[-i/2(\alpha+\gamma)] & -\sin(\beta/2)\exp[-i/2(\alpha-\gamma)] \\ \sin(\beta/2)\exp[i/2(\alpha-\gamma)] & \cos(\beta/2)\exp[i/2(\alpha+\gamma)] \end{pmatrix}$$

will therefore be

$$(11) \qquad
\begin{aligned}
S &= \begin{pmatrix} \dfrac{1-i}{2} & \dfrac{1+i}{2} \\ \dfrac{1-i}{2} & \dfrac{1+i}{2} \end{pmatrix} \\
\text{and} \\
S^{-1} &= \begin{pmatrix} \dfrac{1+i}{2} & \dfrac{1+i}{2} \\ -\dfrac{1-i}{2} & \dfrac{1-i}{2} \end{pmatrix}.
\end{aligned}$$

[15] H. JONES: *The Theory of Brillouin Zones and Electronic States in Crystals* (Amsterdam, 1960), Chap. 7.

The operation of $S^{-1}Q$ on the wave function Ψ will give Ψ multiplied by the character of the operation of Λ_4. In this case

$$(12) \qquad\qquad S^{-1}Q\Psi = -\Psi .$$

This equation can provide us two independent equations of a, b, c, d. Combined with other equations obtained by additional operations, we can solve for the values of a, b, c, d. The irreducible representations in the double group with spin up are

$$(13) \qquad \left\{ \begin{aligned}
&\Psi_1 = \Psi_{\Delta_5 s\uparrow} = \Phi_{\Delta_1}\begin{pmatrix}1\\0\end{pmatrix} = \Phi_{\Delta_1}\,\alpha \,,\\[6pt]
&\Psi_2 = \Psi_{\Delta_5 p\uparrow} = \frac{1}{\sqrt{2}}\,(\Phi^x_{\Delta_5} + i\Phi^y_{\Delta_5})\alpha \,,\\[6pt]
&\Psi_3 = \Psi_{\Sigma_3 s\uparrow} = \Phi_{\Sigma_1}\,\alpha \,,\\[4pt]
&\Psi_4 = \Psi_{\Sigma_3 p\uparrow} = \Phi_{\Sigma_3}\,\alpha \,,\\[4pt]
&\Psi_5 = \Psi_{\Sigma_4 p\uparrow} = \Phi_{\Sigma_4}\,\alpha \,,\\[4pt]
&\Psi_6 = \Psi_{\Lambda_1 p\uparrow} = \Phi_{\Lambda_1}\,\alpha \,,\\[6pt]
&\Psi_7 = \Psi_{\Lambda_4 p\uparrow} = \begin{pmatrix}\Phi^{x-z}_{\Lambda_3} & -\tfrac{1}{2}(\sqrt{2}+1+i) & \Phi^{y-z}_{\Lambda_3}\\[4pt]\dfrac{1-i}{\sqrt{2}}\,\Phi^{x-z}_{\Lambda_3} & -\tfrac{1}{2}(\sqrt{2}+1-i) & \Phi^{y-z}_{\Lambda_3}\end{pmatrix} .
\end{aligned} \right.$$

The spin-down counter-parts of eq. (13) can be obtained by application of the operator $\hat{C}$ ([16]) to eq. (13), where

$$(14) \qquad\qquad \hat{C} = -i\sigma_y K_0 J \,,$$

in which K_0 denotes complex conjugation, J is the inversion operator, and σ_y the y component of the spinor.

The g-shift averaged over the Fermi distribution is given as

$$(15) \qquad\qquad \Delta g = \frac{\displaystyle\sum_r \iiint f_{0r}(k)\,\Delta g_r(k)\,\mathrm{d}^3 k}{\displaystyle\sum_r \iiint f_{0r}(k)\,\mathrm{d}^3 k} \,,$$

where $\Delta g_r(k)$ are the integrals of eq. (4), and $f_{0r}(k)$ is the equilibrium Fermi-Dirac distribution.

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[16] C. KITTEL: *Quantum Theory of Solids*, Chap. 9 (New York, N. Y., 1963).

2'3. Alkali metals doped with impurities. – If the alkali metals are doped with impurities, the Fermi surface will be changed. According to COHEN and HEINE ([17]), the distortion of the Fermi surface depends on the values of s-like and p-like electronic states on the zone face and on the density of the states of solute and solvent. For example, the Fermi surface in pure Cu touches the zone boundary, but it may shrink and become more spherical when impurities are added. We can can successfully use the wave functions at the center of the Brillouin zone with the $k \cdot p$ perturbation method to find the wave function near the center of the zone. To b.c.c. structures, the state wave functions which correspond to the $k = 0$ are Γ_1, Γ_{15}, Γ_{12}, Γ_{25} and Γ'_{25}. The wave functions of the type Γ_1 have the full symmetry of the point group. It is the lowest state of the conduction band and usually corresponds to the atomic s-state in cubic metals. The next lower state of the type Γ_{15} is a threefold degenerate state and is related to the atomic p-state, whereas the Γ'_{25} and Γ_{12} states are equivalent to the atomic d-state.

The above basis functions in free-electron approximation can be constructed in the same manner as discussed in the previous Section. If they are normalized in the unit cell, we have

$$(16) \quad \begin{cases} \Gamma_1 : |0\rangle = (2/3a^3)^{\frac{1}{2}}(\cos bx \cos by + \cos by \cos bz + \cos bz \cos bx)\,, \\[2mm] \Gamma_{15} : |x\rangle = (2/a^3)^{\frac{1}{2}} \sin bx (\cos by + \cos bz)\,, \\[2mm] \Gamma_{12} : |A\rangle = (2/a^2)^{\frac{1}{2}}[\cos bz(\cos bx + \cos by) - 2\cos bx \cos by]\,, \\[2mm] \quad\;\; |B\rangle = (2/z^3)^{\frac{1}{2}} \cos bz(\cos bx - \cos by)\,, \\[2mm] \Gamma'_{25} : |xy\rangle = (4/a^3)^{\frac{1}{2}} \sin bx \sin by\,, \end{cases}$$

where a is the lattice constant and $b = 2\pi/a$.

In order to evaluate eq. (4) we need to know the core wave functions. Let us use the SOPW method which states that

$$(17) \quad |\Gamma_i^j\rangle = C_j^{-\frac{1}{2}}\left(|\Gamma_i^j\rangle - \sum_\lambda \sum_\mu \langle \varphi_{\lambda\mu}^j(r)|\Gamma_i^j\rangle |\varphi_{\lambda\mu}^j(r)\rangle\right)\,,$$

where $|\Gamma_i^j\rangle$ is the j-th component of the i-th irreducible representation of the plane wave function, $\varphi_{\lambda\mu}^j(r)$ denotes the μ-th impurity core states (perhaps different from the free atomic states) with quantum numbers λ and transformed like the Γ_i^j. The normalization factor is

$$(18) \quad C_j^{-\frac{1}{2}} = \left[1 - N \sum_\mu \sum_\lambda C_\mu |\langle \varphi_{\lambda\mu}^j(r)|\Gamma_i^j\rangle|^2\right]^{-\frac{1}{2}}\,,$$

([17]) M. H. COHEN and V. HEINE: *Adv. in Phys.*, **7**, 395 (1958).

where C_μ denotes the atomic concentration of ions of type μ, and N is the total number of ions contained in the volume.

The core states which transform like the Γ_i^j irreducible representations are

$$(19) \quad \begin{cases} \Gamma_1^0 = R_{n0}(r)\,Y_0^0 \,, \\[8pt] \Gamma_{15}^x = \dfrac{1}{\sqrt{2}} R_{n1}(Y_1^1 - Y_1^{-1}) \,, \\[8pt] \Gamma_{15}^y = \dfrac{1}{\sqrt{2}} R_{n1}(Y_1^1 + Y_1^{-1}) \,, \\[8pt] \Gamma_{15}^z = R_{n1}\,Y_1^0 \,, \\[8pt] \Gamma_{12}^A = R_{n2}\,Y_2^0 \,, \\[8pt] \Gamma_{12}^B = \dfrac{1}{\sqrt{2}} R_{n2}(Y_2^2 + Y_2^{-2}) \,, \\[8pt] \Gamma_{25}'^{\,xy} = \dfrac{1}{i\sqrt{2}} R_{n2}(Y_2^2 + Y_2^{-2}) \,, \\[8pt] \Gamma_{25}'^{\,yz} = \dfrac{i}{\sqrt{2}} R_{n2}(Y_2^1 + Y_2^{-1}) \,, \\[8pt] \Gamma_{25}'^{\,zx} = \dfrac{-1}{\sqrt{2}} R_{n2}(Y_2^1 - Y_2^{-1}) \,. \end{cases}$$

With the Bardeen method the periodic part of the wave function of the Schrödinger equation at a point k may be expanded in terms of the complete set of functions associated with the point $k = 0$, i.e. the center of the zone. The Bardeen expansion to second order is

$$(20) \quad u_0(k, r) = |0) + 2i \sum_l{}' \frac{|l)(l|k\cdot\nabla|0)}{E_0 - E_l} - 4 \sum_l{}' \left\{ \sum_n{}' \frac{|l)(k|k\cdot\nabla|n)(n|k\cdot\nabla|0)}{(E_0 - E_l)(E_0 - E_n)} - \right.$$

$$\left. - \frac{|l)(l|k\cdot\nabla|0)(0|k\cdot\nabla|0)}{(E_0 - E_l)^2} - \frac{1}{2}\frac{|0)(0|k\cdot\nabla|l)(l|k\cdot\nabla|0)}{(E_0 - E_l)^2} \right\} \,.$$

Direct calculation shows that the $k\cdot\nabla$ perturbation mixes only Γ_1 and Γ_{15}. If we consider the higher-order terms, $k\cdot p$ will mix Γ_{15} and Γ_{12}, Γ_{25}'. If eqs. (16), (17), (19) are substituted into (20) we find, to second order in k and with neglect of the small terms due to the integration of the core states, that

$$(21) \quad u_0(k, r) = |0) - \frac{i}{\sqrt{3}b}\left[k_x|x) + k_y|y) + k_z|z)\right] +$$

$$+ \frac{1}{2\sqrt{3}b^2}\left[2k_z^2 - k_x^2 - k_y^2)|A) + (k_x^2 - k_y^2)|B)\right] -$$

$$- \frac{1}{\sqrt{6}b^2}\left[k_x k_y|xy) + k_y k_z|yz) + k_x k_z|xz)\right] - \frac{k^2}{6b^2}|0) \,.$$

For monovalent impurities the core wave functions $\varphi_{\lambda\mu}(r)$ in eq. (17) can be the free-atom core states of the impurity atoms. When the valence of the impurity differs from that of the host, the excess or deficiency of ionic charge must be screened; the screening results from a change in the amplitude of the impurity core states. According to ASIK et al. [18] the impurity potential $V_1(r)$ can be represented as

$$(22) \qquad V_1(r) = -\frac{Z_v e^2}{r} \exp[-\alpha r],$$

where Z_v is the difference in the valence of the impurity atom and that of the host. The screening parameter α in each case is adjusted so that the s.p.d., ... phase shifts η_0, η_1, η_2, ..., and thus satisfies the Friedel sum rule [19]

$$(23) \qquad Z_v = \frac{2}{\pi} \sum_{l=0}^{\infty} (2l+1)\eta_l.$$

The optimum-screening parameter and phase shifts for a screened Coulomb potential in Li and Na are tabulated in ref. [18].

The l-th radial wave functions $R_l(r)$ of the impurity atom in the screened potential, by assuming the unit $m = \hbar = 1$, is

$$(24) \qquad \frac{\mathrm{d}^2 R_l}{\mathrm{d}r^2} + k_{\mathrm{F}}^2 R_l + \frac{2Z_v}{a_0 r} \exp[-\alpha r] R_l - \frac{l(l+1)}{r^2} R_l = 0,$$

where a_0 is the Bohr radius. Equation (24) can be numerically integrated by computer by the Milne method [20]. The numerical calculation of the g-shift is like that for pure alkali metals and will not be presented here.

2˙4. *Calculation of the g-shift.* – First let us consider the term

$$(25) \qquad \Delta g_r^1(k) = \frac{2}{i} \int \Psi_r^\dagger (\hat{r} \times \hat{\nabla})_z \Psi_r \, \mathrm{d}^3 r,$$

which is effectively given by the expectation value of the Z-component of the angular momentum (times $2/\hbar$) in the unit cell. The expectation value of the angular momentum of the s-state electron is zero. The explicit forms of eq. (25)

[18] J. R. ASIK, M. A. BALL and C. P. SLICHTER: *Phys. Rev.*, **181**, 645 (1968).

[19] J. FRIEDEL: *Phil. Mag.*, **43**, 153 (1952).

[20] K. S. KUNZ: *Numerical Analysis* (New York, N. Y., 1957), p. 202.

are given as follows:

$$
(26)
\begin{cases}
\int \Psi_2^\dagger \frac{2}{i} (r \times \nabla)_z \Psi_2 \, \mathrm{d}^3 r = \\
\qquad = \int N_{11} N_{12} \left\{ \frac{2\pi}{a} \left[x \sin \frac{2\pi}{a} x \cos \frac{2\pi}{a} y + y \sin \frac{2\pi}{a} y \cos \frac{2\pi}{a} x \right] + \right. \\
\qquad\qquad \left. + \frac{3}{4\pi} \sum_n A_{n11} A_{n12} \frac{x^2 + y^2}{r^2} R_{n1}^2 \right\} \mathrm{d}^3 r + \text{c.c.} , \\[8pt]

\int \Psi_4^\dagger \frac{2}{i} (r \times \nabla)_z \Psi_4 \mathrm{d}^3 r = 2 \int N_{21}^2 k_\eta (x - y) \sin^2 \frac{2\pi z}{a} \cos^2 \frac{2\pi}{a} (x - y) \mathrm{d}^3 r + \text{c.c.} , \\[8pt]

\int \Psi_5^\dagger \frac{2}{i} (r \times \nabla)_z \Psi_5 \mathrm{d}^3 r = 2 N_{22}^2 \int \left\{ \cos k_\eta (x + y) \cos \frac{2\pi}{a} z \sin \frac{2\pi}{a} (x - y) - \right. \\
\qquad\qquad - \sqrt{\frac{3}{4\pi}} \sum_n A_{n22} \frac{x - y}{r} R_{n1} \left\} \right\{ k_\eta (x - y) \cos k_\eta (x + y) - \\
\qquad\qquad \left. - \frac{2\pi}{a} (x + y) \sin k_\eta (x + y) \cos \frac{2\pi}{a} z \cos \frac{2\pi}{a} (x - y) \right\} \mathrm{d}^3 r + \text{c.c.} , \\[8pt]

\int \Psi_7^\dagger \frac{2}{i} (r \times \nabla)_z \Psi_7 \mathrm{d}^3 r = 4 \int N_{31}^2 \left\{ \cos k_\xi (x + y + z) \sin \frac{2\pi}{a} (x - z) - \right. \\
\qquad\qquad - \sqrt{\frac{3}{4\pi}} \sum_n A_{n31} \frac{x - z}{r} R_{n1} \left\} \right\{ k_\xi (x - y) \cos k_\xi (x + y + z) \sin \frac{2\pi}{a} (x - z) - \\
\qquad\qquad \left. - \frac{2\pi}{a} y \sin k_\xi (x + y + z) \cos \frac{2\pi}{a} (x - z) \right\} \mathrm{d}^3 r + \\
\qquad\qquad + 2(2 + \sqrt{2}) \int N_{32}^2 \left\{ \cos k_\xi (x + y + z) \sin \frac{2\pi}{a} (y - z) - \right. \\
\qquad\qquad \left. - \sqrt{\frac{3}{4\pi}} \sum_n A_{n32} \frac{y - z}{r} R_{n1} \right\} \cdot \\
\qquad\qquad \cdot \left\{ k_\xi (x - y) \cos k_\xi (x + y + z) \sin \frac{2\pi}{a} (y - z) + \right. \\
\qquad\qquad \left. + \frac{2\pi}{a} x \sin k_\xi (x + y + z) \cos \frac{2\pi}{a} (y - z) \right\} \mathrm{d}^3 r + \text{c.c.} ,
\end{cases}
$$

where c.c. is the complex conjugate.

The second term is

$$
(27) \qquad \Delta g_r^2(k) = \frac{1}{2 m_r^* c^2} \int \Psi_r^\dagger \left[x \frac{\partial V}{\partial x} + y \frac{\mathrm{d} V}{\partial y} \right] \Psi_r \, \mathrm{d}^3 r ,
$$

where m_r^* is the cyclotron effective mass in the r-th band. Equation (27) comes from the spin-orbit coupling energy

$$
(28) \qquad \frac{\hbar}{4 m^2 c^2} \hat{\sigma} \cdot [\hat{\nabla} V \times \hat{p}] .
$$

This term calculated by OVERHAUSER *et al.* [4] is smaller than that calculated by YAFET [2] and in subsequent works [3] by a factor of 2. We can assume the potential to be of the form

$$(29) \qquad V(r) = -\left[\frac{r_s}{r} + \frac{1}{2}\left(\frac{r}{r_s}\right)^2 - \frac{3}{2}\right]\frac{ne^2}{r_s} - \frac{\mu e^2}{r}\exp\left[-r/\lambda\right].$$

The first term represents the potential of n nuclear charges screened by an electronic charge distributed uniformly throughout the Wigner-Seitz sphere of radius r_s. The second term represents crudely the potential of n nuclear charges by the ion core. The operator is

$$(30) \qquad x\frac{\partial V}{\partial x} + y\frac{\partial V}{\partial y} = e^2\left[n\left(\frac{1}{r} - \frac{r^2}{r_s^3}\right) + \mu\left(\frac{1}{r} + \frac{1}{\lambda}\right)\exp\left[-r/\lambda\right]\right]\sin^2\theta.$$

Equation (27) can then be easily evaluated by use of eq. (30).

The third term is

$$(31) \qquad \Delta g_r^3(k) = -\frac{1}{m_r^{*2}c^2}\int_{\Omega}\Psi_r^{\dagger}p^2\Psi_r\,\mathrm{d}^3r.$$

Since $p^2\Psi = -\hbar^2\Delta^2\Psi = 2m(E - V)\Psi$, eq. (31) can be readily evaluated, and we find that

$$(32) \quad \begin{cases} \Delta g_1^3 = -\dfrac{N_1^2}{m_\Delta^{*2}c^2}\left\{\hbar^2\left(\left(\dfrac{2\pi}{a}\right)^2 + k_\zeta^2\right)\Omega + 2m_\Delta^*\sum_n B_{n1}^2\int(E_{ns} - V)R_{n0}^2\,\mathrm{d}^3r\right\}, \\[2ex] \Delta g_2^3 = -\dfrac{1}{2m_\Delta^{*2}c^2}\left\{\hbar^2(N_{11}^2 + N_{12}^2)\left(k_\zeta^2 + \left(\dfrac{2\pi}{a}\right)^2\right)\cdot\right. \\[2ex] \qquad\qquad \left.\cdot\,\Omega + 2m_\Delta^*\sum_n(A_{n11}^2N_{11}^2 + A_{n12}^2N_{12}^2)\int(E_{np} - V)R_{n1}^2\,\mathrm{d}^3r\right\}, \\[2ex] \Delta g_3^3 = -\dfrac{N_2^2}{m_\Sigma^{*2}c^2}\left\{\hbar^2\left(2k_\eta^2 + 3\left(\dfrac{2\pi}{a}\right)^2\right)\Omega + 2m_\Sigma^*\sum_n B_{n2}^2\int(E_{ns} - V)R_{n0}^2\,\mathrm{d}^3r\right\}, \\[2ex] \Delta g_4^3 = -\dfrac{N_{21}^2}{m_\Sigma^{*2}c^2}\left\{\hbar^2\left(2k_\eta^2 + 3\left(\dfrac{2\pi}{a}\right)^2\right)\Omega + 2m_\Sigma^*\sum_n A_{n21}^2\int(E_{np} - V)R_{n1}^2\,\mathrm{d}^3r\right\}, \\[2ex] \Delta g_5^3 = -\dfrac{N_{22}^2}{m_\Sigma^{*2}c^2}\left\{\hbar^2\left(2k_\eta^2 + 3\left(\dfrac{2\pi}{a}\right)^2\right)\Omega + 2m_\Sigma^*\sum_n A_{n22}^2\int(E_{np} - V)R_{n1}^2\,\mathrm{d}^3r\right\}, \\[2ex] \Delta g_6^3 = -\dfrac{N_3^2}{m_\Lambda^{*2}c^2}\left\{\hbar^2\left(3k_\xi^2 + 2\left(\dfrac{2\pi}{a}\right)^2\right)\Omega + 2m_\Lambda^*\sum_n B_{n3}^2\int(E_{ns} - V)R_{n0}^2\,\mathrm{d}^3r\right\}, \\[2ex] \Delta g_7^3 = -\dfrac{2}{m_\Lambda^{*2}c^2}\left\{\hbar^2\left(3k_\xi^2 + 2\left(\dfrac{2\pi}{a}\right)^2\right)(N_{31}^2 + (2 + \sqrt{2})N_{32}^2)\cdot\right. \\[2ex] \qquad\qquad \left.\cdot\,\Omega + 2m_\Lambda^*\sum_n(A_{n31}^2N_{31}^2 + (2 + \sqrt{2})N_{32}^2A_{n32}^2)\int(E_{np} - V)R_{21}^2\,\mathrm{d}^3r\right\}, \end{cases}$$

where Ω is the volume of the Wigner-Seitz sphere.

The last term S, which was the contribution of the surface integral over the cellular polyhedron, can be neglected since the amplitude of the wave functions calculated by the tight-binding method at the boundary is negligibly small.

The g-shift contributions from electrons with their momenta extend from $k = 0$ to $k = k_{\mathrm{F}}$. The most effective contribution comes from the electrons with their wave vectors near the Fermi surface. The mean value of the g-shift over the [100], [110], [111] directions is

$$(33) \qquad \Delta g = \frac{\iint \sum_r f_{0r}(k)_\Delta \, g_r(k) \, \mathrm{d}A_k \, \mathrm{d}k_\perp}{\iint \sum_r f_{0r}(k) \Psi_r^\dagger \Psi_r \, \mathrm{d}A_k \, \mathrm{d}k_\perp \, \mathrm{d}^3 r} \, ,$$

where $f_{0r}(k)$ is the equilibrium Fermi-Dirac distribution of the form

$$(34) \qquad f_{0r}(k) = 1/[\exp{[(E_{rk} - \zeta_{rf})/K_{\mathrm{B}} T]} + 1] \, .$$

Here $E_{rk} = \hbar^2 k^2 / 2 m_r^*$, and ζ_{rf} is the Fermi potential at the r-th band. The Fermi potential is related to the Fermi energy by the following formula [21]:

$$(35) \qquad \zeta_f = E_{\mathrm{F}} - \frac{\pi^2}{6} (K_{\mathrm{B}} T)^2 \left[\frac{\partial}{\partial E} \ln N(E) \right]_{E = E_{\mathrm{F}}} + \dots \, ,$$

where $N(E)$ is the density of states. For metals at ordinary temperature we have $K_{\mathrm{B}} T \ll E_{\mathrm{F}}$ (as an example, for lithium,

$$E_{\mathrm{F}} = 9.45 \cdot 10^{-11} \, \mathrm{erg} \, , \qquad K_{\mathrm{B}} T = 4.1 \cdot 10^{-14} \, \mathrm{erg}) \, ,$$

so that $\zeta_f \approx E_{\mathrm{F}}$. The temperature dependence of the g-shift is apparent from examination of the following formula:

$$(36) \qquad \bar{Q} = \frac{1}{4\pi^3} \int_0^{E_{\mathrm{F}}} Q f_0(E_k) \, \mathrm{d}^3 k = \frac{1}{4\pi^3} \int_0^{E_{\mathrm{F}}} Q \, \mathrm{d}^3 k + \frac{\pi^2}{6} (K_{\mathrm{B}} T)^2 \left[\frac{\partial}{\partial E} Q \right]_{E = E_{\mathrm{F}}} =$$

$$= \frac{1}{4\pi^3} \int_0^{E_{\mathrm{F}}} Q \, \mathrm{d}^3 k + \frac{\pi^2}{6} (K_{\mathrm{B}} T)^2 \left[\frac{1}{\nabla_k E} \frac{\partial}{\partial k_n} Q \right]_{E = E_{\mathrm{F}}} \, .$$

As an application to lithium, the calculations were carried out on an IBM 1130 digital computer. The radial-wave functions are from the work of HERMAN and SKILLMAN [22], and the structure constants and other parameters of Li and Na are given in Table III.

[21] J. M. ZIMAN: *Principle of the Theory of Solids* (Cambridge, Mass., 1965), p. 119.
[22] F. HERMAN and S. SKILLMAN: *Atomic Structure Calculations* (Englewood Cliffs, N. J., 1963).

TABLE III. – *The structure constants and parameters for calculating the g-shift of conduction electrons in lithium and sodium.*

Description	Symbol	Li	Na
Lattice constant	a (atomic units)	6.651	8.109 [a]
Radius of Wigner-Seitz sphere	r_s (atomic units)	3.26	3.97
Ratio of cyclotron effective mass to free-electron mass	m^*_{110}/m_0	1.48	1.00 [a]
	m^*_{100}/m_0	1.65	1.00
	m^*_{111}/m_0	1.82	1.00
Ratio of the extreme area of cross-section A of the Fermi surface to area of the free-electron Fermi sphere	A_{110}/A_0	0.976	1.00 [a]
	A_{100}/A_0	0.993	1.00
	A_{111}/A_0	1.011	1.00
Ratio of the wave vector on the Fermi surface in the $[n_1 n_2 n_3]$ direction to the free-electron wave vector	k_{110}/k_F	1.023	1.00 [a]
	k_{100}/k_F	0.973	1.00
	k_{111}/k_F	0.983	1.00
Fermi energy of free electron in alkali metals	E_F (eV)	4.76	3.20 [b]
Ratio of energy at Fermi surface to free-electron energy	E_{110}/E_F	0.754	1.065 [b]
	E_{100}/E_F	0.750	1.240
	E_{111}/E_F	0.760	1.070
Screen radius	(atomic units)	0.763	0.294 [c]
Effective charge		2	0.12

(a) Ref. [11].
(b) Ref. [5].
(c) Ref. [4].

3. – Experimental details.

We have measured the temperature dependence of the g-shift of conduction electrons in sodium. The sample preparation is the same as in our other works [23]. Resistivity measurements of the material by eddy-current decay method [24] gave a resistivity ratio $\varrho_{300\,°K}/\varrho_{4.2\,°K} \approx 6000$.

At temperature above 100 °K the measurements were performed by use of a Varian X-band homodyne reflection spectrometer. The sodium samples surrounded by a quartz Dewar were mounted in a multipurpose rectangular cavity of mode TE_{102}. A 100 kHz modulation field is used for improvement of the signal-to-noise ratio. Use of highly attenuated microwave power prevents the saturation effect. In our measurements the microwave power is attenuated

[23] J. T. LUE: *The spin-lattice relaxation time of conduction electrons in alkali metals: sodium* (to be published).

[24] C. P. BEAN, P. W. DEBLOIS and C. B. NESBIT: *Journ. Appl. Phys.*, **30**, 1976 (1959).

25 db down from a 400 MW klystron. Since the relaxation time is short enough above 100 °K, there is no saturation problem when this power level is used with a homodyne detector. Increasing the modulation field greatly distorts the line shape. In our system we took the 100 kHz modulation field at a.c. 13 G so that there was no sacrifice of the signal-to-noise ratio to avoid the line broadening. The temperature variation arrangement was similar to that of WALSH, JEENER and BLOEMBERGEN ([25]). Signals proportional to the derivative of the real part of the surface impedance of the sample were obtained by the locking of the microwave klystron to the cavity resonance frequency.

At low temperatures the CESR (conduction electron spin resonance) signals were measured by a two-klystron superheterodyne ESR spectrometer operating at X-band, a design very similar to that described by FEHER ([26]). The microwave cavity was surrounded by two concentric pyrex-glass Dewars filled with liquid nitrogen and liquid helium. For operation at a temperature intermediate between 4.2 °K and 50 °K, the inner Dewar was filled with activated charcoal ([27]) which then surrounded the microwave cavity. The charcoal can absorb cold helium gas and can provide a large thermal reservoir. With this installation we can measure the CESR at an elevated temperature after waiting for equilibrium to be established. The inside of the cavity and the wave guide dipped in the Dewar were filled with styrofoam to prevent the bubbling of liquid helium.

Precise measurement of g values requires careful determination of the magnetic field and the microwave frequency at which resonance occurs. The best accuracy in the determination of the absolute magnitude of a magnetic field is obtained with an NMR fluxmeter. Our home-made fluxmeter ([28]) has the stability of the frequency of the protons of one part in 10^8. The gyromagnetic ratio of the proton is known only to one part in 10^5, resulting in an absolute accuracy in measurement of the field of two parts in 10^5. To measure the microwave frequency, a Hewlett-Packard 5257A transfer oscillator accompanied with a 5245M electronic counter was used. The frequency measured can have accuracies of 1 part in 10^5.

4. – The experimental and theoretical results and discussions.

4'1. *The determination of the g value from the experimental line shape.* – DYSON ([29]) has solved the line shapes of the power absorbed by a flat metal plate

([25]) W. M. WALSH jr., J. JEENER and N. BLOEMBERGEN: *Phys. Rev.*, **139**, A 1338 (1965).
([26]) G. FEHER: *Bell System Tech. Journ.*, **36**, 449 (1957).
([27]) G. WHITE: *Experimental Techniques in Low Temperature Physics* (Oxford, 1959), p. 213.
([28]) J. T. LUE: *A simple circuit of crystal oscillator and its application to a high resolution NMR spectrometer* (to be published).
([29]) F. J. DYSON: *Phys. Rev.*, **98**, 349 (1955).

of arbitrary thickness with the external d.c. field perpendicular to the face and a linear polarized r.f. field H_1 parallel to it. In our case the sample is a cylindrical rod with H_0 arbitrarily oriented with respect to the rod axis and a coaxial r.f. field around it. Since the skin depth is small compared to the radius of the cylinder, we can approximately replace the cylinder with a flat plate. Furthermore, since it is experimentally observed that the line shape does not depend on the orientation of H_0, we can take H_0 perpendicular to the plate. Thus Dyson's result would apply except that the boundary conditions are different. In this theory he assumes the r.f. field is the same on both faces of the plate. For the cylindrical rod the r.f. fields on the two sides are opposite in sign.

From Dyson's calculation the line shape of CESR is a function of skin depth δ and spin diffusion depth in one relaxation time δ_e. The electronic thermal scattering would greatly reduce the value of δ_e and increase the value of δ; therefore the line shape is also a function of temperature. The true resonance center of the spectrum line (the point from which we calculate the g value) does not coincide with the point of maximum absorption (the zero of the derivative curve). The theoretical curve is fitted once the ratio of the relative heights of the low-field and high-field peaks is experimentally determined. The dependence of the shift of the true resonance center from the point of maximum absorption as a function of the peak-to-peak ratio is given by Pressley ([30]).

4'2. *Theoretical prediction of the g-shift of conduction electrons.* – We have used the wave functions in the first excited band to calculate the g-shift, since the wave functions in the first occupied band (Γ-states) are valid only for the wave vector k near zero, which are inapplicable to alkali metals where the Fermi surface almost touch the Brillouin zone. The contributions of the g-shift from the Γ-states have been included automatically in the integration of eq. (33), because of the Δ, Σ, Λ states in the first band are compatible to the Γ-states as $k \to 0$. In metals the energy levels are quasi-continuous, the resonance spectrum can be contributed from different bands which may have a wide range of g values. The spectrum line is not come from any specific band. But the majority of the spin resonance experiments carried out so far show only one narrow line. The simplicity comes from experimental conditions, *i.e.* if the spin-lattice relaxation time is larger than the electron scattering time (τ_c) between two Landau levels without spin reversal, and if $\tau_c \delta\omega$, where $\delta\omega$ is the distribution of resonance linewidth from different bands. The center of the line, therefore, is at the weighted average frequency and is very narrow.

In an application to the theory given in Sect. **2** we have calculated the temperature dependence of the g-shift of conduction electrons in lithium.

([30]) K. J. PRESSLEY and H. L. BERK: *Phys. Rev.*, **140**, A 1207 (1965).

Our calculation shows that the contributions of the Margenau term $\Delta g^2 + \Delta g^3$ of lithium is 43.6% along the [110] direction and is 15.7% along the [111]
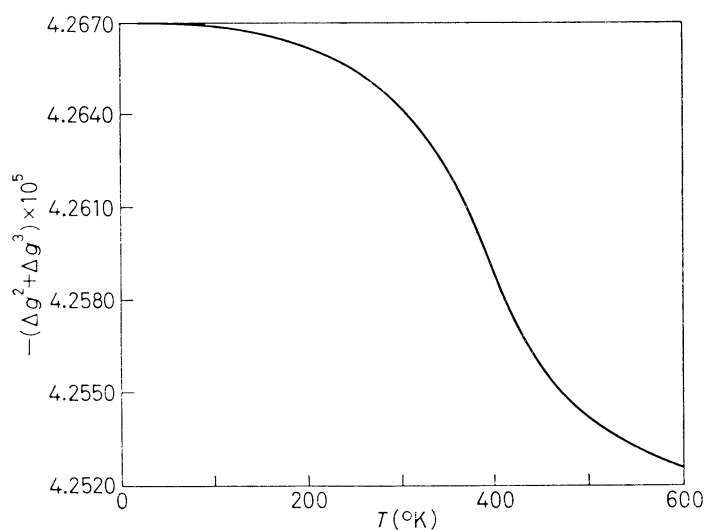

Fig. 2. – The calculated temperature dependence of the g-shift of conduction electrons in lithium.

direction corresponding to the largest and smallest terms respectively, with wave functions of Li stated by HERMAN and SKILLMAN do not permit us to an average value of $- 4.2 \cdot 10^{-5}$ for the Margenau term. Since the s-state elec-
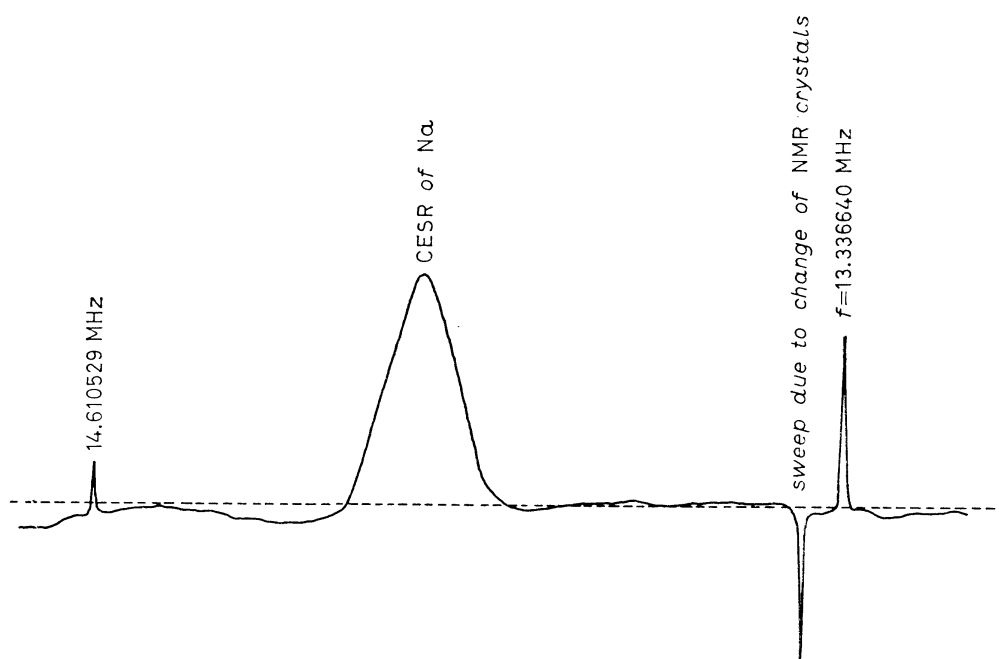

Fig. 3. – The conduction-electron spin resonance line of sodium at room temperature accompanied by two NMR marks.

trons have no contribution to the first term $\Delta g^1 = (2/i)\int \Psi^\dagger(\hat{r}\times\hat{\nabla})_z\Psi_r\,\mathrm{d}^3r$, the estimate the value of Δg^1. BIENENSTOCK and BROOK [3] using the quantum defect method found that $\Delta g^1 = -2.5\cdot10^{-5}$. This value combined with our result $-4.2\cdot10^{-5}$ would give $-6.7\cdot10^{-5}$, which is in satisfactory agreement with the experimental result $(-6.1\pm0.2)\cdot10^{-5}$ [31].

The calculated temperature dependence of the g-shift for Li was shown in Fig. 2. The shift from 4 °K to 500 °K is only about 0.3 %. The g-shift arising from the atomic spin-orbit interaction is less influenced by the temperature change of the lattice constant. Since the Fermi temperature of alkali metals may be as high as $4\cdot10^4$ °K, this is the reason why the effect on the g-shift by the Fermi-Dirac distribution of the conduction electrons in the temperature range from 4 °K to 500 °K is very small. An inspection of the theoretical result would show that the g-shift decreases in magnitude as the temperature increases and asymptotically approaches to a final value; the increase in temperature causes the conduction electrons to behave more like free electrons.

$$* * *$$

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[31] N. S. VANDER VEN: Phys. Rev., **168**, 787 (1968).

● RIASSUNTO (*)

Si sono calcolati gli spostamenti g degli elettroni di conduzione nei metalli alcalini puri e impuri facendo la media sulla superficie di Fermi lungo le direzioni [100], [110] e [111]. Le funzioni d'onda degli elettroni di conduzione, che si sono approssimate con onde piane ortogonalizzate ortogonali agli stati interni, sono le rappresentazioni non riducibili nel gruppo doppio. Si ha per il Li il valore calcolato dello spostamento g di $-6.7\cdot10^{-5}$, che coincide entro limiti soddisfacenti col valore sperimentale $(-6.1\pm0.2)\cdot10^{-5}$. Si ottiene la dipendenza dalla temperatura dello spostamento g quando l'integrazione operata sul vettore K coinvolge la distribuzione di Fermi-Dirac. Il valore di g per il Li si sposta solo di circa lo 0.3% andando da una temperatura di 4 °K a una di 500 °K. Si ottengono le funzioni d'onda per i metalli alcalini impuri per mezzo dello sviluppo di Bardeen del secondo ordine intorno al centro della zona di Brillouin.

(*) Traduzione a cura della Redazione.

Зависимость от температуры g **сдвигов для электронов проводимости в чистых и нечистых щелочных металлах.**

Резюме (*). — Проводится вычисление g сдвигов для электронов проводимости в чистых и нечистых щелочных металлах с помощью усреднения по поверхности Ферми вдоль направлений [100], [110] и [111]. Волновые функции электронов проводимости аппроксимируются с помощью ортогонализованных плоских волн, ортогональных состояниям остова, и образуют неприводимые представления в двойной группе. Вычисленный g сдвиг для Li составляет $-6.7\cdot10^{-5}$, что удовлетворительно согласуется с экспериментальным результатом $(-6.1\pm0.2)\cdot10^{-5}$. Температурная зависимость g сдвига получается после интегрирования по всем векторам K, входящим в распределение Ферми-Дирака. Величина g для лития изменяется только на 0.3% при изменении температуры от $4\,°K$ до $500\,°K$. Волновые функции для щелочных металлов с примесями получаются с помощью разложения Бардина второго порядка вблизи центра зоны Бриллюэна.

(*) *Переведено редакцией.*