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Knight Shifts and Pauli Susceptibilities in Alkali Metals and Alloys*

J. P. Perdew[†] and J. W. Wilkins

Laboratory of Atomic and Solid State Physics, Cornell University, Ithaca, New York 14850 (Received 11 August 1972)

An expression for the contact density, or Fermi-surface electron probability density at the nucleus, is developed to first order in the pseudopotential for a metal with a spherical Fermi surface, and applied to solid alkali metals and liquid binary alkali alloys at all concentrations. The explicit orthogonalization of the pseudo-wave-functions to the ionic core states permits the use of a local empirical pseudopotential. The contact density samples the Fourier transform of the pseudopotential primarily in the region just above $2k_{F}$; consequently the large changes in k_{F} which occur upon alloying in the alkali metals are dominant over the details of the ionic environment in determining the behavior of the contact density. The calculated contact densities, when combined with measured alloy Knight shifts, imply a unique and roughly free-electron-like dependence of the Pauli electron-spin susceptibility upon the interelectron spacing r_s in the range 4.0 $< r_s < 5.8$. The polarizability of the ions may introduce an effective value of r_s in the range $3.8 < r_s < 4.6$. The deduced susceptibilities are consistent with a simple picture in which the electron-ion effective masses of Na, K, Rb, and Cs are close to unity; the susceptibilities agree in this picture with a recent analysis of the observed enhancement of the Korringa constant. The calculation is in some important respects insensitive to the choice of pseudopotentials, structure factors, and core-state wave functions. The temperature dependence and change upon melting of the Knight shift are also estimated, and the extension of the calculation to other metals is briefly discussed.

I. INTRODUCTION

The Knight shift¹ of the NMR frequency in a metal depends upon the electron-spin susceptibility and the contact density or probability density for Fermi-surface electrons at the nucleus. While the contact densities in perfect solid metals may be calculated by the techniques of band theory,^{2,3} the contact densities in disordered systems such as vibrating solids, liquids, and alloys are more naturally treated by pseudopotential perturbation theory.⁴ Faber⁵ has taken a pseudopotential approach to calculate the change in the contact density of an ion due to changes upon alloying in the scattering from neighboring ions. His method is similar in principle to the phase-shift method of Blandin and Daniel.⁶

If the changes in the environment of an ion due to alloying, melting, etc., are associated with large changes in the Fermi wave vector k_F , then changes in the contact density of an ion are not adequately described by the scattering from neighboring ions, and the full pseudopotential perturbation theory must be employed. This approach additionally provides an estimate of the magnitude of the contact density in the pure metal and at all alloy concentrations; it has been applied to cadmium by Kasowski,⁷ to the alkali metals by Perdew and Wilkins,⁸ to sodium by Ritter and Gardner,⁹ and to magnesium by Jena and Halder.¹⁰

The Knight shift is discussed in Sec. II. Expressions for the contact density in a binary alloy with a spherical Fermi surface are derived in Sec. III, and applied in Sec. IV to the liquid alkali metals, which exhibit large changes in k_F upon alloying. It is shown that the explicit orthogonalization of the pseudo-wave-function to the ionic core states suppresses the higher Fourier components of the pseudopotential and thereby permits the use of a local empirical pseudopotential in the calculation. The numerical results are combined with measured Knight shifts to extract information about the Pauli susceptibility. Then the sensitivity of the calculation to various input parameters is explored. The temperature dependence of the Knight shift is also discussed in Sec. IV. The change in the Knight shift upon melting is considered in Sec. V. Appendix C should be consulted for a discussion of the effective r_s values resulting from ion polarizability in the dielectric response.

II. KNIGHT SHIFT

The electron-spin magnetic-moment density

$$\vec{\mathbf{M}}_{s}(\vec{\mathbf{r}}) = \left\langle \sum_{i} \gamma_{e} \hbar \vec{\mathbf{S}}_{i} \delta(\vec{\mathbf{r}} - \vec{\mathbf{r}}_{i}) \right\rangle$$
(2.1)

in paramagnetic cubic and liquid metals is proportional to the applied magnetic field \vec{H}_0 :

$$\vec{\mathbf{M}}_{s}(\vec{\mathbf{r}}) = \chi(\vec{\mathbf{r}})\vec{\mathbf{H}}_{0} \quad (2.2)$$

If χ_P is the Pauli susceptibility, i.e., the actual electron-spin susceptibility of the system, one may write

$$\chi(\mathbf{\ddot{r}}) = \chi_P f(\mathbf{\ddot{r}}) , \qquad (2.3)$$

where

$$\int_{V} d^{3} \gamma f(\mathbf{\tilde{r}}) = V .$$
(2.4)

The Pauli susceptibility is enhanced over its freeelectron value by electron-ion and electron-electron interactions. If the Fermi surface is nearly spherical and if the principal effect of the static electron-ion interaction is to enhance the Fermilevel density of states by a factor $(m^*/m)_{e^+}$, then

$$\chi_P \approx \frac{(m^*/m)_{e-i} \left[1 + F_1(r_s)\right]}{1 + (m^*/m)_{e-i} G_0(r_s)} \chi_P^0(r_s) , \qquad (2.5)$$

where F_1 and G_0 are jellium Fermi-liquid parameters, ¹¹ and

$$\chi_P^0(r_s) = 2.589 \times 10^{-6} / r_s \tag{2.6}$$

is the free-electron spin susceptibility. The interelectron spacing r_s is related to the average volume Ω_0 of metal per ion, the average valence z, and the Fermi wave vector k_F :

$$\Omega_0 / z = \frac{4}{3} \pi (r_s a_0)^3 = 3\pi^2 / k_F^3 , \qquad (2.7)$$

where a_0 is the Bohr radius.

In the nonrelativistic one-electron approximation with identical spatial wave functions for spin-up and spin-down electrons, it is easily shown that

$$f(\mathbf{\tilde{r}}) = \langle |\Psi_{\mathbf{\tilde{r}}}(\mathbf{\tilde{r}})|^2 \rangle_{\mathrm{FS}} , \qquad (2.8)$$

where $\Psi_{\vec{k}}$ is a one-electron wave function normalized in unit volume, and the brackets indicate a Fermi-surface average followed by a configuration average. In simple metals, it is now known³ that exchange polarization, relativity, and electron correlation enhance $f(\vec{r})$ by a factor $\Lambda(\vec{r})$ of order unity.

The Knight shift due to hyperfine contact interaction between a nucleus at the origin and the electrons which surround it is

$$K = \frac{8}{3} \pi \chi(0) = \frac{8}{3} \pi \chi_P \left\langle \left| \Psi_{\vec{k}}(0) \right|^2 \right\rangle_{\rm FS} \Lambda .$$
 (2.9)

The quantity $\langle |\Psi_{\vec{k}}(0)|^2 \rangle_{\rm FS}$ is called the contact density.

III. CONTACT DENSITY IN BINARY ALLOY

The system considered here is a macroscopic unit volume of an alloy of metals A and B with concentrations $1 - C_B$ and C_{B_r} respectively, in which the average volume per ion is Ω_0 . There are $N_A = (1 - C_B)/\Omega_0$ ions of type A with coordinates \vec{R}_I^A .

The Knight shift of component A is

$$K_A(C_B) = \frac{8}{3} \pi \chi_P \left\langle \left| \Psi_{\vec{k}}(\vec{\mathbf{R}}_i^A, C_B) \right|^2 \right\rangle_{\text{FS}} \Lambda_A .$$
 (3.1)

An expression for the contact density will now be developed to first order in the electron-ion pseudopotential. If the pseudopotential were strictly zero, then the pseudo-wave-functions would be plane waves $|\vec{k}\rangle$:

$$\langle \mathbf{\tilde{r}} \, | \, \mathbf{\tilde{k}} \rangle = e^{i \mathbf{\tilde{k}} \cdot \mathbf{r}} \,, \tag{3.2}$$

and the true wave functions for the conduction electrons would be orthogonalized plane waves:

$$|\Psi_{\vec{k}}^{1-\text{OPW}}\rangle = [N_{\vec{k}}^{0}(C_{B})]^{-1/2}(1-P)|\vec{k}\rangle,$$
 (3.3)

where $N_{k}^{Q}(C_{B})$ is a normalization factor of order unity and

$$P = \sum_{l,c} |u_{c,l}^{A}\rangle \langle u_{c,l}^{A}| + \sum_{l',c'} |u_{c',l'}^{B}\rangle \langle u_{c',l'}^{B}| \qquad (3.4)$$

is the projection operator onto the ionic core states $[\langle \vec{\mathbf{r}} | u_{c,l}^A \rangle = u_c^A (\vec{\mathbf{r}} - \vec{\mathbf{R}}_l^A)]$. The contact density is then

$$|\Psi_{k_F}^{1-\text{OPW}}(\vec{\mathbf{R}}_l^A, C_B)|^2 = \gamma_A^2(k_F)/N_{k_F}^0(C_B)$$
. (3.5)

If the core-state wave functions of neighboring ions do not overlap, then the "orthogonalization factor"

$$\gamma_{A}(k) = 1 - \sum_{c} u_{c}^{A}(0) \langle u_{c}^{A} | \vec{\mathbf{k}} \rangle$$
$$= 1 - \sum_{n} u_{ns}^{A}(0) \langle u_{ns}^{A} | \vec{\mathbf{k}} \rangle$$
(3.6)

involves only s-like core states on ion A, and the OPW normalization factor becomes

$$N_{k}^{0}(C_{B}) = \langle \vec{\mathbf{k}} | (1-P)^{2} | \vec{\mathbf{k}} \rangle = \langle \vec{\mathbf{k}} | (1-P) | \vec{\mathbf{k}} \rangle$$
$$= 1 - \frac{1}{\Omega_{0}} \left((1-C_{B}) \sum_{c} |\langle \vec{\mathbf{k}} | u_{c}^{A} \rangle |^{2} + C_{B} \sum_{c'} |\langle \vec{\mathbf{k}} | u_{c'}^{B} \rangle |^{2} \right). \quad (3.7)$$

In a solid, a single OPW may be the proper zeroth-order approximation to the conduction-electron wave function, but in a disordered system the Bloch wave vector \vec{k} is no longer a good quantum number, and the proper zeroth-order wave function is a linear combination of OPW's having the same $|\vec{k}|$. However, it can be shown¹² that to first order in the pseudopotential the expectation value of any Hermitian operator averaged over a spherical Fermi surface may be computed by evaluating the principal part of the expression obtained formally from nondegenerate plane-wave perturbation theory. The operator $(1-P)|\vec{R}_t^A\rangle$ $\times \langle \vec{R}_t^A|(1-P)$ which yields the contact density is of course Hermitian.

First-order principal-part plane-wave perturbation theory in the pseudopotential V_{ps} yields a pseudo-wave-function

$$\left| \phi_{\vec{k}} \right\rangle = \left| \vec{k} \right\rangle + \vartheta \sum_{\vec{q}} \left| \vec{k} + \vec{q} \right\rangle \frac{\langle \vec{k} + \vec{q} | V_{ps} | \vec{k} \rangle}{E(\vec{k}) - E(\vec{k} + \vec{q})} , \quad (3.8)$$

where $E(\vec{k}) = \hbar^2 |\vec{k}|^2 / 2m$ and \mathcal{O} indicates the principal value of the sum. The true wave function is obtained by orthogonalizing (3.8) to the core states and normalizing the result:

$$\Psi_{\vec{k}}(\vec{R}_{l}^{A}, C_{B}) = [N_{k}(C_{B})]^{-1/2} \gamma_{A}(k) e^{i\vec{k}\cdot\vec{R}_{l}^{A}}$$
$$\times \left(1 + \mathfrak{O} \sum_{\vec{a}} \frac{\gamma_{A}(\vec{k}+\vec{q})}{\gamma(k)} e^{i\vec{q}\cdot\vec{R}_{l}^{A}} \frac{\langle\vec{k}+\vec{q}|V_{B}|\vec{k}\rangle}{E(\vec{k}) - E(\vec{k}+\vec{q})}\right). \quad (3.9)$$

[A factor $\gamma_A(k)$ has been taken out in front of the first-order correction for convenience.] The normalization factor is $N_k(C_B) = N_k^0(C_B) + \delta N_k(C_B)$, where

$$\delta N_k(C_B) = -2 \operatorname{Re} \mathscr{O} \sum_{\vec{q}} \langle \vec{k} | P | \vec{k} + \vec{q} \rangle \frac{\langle \vec{k} + \vec{q} | V_{ps} | \vec{k} \rangle}{E(\vec{k}) - E(\vec{k} + \vec{q})} .$$
(3.10)

Since V_{ps} and P are superpositions of individual ionic operators, their matrix elements are

$$\langle \vec{\mathbf{k}} + \vec{\mathbf{q}} | V_{ps} | \vec{\mathbf{k}} \rangle = \rho_{\vec{\mathbf{q}}}^{A} \langle \vec{\mathbf{k}} + \vec{\mathbf{q}} | v_{A} | \vec{\mathbf{k}} \rangle + \rho_{\vec{\mathbf{q}}}^{B} \langle \vec{\mathbf{k}} + \vec{\mathbf{q}} | v_{B} | \vec{\mathbf{k}} \rangle ,$$

$$(3.11)$$

$$\langle \vec{\mathbf{k}} | P | \vec{\mathbf{k}} + \vec{\mathbf{q}} \rangle = \rho_{-\vec{\mathbf{q}}}^{A} \langle \vec{\mathbf{k}} | p_{A} | \vec{\mathbf{k}} + \vec{\mathbf{q}} \rangle + \rho_{-\vec{\mathbf{q}}}^{B} \langle \vec{\mathbf{k}} | p_{B} | \vec{\mathbf{k}} + \vec{\mathbf{q}} \rangle ,$$

where v_A and p_A are, respectively, the pseudopotential and projection operator of a screened ion of type A at the origin, and

$$\rho_{\vec{q}}^{A} = \sum_{l} e^{-i\vec{q} \cdot \vec{R}_{l}^{A}} .$$
(3.12)

The expression (3.9) must now be squared, linearized, and averaged to yield the contact density:

$$\langle |\Psi_{\vec{k}}(\vec{R}_{l}^{A}, C_{B})|^{2} \rangle_{\text{FS}} = |\Psi_{k_{F}}^{1-\text{OPW}}(\vec{R}_{l}^{A}, C_{B})|^{2}$$

$$\times \frac{1 + \sum_{A} (k_{F}) + \Delta_{AB} (k_{F}, C_{B})}{1 + \delta N_{k_{F}} (C_{B}) / N_{k_{F}}^{0} (C_{B})} , \quad (3.13)$$
where

where

$$\Sigma_{A}(k_{F}) = 2 \int \frac{d\hat{k}_{F}}{4\pi} \otimes \sum_{\vec{q}} \frac{\gamma_{A}(\vec{k}_{F} + \vec{q})}{\gamma_{A}(k_{F})} \frac{\langle \vec{k}_{F} + \vec{q} \mid v_{A} \mid \vec{k}_{F} \rangle}{E(\vec{k}_{F}) - E(\vec{k}_{F} + \vec{q})} ,$$
(3.14)

$$\Delta_{AB}(k_{F}, C_{B}) = 2 \int \frac{d\hat{k}_{F}}{4\pi} \, \mathfrak{G} \sum_{\vec{q}} \frac{\gamma_{A}(\vec{k}_{F} + \vec{q})}{\gamma_{A}(k_{F})} \left[\left[S_{AA}(\vec{q}) - 1 \right] \langle \vec{k}_{F} + \vec{q} \mid v_{A} \mid \vec{k}_{F} \rangle + \left(\frac{C_{B}}{1 - C_{B}} \right)^{1/2} S_{AB}(\vec{q}) \, \langle \vec{k}_{F} + \vec{q} \mid v_{B} \mid \vec{k}_{F} \rangle \right] \left[E(\vec{k}_{F}) - E(\vec{k}_{F} + \vec{q}) \right]^{-1}, \quad (3.15)$$

$$\delta N_{k_{F}}(C_{B}) = -2 \int \frac{d\hat{k}_{F}}{4\pi} \frac{1}{\Omega_{0}} \, \mathfrak{G} \sum_{\vec{r}} \left\{ (1 - C_{B}) \, \langle \vec{k}_{F} \mid p_{A} \mid \vec{k}_{F} + \vec{q} \rangle \right\}$$

$$\times \left[S_{AA}(\vec{q}) \langle \vec{k}_{F} + \vec{q} | v_{A} | \vec{k}_{F} \rangle + \left(\frac{C_{B}}{1 - C_{B}}\right)^{1/2} S_{AB}(\vec{q}) \langle \vec{k}_{F} + \vec{q} | v_{B} | \vec{k}_{F} \rangle \right] \\ + C_{B} \langle \vec{k}_{F} | p_{B} | \vec{k}_{F} + \vec{q} \rangle \left[S_{BB}(\vec{q}) \langle \vec{k}_{F} + \vec{q} | v_{B} | \vec{k}_{F} \rangle + \left(\frac{1 - C_{B}}{C_{B}}\right)^{1/2} S_{AB}(\vec{q}) \langle \vec{k}_{F} + \vec{q} | v_{A} | \vec{k}_{F} \rangle \right] \right] \left[E(\vec{k}_{F}) - E(\vec{k}_{F} + \vec{q})]^{-1} \cdot (3.16)$$

These expressions involve the partial structure factors

$$S_{AA}(\mathbf{\bar{q}}) = N_A^{-1} \left\langle \left\langle \rho_{\mathbf{q}}^A \rho_{-\mathbf{q}}^A \right\rangle \right\rangle , \qquad (3.17)$$

$$S_{AB}(\vec{\mathbf{q}}) = (N_A N_B)^{-1/2} \langle \langle \rho^B_{\vec{\mathbf{q}}} \rho^A_{-\vec{\mathbf{q}}} \rangle \rangle = S_{BA}(\vec{\mathbf{q}}) , \qquad (3.18)$$

in which double brackets indicate a configuration average.

For discussion purposes, the first-order correction to the contact density has been separated into two pieces. The "self-term" $\Sigma_A(k_F)$ represents the influence of the pseudopotential of the single ion at \vec{R}_i^A on its own Knight shift. Physically, $\gamma_A^2(k_F)[1+\Sigma_A(k_F)]$ is the contact density for a single screened ion A immersed in an otherwise uniform electron gas. The "distinct term" $\Delta_{AB}(k_F)$, C_B) is a fractional correction due to scattering

from the other ions in the metal. The Faber scattering theory⁵ (as generalized by Halder¹³) is obtained in essence from (3.15) upon the substitution $\gamma_A(\vec{k}_F + \vec{q}) - \gamma_A(k_F)$. Retention of $\gamma_A(\vec{k}_F + \vec{q})$ in (3.15) corresponds to a sort of "multiple scattering": The scattered waves arriving from the other ions are somewhat distorted by the single ion of interest. [Faber actually employs a damped Green's function which introduces a relaxation time into the energy denominator of (3.15). Calculations indicate that this relaxation time is too long to be important in the alkali metals.]

Expressions (3.14)-(3.16) simplify under certain approximations. In the remainder of this paper, the small normalization correction is approximated by

$$\delta N_{k_F}(C_B) = (1/\Omega_0) \left[(1 - C_B) \Omega_0^A \delta N^A + C_B \Omega_0^B \delta N^B \right],$$
(3.19)

where δN^A is the normalization correction calculated for pure metal *A*; more significantly, the pseudopotential is assumed to be effectively local:

$$\langle \vec{\mathbf{k}}_{F} + \vec{\mathbf{q}} | v_{A} | \vec{\mathbf{k}}_{F} \rangle = v_{A}(q) = \int d^{3}r e^{-i\vec{\mathbf{q}} \cdot \vec{\mathbf{r}}} v_{A}(r) .$$
(3.20)

The latter approximation leads to simple expressions for (3.14)-(3.16) in terms of the dimensionless angular integrals

$$\Gamma_{A}(k_{F}, q) = \mathfrak{O} \int \frac{d\hat{q}}{2\pi} \frac{\gamma_{A}(\vec{k}_{F} + \vec{q})}{\gamma_{A}(k_{F})} \frac{E(\vec{q})}{E(\vec{k}_{F}) - E(\vec{k}_{F} + \vec{q})},$$

$$(3.21)$$

$$\Pi_{A}(k_{F}, q) = \mathfrak{O} \int \frac{d\hat{q}}{2\pi} \frac{\langle \vec{k}_{F} | p_{A} | \vec{k}_{F} + \vec{q} \rangle}{\langle \vec{k}_{F} | p_{A} | \vec{k}_{F} + \vec{q} \rangle}$$

$$A^{(k_F, q) = \Phi} \int \frac{1}{2\pi} \frac{F + A - F}{\Omega_0} \times \frac{E(\vec{q})}{E(\vec{k}_F) - E(\vec{k}_F + \vec{q})} \quad . \quad (3.22)$$

These integrals are evaluated analytically in Appendix A for Slater-like analytic core wave functions. Finally, it is convenient for discussion purposes to separate (3.21) into two factors:

$$\Gamma_A(k_F, q) = \left(\frac{q}{2k_F} \ln \left|\frac{1-q/2k_F}{1+q/2k_F}\right|\right) f_A(k_F, q) .$$
(3.23)

The factor in large round parentheses is the value that (3.21) would take under the substitution $\gamma_A(\vec{k}_F + \vec{q}) \rightarrow \gamma_A(k_F)$; the departure of the factor $f_A(k_F, q)$ from unity thus measures the influence of explicit orthogonalization on the first-order corrections to the contact density.

Henceforth it will be convenient to work with the dimensionless "form factor"

$$\tilde{v}_{A}(q) = \frac{z}{\frac{2}{3}E(k_{F})\Omega_{0}} v_{A}(q) = \frac{mk_{F}}{\pi^{2}\hbar^{2}} v_{A}(q) , \qquad (3.24)$$

which for Lindhard-screened pseudopotential tends to -z in the limit q - 0.

IV. LIQUID ALKALI METALS

In liquid metals the sums in Sec. III may be converted to integral form through the transformation

$$\mathscr{O}\sum_{\vec{q}} - \frac{1}{(2\pi)^3} \mathscr{O}\int_0^\infty dq \, q^2 \int d\hat{q} \, , \qquad (4.1)$$

with the results

$$\Sigma_A(k_F) = 2\mathscr{O} \int_0^\infty d\left(\frac{q}{2k_F}\right) \Gamma_A(k_F, q) \widetilde{v}_A(q) , \qquad (4.2)$$

$$\Delta_{AB}(k_F, C_B) = 2 \mathcal{P} \int_0^\infty d\left(\frac{q}{2k_F}\right) \Gamma_A(k_F, q) \\ \times \left[\left[S_{AA}(q) - 1 \right] \tilde{v}_A(q) + \left(\frac{C_B}{1 - C_B}\right)^{1/2} S_{AB}(q) \tilde{v}_B(q) \right],$$

$$(4.3)$$

$$\delta N^{A} = -2 \mathscr{O} \int_{0}^{\infty} d\left(\frac{q}{2k_{F}^{A}}\right) \Pi_{A}(k_{F}^{A}, q) S_{AA}(q) \tilde{v}_{A}(q) , \quad (4.4)$$

where (4.4) is evaluated only once for each pure metal A.

The integrals (4.2)-(4.4) have been evaluated numerically for the liquid alkalis Na, K, Rb and their binary alloys, and combined with Eqs. (3, 13)and (3.19) to yield the contact densities. Lithium was excluded because of the strength and nonlocality of its pseudopotential, as well as the absence of measurements for the liquid lithium-alkali alloys. Cesium was excluded because of the lack of suitable analytic core wave functions; however, it was possible to calculate the contact density at nucleus A in A-Cs alloys by assuming that the Cs contribution to the normalization factor is $-C_{Cs}(130a_0^3/\Omega_0)$, in keeping with the trend in the other alkalis. For Na^* and K^* the core wave functions of Bagus¹⁴ were used, and for Rb⁺ those of Watson and Freeman¹⁵ (see Figs. 1 and 2).

The pseudopotentials employed here were those of Ashcroft,¹⁶ in which the unscreened pseudopotential equals the Coulomb potential for $r > R_c$ and equals zero for $r < R_c$; Lindhard screening is assumed (Fig. 3). The model radius R_c is determined from the measured [110] band gaps (occurring at $q/2k_F = 1.14$) in pure solid Na, K, and Rb, and from the observed resistivity in Cs. These potentials have a claimed reliability for $q/2k_F \leq 2$.

It is apparent from Figs. 2 and 4 that the region just above $q/2k_F \approx 1$ is weighted very heavily in (4.2) and (4.3); fortunately, this is just the region in which the pseudopotential is known empirically in the pure metals. In practice, one finds-by examining the partial sums of (4.2) and (4.3)-that Δ_{AB} attains a value within 5% of its final value at $q/2k_F \approx 1.5$ and has effectively converged at $q/2k_F$ \approx 2, while 1 + Σ_A attains a value within 5% of its final value at $q/2k_F \approx 2$ and then undergoes small oscillations up to $q/2k_F \approx 8$. These small oscillations result from the discontinuity in the pseudopotential and are not physically meaningful; accordingly, the Ashcroft form factor has been set equal to zero beyond its second node, which occurs at $q/2k_{\rm F}\approx 3$ in the pure metals. The explicit orthogonalization acts as an important convergence factor; indeed, if the full form factor is employed and $f_A(k_F, q)$ is replaced by unity, then $1 + \Sigma_A$ converges slowly to unrealistic values. The present approach succeeds because of the strong orthogonality constraint on the wave function near the nucleus.

The largest individual contribution to the change in the Knight shift upon alloying in the alkali metals is found to be the change in the self-term $\Sigma_A(k_F)$ (see Table I), although other contributions are not negligible. The behavior of $\Sigma_A(k_F)$ can be understood from Fig. 3. Consider the alloy Na-Cs;



FIG. 1. Orthogonalization functions $\gamma_A(q)$ [Eq. (3.6)], where q is measured in units of k_F appropriate to the pure liquid metals.

as the Cs concentration increases and k_F decreases, the node of the Na pseudopotential is displaced toward larger values of $q/2k_F$, and the pseudopotential in the important region just above $2k_F$ becomes more attractive—consequently the

contact density increases. At the same time, the maximum of the repulsive part of the form factor, Eq. (3.24), is reduced, and changes also occur in the dependence of $f_A(k_F, q)$ upon $q/2k_F$ (Fig. 5).

The partial structure factors employed in the calculation were those of Ashcroft and Langreth,¹⁷ based on the solution of the Percus-Yevick equation for a binary fluid of hard spheres of two different diameters. The calculated contact densities varied at most by about 3% as the packing fraction and the ratio of hard-sphere diameters were varied over a permissible range; the results presented here are for a packing fraction $\eta = 0.45$ and a hard-sphere ratio of unity. The latter condition defines the "modified substitutional model," in which

$$S_{AA}(q) = 1 + (1 - C_B) [S(\sigma, q) - 1], \qquad (4.5)$$

$$S_{AB}(q) = [C_B(1 - C_B)]^{1/2} [S(\sigma, q) - 1], \qquad (4.6)$$

and the hard-sphere diameter σ varies with the atomic volume Ω_0 . A linear variation of Ω_0 with concentration has been assumed.

Some of the calculated contact densities are presented in Table I. Conventionally, results are expressed in terms of the quantity

$$P_F^d = \langle |\Psi_{\vec{k}}(\vec{R}_l)|^2 \rangle_{\rm FS} a_0^3 / \Omega_0 , \qquad (4.7)$$

 TABLE I. Intermediate quantities and results from the calculation of contact densities in liquid binary alkali alloys, with

 Pauli-susceptibility enhancements inferred from alloy Knight shifts.

A	B	rs	CB	Ω_0/a_0^3	$\gamma_A(k_F)$	N^0_{k}	$(P_F^d)^{1-\mathrm{OPW}}$	$(1 + \delta N_k / N_k^0)^{-1}$	$1 + \Sigma_A$	Δ_{AB}	P_F^d	Λ_A	χ_P/χ_P^0
Na	Na	4.045	0	277.1	11.82	0.928	0.544	0,965	0.989	-0.289	0.368	1.228	1.730
К	K	5.018	0	529.1	-19.35	0.864	0.820	0.934	0.932	-0.285	0.495	1.485	1.573
Rb	Rb	5.371	0	649.1	25.35	0.832	1.192	0.951	1.290	-0.239	1.190	1.340	1.582
Na	К	4.362	0.280	347.7	12.03	0.900	0.462	0.952	1.140	-0.318	0.362		1.636
		4.887	0.840	488.8	12.30	0.870	0.356	0.937	1.414	-0.368	0.349		1.573
Na	Rb	4.695	0.420	433.4	12.21	0.866	0.398	0.947	1.311	-0.341	0.368		1.561
		5.044	0.700	537.5	12.37	0.846	0.336	0.953	1.500	-0.368	0.363		1.536
		5.351	0.980	641.7	12.48	0.833	0.292	0.951	1.673	-0.391	0.355		1.544
Na	Cs	4.242	0.080	319.7	11.96	0.910	0.492	0.971	1.081	-0.305	0.371		1.671
		5.373	0.700	649.5	12.48	0.851	0.282	0.995	1.685	-0.378	0.366		1.580
ĸ	Na	4 485	0 600	377 9	-18 58	0 891	1 026	0.948	0.753	-0 215	0 523		1 565
	Ila	4.937	0.100	503.9	-19.25	0.867	0.848	0.936	0.902	-0.274	0.498		1.575
к	Rh	5.055	0.100	541.1	-19.40	0.860	0.808	0.936	0.946	-0.288	0.498		1.574
	100	5.291	0.760	620.3	-19.67	0.838	0,743	0.948	1.039	-0.303	0.518		1.559
к	Cs	5.122	0.120	562.7	-19,48	0.860	0.784	0.944	0.972	-0.293	0.502		1.573
		5.644	0.800	753.1	-20.01	0.844	0.630	0.990	1.189	-0.322	0.533		1.603
ու	NTo	4 501	0 500	440 0	00.00	0 004	1 500	0.050	1 005	0 140	1 010		1 500
пo	INA	4.741	0.040	440.0	23.92	0.004	1.010	0.950	1.000	-0.149	1.310		1.573
		5.330	0.040	634.2	25.27	0.833	1.210	0.951	1.274	-0.233	1.196		1.583
Rb	К	5.092	0.800	553.1	24.80	0.856	1.300	0.938	1.186	-0.214	1.184		1.559
		5.351	0.060	641.9	25.31	0.833	1.198	0.950	1,282	-0.237	1.189		1.582
Rb	Cs	5.406	0.080	661.9	25.41	0.833	1.171	0.956	1.303	-0.242	1,188		1.592
		5.750	0.920	796.3	25.99	0.839	1.011	0.997	1.443	-0.267	1.186		1.690



FIG. 2. Functions $f(k_F, q)$ [Eq. (3.23)] appropriate to Na, K, and Rb. There is a very weak singularity at $q = 2k_F$.

which corresponds to wave-function normalization in the Wigner-Seitz cell. The values for P_F^d in Table I are in excellent agreement with the recent real-potential calculations by Moore and Vosko² for solid Na (0.364) and K (0.483), and by Mahanti, Tterlikkis, and Das³ for solid Rb (1.137); however, this excellent agreement must be regarded as fortuitous to some extent.

It should also be noted that P_F^d varies by 10% or less upon alloying, although the average atomic volume Ω_0 varies strongly (by more than 100% in

Na-Cs). This is a rather surprising result, for the constancy of P_F^d can be characterized as tightbinding behavior. This behavior of the contact density appears to be a mere numerical consequence of the pseudopotential calculation, without a simple interpretation.

The Knight-shift measurements in binary alkali alloys, including the empirical relation¹⁸

$$\frac{1}{K_A(C_B)} \left. \frac{dK_A}{dC_B} \right|_{C_B=1} \approx \frac{1}{K_B(C_B)} \left. \frac{dK_B}{dC_B} \right|_{C_B=1}, \quad (4.8)$$



FIG. 3. Ashcroft form factor [Eq. (3.24)] for Na at electron densities corresponding to Na, K, and Cs.

as well as the Knight-shift measurements in ternary alkali alloys,¹⁹ can be simply interpreted if P_F^d for each alkali varies in proportion to some function of k_F which is the same for all alkalis. Kaeck²⁰ has extracted the Pauli susceptibilities from his measured binary-alloy Knight shifts upon the assumption that this function is constant, i.e., that P_F^d for a given nucleus A remains constant upon alloying; this assumption is supported by the present calculation.

The Pauli susceptibilities have been extracted from Eq. (3.1) by combining measured alloy Knight shifts with calculated contact densities. The Knight shift varies linearly with concentration in the observed concentration range for the alkali alloys. The values of $[1/K_A(0)](dK_A/dC_B)$ were taken from Ref. 18; for A = Na, B = Cs, the value $[1/K_A(0)](dK_A/dC_B) = 0.87$ was read from the data in Ref. 20.

No attempt has been made here to calculate the

indirect contributions to the Knight shift subsumed under Λ_A . Instead, it has been assumed that Λ_A depends only upon the nature of ion A, and not upon the details of the metallic environment in which it is found; this seems as plausible as the more conventional assumption² that Λ_A is the same for the free atom as for that atom in the pure metallic state. The Schumacher-Vehse²¹ direct measurement of the Pauli susceptibility for pure Na (χ_P/χ_P^0) = 1.73 ± 0.08) was used as a calibration point to determine $\Lambda_A = 1.23$ for Na. Then the Knight-shift measurements for Na in Na-K were used to determine a susceptibility for pure K, which led to a value of Λ_A for K; this process of "alloy extrapolation" was repeated to obtain Λ_A for Rb. The values for Λ_A found in this way (Table I) may be compared with the theoretical results of Mahanti, Tterlikkis, and Das³ based upon core-polarization and relativistic effects: Na, 1.26; K, 1.27; Rb 1.33. The agreement is good except in K; how-







FIG. 5. Orthogonalization function $f(k_F, q)$ for Na at electron densities appropriate to Na and K.

ever, the values of Λ_A calculated here must surely contain some of the errors in the calculated contact densities. (A value $\Lambda_A = 1.53$ for Cs may be determined from the susceptibility of Cs deduced here, the observed Knight shift, and the theoretical value of P_F^d from Ref. 3. This result compares well with the value $\Lambda_A = 1.54$ expected³ from core polarization and relativity.)

The deduced enhancement of the Pauli susceptibility is presented as a function of r_s in Fig. 6.

The calculation implies (to within a few percent) the same Pauli susceptibility for a particular alloy as deduced separately from the Knight shifts of the two alloy components, as it must if the calculation is to be believed. Moreover, the deduced susceptibilities are found to define a nearly unique function of r_s . This is just what would be expected from Eq. (2.5) if $(m^*/m)_{e-i}$ is close to unity in all the alkali metals from Na to Cs, as suggested by the pseudopotential density-of-states calculations



of Timbie and White²² and Weaire.²³ The deduced susceptibility enhancements χ_P/χ_P^0 in Fig. 5 are in rough agreement with the spin-wave measurements of Schultz and Dunifer²⁴; Na, 1.57±0.08; K, 1.68±0.10; Rb, 1.71±0.16; Cs, 2.05±0.2. However, the 10% decrease in the deduced enhancements from Na to K is puzzling in view of the slight increase in the measured enhancements and in the theoretical enhancements for an interacting electron gas.²⁵

It is revealing to explore the sensitivity of the calculation to the various input parameters. The insensitivity to liquid structure has already been discussed. The calculation is similarly insensitive to the dielectric function which screens the pseudo-potential: The inclusion of the Sham-Hubbard exchange²⁶ in the Lindhard dielectric function increases the magnitude of the pseudopotential by a q-dependent factor of the order of 1.10 to 1.05 in the range $1.0 < q/2k_F < 1.25$, but changes the calculated contact densities only about 3%.

Often it is found that the magnitude of the calculated contact density is sensitive to the input parameters while its fractional variation upon alloying is not. For example, the simple Slaterrule core wave functions yield values of $\gamma_A^2(k_F)$ differing by as much as 20% from those calculated from the more sophisticated Bagus¹⁴ functions, but do not significantly affect the fractional variation in contact density. Similarly, a 5% reduction in the Ashcroft core radius R_c was found to increase P_F^d by about 20% in all the alkalis (mainly through the self-term Σ_A), but the ratios $P_F^d(C_B)/P_F^d(0)$ were unaffected to within about 2%. The calculations were repeated using the two-parameter local Cohen pseudopotential²⁷ derived from spectroscopic data; again, the magnitudes P_F^d differed by as much as 20% from the values in Table I, while the ratios $P_F^d(C_R)/P_F^d(0)$ were unaffected.

A possibly serious source of error is the neglect of any energy dependence in the pseudopotential. Evidence from the thermopower¹⁶ indicates that this dependence is probably small, at least in Na and K. However, it should be evident from the preceding paragraph that a variation of even 5% in R_c upon alloying could seriously affect the deduced Pauli susceptibilities.

Finally, calculations have been attempted for the temperature dependence of the Knight shift in pure liquid alkali metals near the melting point. This temperature dependence has been assumed to arise through the temperature dependence of the interelectron spacing r_s (which is known from the observed thermal expansion)²⁸ and of the hardspheres packing fraction (which is found from compressibility data for Na and K, and from neutron-diffraction data for Rb).²⁹ The values of $(d \ln K/dT) \times 10^4$ calculated in this way are as follows: Na, 2.6; K, 3.8; Rb, 2.7. The corresponding values calculated neglecting the temperature dependence of the packing fraction are as follows: Na, 1.4; K, 0.9; Rb, 1.2. These values bracket the experimental values, which have been estimated from the data of Ref. 30: Na, 1.9; Rb, 1.5. Unlike the change upon alloying of the Knight shift, the temperature dependence is small but highly sensitive to the details of liquid structure, as Ritter and Gardner⁹ have observed.

V. SOLID ALKALI METALS

The structure factor for a perfect Bravais lattice is

$$S(\mathbf{\bar{q}}) = N \sum_{\mathbf{\bar{d}}} \delta_{\mathbf{\bar{d}},\mathbf{\bar{d}}} , \qquad (5.1)$$

where the sum is over all reciprocal-lattice vectors \vec{G} . Consequently, Eqs. (3.14) and (3.15) become

$$\Sigma_A + \Delta_{AA} = \frac{1}{6z} \sum_{G \neq 0} M(G) \left(\frac{2k_F}{G}\right)^2 \Gamma_A(k_F, G) \tilde{v}_A(G) ,$$
(5.2)

where the sum is over shells of reciprocal-lattice vectors and M(G) is the number of reciprocal-lattice vectors of length G. The function Γ_A [Eq. (3.21)] appears again as in Sec. IV, this time because of the average over the assumed spherical Fermi surface. Table II exhibits the convergence of the partial sum of $1 + \Sigma_A + \Delta_{AA}$ as a function of the largest included reciprocal-lattice vector; the dominance of the first few shells is evident.

A more realistic model for a solid near the melting point is the Einstein model³¹ of independent atomic oscillators. It is easy to show that the structure factor for this model is

$$S(\vec{\mathbf{q}}) = 1 + \left| \left\langle \left\langle e^{i \vec{\mathbf{q}} \cdot \vec{\mathbf{u}}} \right\rangle \right\rangle \right|^2 \left(-1 + N \sum_{\vec{\mathbf{q}}} \delta_{\vec{\mathbf{q}},\vec{\mathbf{q}}} \right) , \qquad (5.3)$$

where $\mathbf{\tilde{u}}$ is the displacement of an ion from its equilibrium position. The configuration average $\langle \langle e^{i\mathbf{\tilde{q}}\cdot\mathbf{\tilde{u}}} \rangle \rangle$ can be expressed in terms of the Einstein

TABLE II. Convergence of the partial sum of $1 + \Sigma_A$ + Δ_{AA} as a function of the largest included reciprocallattice vector $G/2k_F$ in perfect bcc solid alkalis [see Eq. (5.2)].

		$1 + \Sigma + \Delta A$					
$G/2k_F$	M(G)	Na $(P_F^d = 0.331)$	- A - AA K (0.432)	Rb (1.099)			
1.1398	12	0.659	0.540	0.751			
1.6120	6	0.607	0.497	0.746			
1.9743	24	0.587	0.516	0.854			
2.2797	12	0.596	0.532	0.897			
2.5488	24	0.612	0.549	0.945			
2.7921	8	0.614	0.550	0.952			
3.0158	48	0.614	0.550	0.957			

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temperature, but this temperature is not known empirically. It is necessary to appeal to the Debye approximation, in which at high temperatures³¹

$$\langle \langle e^{i\vec{\mathfrak{q}}\cdot\vec{\mathfrak{u}}} \rangle \rangle = \exp\left(-\frac{3}{2} \frac{\hbar^2 T q^2}{M k_B \Theta_D^2}\right)$$
 (5.4)

Equations (5.3) and (5.4) have been used along with Debye temperatures Θ_D determined from the specific heat³² to calculate contact densities for the solid alkali metals at the melting point. The values of P_F^d calculated in this way are comparable to those found in the liquid state, and hence about 10% larger than those calculated for the "perfect solids"; the explanation for this difference is that vibrations tend to wash out part of the distinct term Δ_{AA} , which is negative.

[An expression for $S(\vec{q})$ may be derived for a harmonic solid.³³ The exact expression, which is rather difficult to evaluate, tends to unity at large q, as do the Einstein solid and liquid structure factors. This harmonic expression is often estimated by neglecting "multiple phonon effects,"^{9,33} but the resulting approximation tends to zero at large q— this erroneous limiting behavior may destroy some of the large-q contribution to the self-term in the contact density, and lead to spurious contributions to the calculated change in contact density upon melting. This may be the reason why Ritter and Gardner⁹ overestimate the change in the Knight shift of Na upon melting by a factor of 3; however, we have not investigated this question numerically.]

Finally, the melting change of the Knight shift has been calculated under the assumption

$$\frac{K^{1iq}}{K^{sol}} = \frac{(m^*_{e-i})^{1iq}}{(m^*_{e-i})^{sol}} \frac{\chi_P(r_s^{1iq})}{\chi_P(r_s^{sol})} \frac{(P_F^d\Omega_0)^{1iq}}{(P_F^d\Omega_0)^{sol}} , \qquad (5.5)$$

where the superscripts refer to the liquid and solid metals at the melting point, $\chi_P(r_s)$ is the function presented in Fig. 5, and the electron-ion effective masses m^*_{e-i} are those calculated by Timbie and White.²² The calculated values of K^{11q}/K^{sol} are as follows: Na, 1.021; K, 1.023; Rb, 1.025, which may be compared with experimental values read from the data of Ref. 29: Na, 1.022; K, 1.02; Rb, 1.015. The calculated value for Rb can be fitted to experiment by a 7% decrease in Θ_D . The largest part of the change in the Knight shift upon melting comes from the change in the volume Ω_0 ,³⁴ although changes in m^*_{e-i} and P^d_F are individually of the order of 0.5%.

VI. CONCLUSION AND EXTENSION TO OTHER METALS

An expression for the contact density in a metal with a spherical Fermi surface has been developed to first order in the pseudopotential. (The extension to a solid metal with a nonspherical Fermi surface is trivial.) This expression may be applied to solid and liquid metals, and to alloys at all concentrations, even when k_F varies strongly upon alloying.

Calculations for the alkali metals have been carried out using simple analytic expressions for the core wave functions, pseudopotentials, and structure factors. Under the assumption of a local pseudopotential, it is found that the contact density samples the Fourier transform of the pseudopotential primarily just above $2k_F$, where it is known empirically in the pure metals; as k_F varies upon alloying, different regions of the pseudopotential are sampled and important changes occur in the contact density, especially through the self-term and the one-OPW prefactor. It is to be expected that core orthogonalization will hasten convergence in momentum space, and that large changes in k_F will control changes in the contact density, even in metals which cannot be described by local pseudopotentials. If necessary, the angular integrations in Eqs. (3.14) and (3.15) can be performed numerically for such metals in the liquid state.

Reasonable values are produced for the contact density in each pure alkali metal and in the binary liquid alloys. The Pauli susceptibilities are deduced from the observed alloy Knight shifts; the enhancement of the Pauli susceptibility over its free-electron value appears to be a weak but almost unique function of the interelectron spacing r_s in the range $4.0 < r_s < 5.8$. Confidence in the deduced Pauli susceptibilities is strengthened by the insensitivity of the fractional variation in contact density upon alloying to the choice of pseudopotentials, structure factors, and core-state wave functions. The calculation is able to account in part for the observed temperature dependence and change upon melting of the Knight shift.

Recently, Host and Styles³⁵ have applied our formulation to their measurements of the Knight shifts in liquid alloys of the noble metals with In and Sn. Their calculations employ a local energy-independent pseudopotential, and thereby fail for the noble metals, as expected. On the other hand, they calculate reasonable values for the contact densities of pure In and Sn. Their calculated fractional changes in the contact densities of In and Sn as a function of noble-metal concentration are qualitatively similar to, but somewhat larger than, the measured (and highly nonlinear) changes in the Knight shifts of these metals.

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APPENDIX A: ORTHOGONALIZATION AND NORMALIZATION INTEGRALS

The Slater-like analytic core wave functions take the form

$$u_{nlm}(\hat{\mathbf{r}}) = (4\pi)^{1/2} \chi_{nl}(\mathbf{r}) Y_{lm}(\hat{\mathbf{r}}) , \qquad (A1)$$

$$\chi_{nI}(r) = \sum_{p} a_{nI}(N_{p}, \zeta_{p}) (\zeta_{p}r)^{N_{p}} e^{-\xi_{p}r} , \qquad (A2)$$

where the N_p 's are integers, $N_p \ge l$.

Overlap amplitudes. It is easy to show that

$$\langle u_{nIm} | \vec{k} \rangle = i^{l} (4\pi)^{1/2} Y_{Im}^{*}(\hat{k}) b_{nI}(k) ,$$
 (A3)

where

$$b_{nl}(k) = \sum_{p} a_{nl}(N_{p}, \xi_{p}) B_{l}(N_{p}, \xi_{p}, k) , \qquad (A4)$$

and

$$B_{l}(N, \zeta, k) = \int_{0}^{\infty} dr \, 4\pi \, r^{2} (\zeta r)^{N} e^{-\xi r} \, j_{l}(kr) \tag{A5}$$

is evaluated at the end of this appendix. Orthogonalization functions. From the defini-

tion (3.6), the orthogonalization factor is

$$\gamma(k) = 1 - \sum_{n} \chi_{n0}(0) b_{n0}(k) .$$
 (A6)

Next consider the angular integral (3.21). By the change of variable $y = -\hat{k} \cdot \hat{q}$, one finds

$$\Gamma(k, q) = \frac{1}{\gamma(k)} \left(\frac{q}{2k} \ln \left| \frac{1 - q/2k}{1 + q/2k} \right| -\sum_{n} \chi_{n0}(0) c_{n0}(k, q) \right) , \quad (A7)$$

where

$$c_{nl}(k, q) = \sum_{p} a_{nl}(N_{p}, \zeta_{p}) C_{l}(N_{p}, \zeta_{p}, k, q) , \qquad (A8)$$

and

$$C_{l}(N, \zeta, k, q) = \mathcal{O} \int_{-1}^{1} dy P_{l} \left(\frac{k - qy}{(k^{2} + q^{2} - 2kqy)^{1/2}} \right)$$
$$\times \frac{B_{l}(N, \zeta, (k^{2} + q^{2} - 2kqy)^{1/2})}{(2k/q)y - 1} \quad (A9)$$

is evaluated at the end of this appendix.

Normalization functions. The one-OPW normalization factor (3.7) involves only

$$\frac{1}{\Omega_0} \sum_{nlm} \left| \left\langle u_{nlm} \right| \vec{\mathbf{k}} \right\rangle \right|^2 = \frac{1}{\Omega_0} \sum_{nl} (2l+1) b_{nl}^2(k) . \quad (A10)$$

The first-order correction to the normalization (4, 4) involves angular integrals of the type (3.22):

$$\Pi(k, q) = \frac{1}{\Omega_0} \sum_{nl} (2l+1) b_{nl}(k) c_{nl}(k, q) .$$
 (A11)

Evaluation of $B_l(N, \xi, k)$, Eq. (A5). First consider l=0:

$$B_{0}(N, \zeta, k) = \frac{4\pi}{\zeta^{3}} p^{N+3} \int_{0}^{\infty} dz \, z^{N+1} e^{-pz} \sin z \big|_{p=\zeta/k}$$

$$=\frac{4\pi}{\zeta^{3}}p^{N+3}(-1)^{N+1}\frac{\partial^{N+1}}{\partial p^{N+1}}\frac{1}{1+p^{2}}\Big|_{p=\zeta/k}$$
(A12)

The identity $(d/dx) j_0(x) = -j_1(x)$ implies that

$$B_{1}(N, \xi, k) = (\xi/k) [(N+2)B_{0}(N-1, \xi, k) - B_{0}(N, \xi, k)].$$
(A13)

Finally, the identity $j_{l+1}(x) = [(2l+1)/x]j_l(x) - j_{l-1}(x)$ implies the recursion relation

$$B_{l+1}(N, \,\xi, \,k) = (2l+1) \left(\,\xi/k \right) B_l(N-1, \,\xi, \,k) \\ - B_{l-1}(N, \,\xi, \,k) \ . \tag{A14}$$

Equations (A12)-(A14) quickly generate the B_i 's, which are simple algebraic functions.

Evaluation of $C_1(N, \zeta, k, q)$, Eq. (A9). By the method of partial fractions, one may write $C_1(N, \zeta, k, q)$ as a sum of integrals of the type

$$A_{m}(\zeta, k, q) = \mathcal{O} \int_{-1}^{1} dy \left[\left(1 + \frac{k^{2} + q^{2} - 2kqy}{\zeta^{2}} \right)^{m} \times \left(\frac{2k}{q} y - 1 \right) \right]^{-1} .$$
 (A15)

These functions A_m are generated by a simple recursion relation:

$$A_{m} = \left(1 + \frac{k^{2}}{\zeta^{2}}\right)^{-1} \times \left[\frac{1}{m-1} \frac{q}{2k} \left(1 + \frac{(k-qy)^{2}}{\zeta^{2}}\right)^{-m+1} \Big|_{-1}^{1} + A_{m-1}\right],$$
(A16)

$$A_{1} = \left(1 + \frac{k^{2}}{\zeta^{2}}\right)^{-1} \frac{q}{2k} \ln \left| \frac{(1 - q/2k) \left[1 + (k+q)^{2}/\zeta^{2}\right]}{(1 + q/2k) \left[1 + (k-q)^{2}/\zeta^{2}\right]} \right|$$
(A17)

APPENDIX B: EFFECTIVE MASSES OF ALKALI METALS; KORRINGA RELATION

The results of this paper indicate that the Pauli susceptibility depends primarily upon r_s in the binary alkali alloys, and not upon the identity of the two alloy components. This kind of behavior is predicted by Eq. (2.5) provided that $(m^*/m)_{e^{-i}}$ is close to unity in all the alkali metals (except possibly Li).

The effective mass $(m^*/m)_{e^{-i}}$ depends upon the gradient of the single-electron energy at the Fermi surface with respect to \vec{k} ; this energy may be evaluated to second order in the pseudopotential. Weaire²³ has evaluated the contribution from the first-order term using the nonlocal Heine-Abaren-kov potential. Timble and White²² have evaluated the contribution from the second-order term using an effectively localized Heine-Abarenkov potential. Both kinds of contributions are found to be small

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except in Li; we have combined them in the proper way to yield the following values of $(m^*/m)_{e-i}$: Li, 1.46; Na, 1.025; K, 1.00; Rb, 0.98; Cs, 0.99.

Recently Shaw and Warren³⁶ have calculated the enhancement factor for the Korringa relation due to electron-electron interactions of finite range. Their result depends upon $(m^*/m)_{e-i}$ and upon the exchange parameter $\alpha' = (m^*/m)_{e-i} G_0(r_s)$. They used Ham's values of $(m^*/m)_{e-i}$ and found values of α' , and hence of χ_P , which are not in agreement with our results. However, with the values of $(m^*/m)_{e-i}$ given in the last paragraph, their analysis (slightly extended to include the small effect due to exchange core polarization³) yields the following values of χ_P/χ_D^0 : Na, 1.77; K, 1.66; Rb, 1.64; Cs, 1.76, in striking agreement with the values obtained here from the alloy Knight shifts.

APPENDIX C: SCREENING BY DIELECTRIC CORE POLARIZATION

Hedin and Brinkman³⁷ have suggested that the proper electron-gas parameter in the alkali metals is not r_s but $r_s^* = r_s/(1+4\pi\alpha)$, where α is the polarizability of the ionic lattice. Thus $F_1(r_s)$ and $G_0(r_s)$ in Eq. (2.5) should be replaced by $F_1(r_s^*)$ and $G_0(r_s^*)$.

A brief plausibility argument will now be given: Consider a cubic solid metal in which the lattice is composed of neutral polarizable ions (embedded in

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- [†]Present address: Physics Department, University of Toronto, Toronto 181, Ontario, Canada.
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a uniform positive background to ensure charge neutrality). The Hartree-Fock wave functions of the conduction electrons are simply plane waves. Defining $v_{eff}(\vec{x}_1, \vec{x}_2)$ as the mean potential produced at \vec{x}_2 when an electron is held fixed at \vec{x}_1 , one may easily show that

$$\begin{aligned} v_{\rm eff}(\vec{q}) &= \int d^3 x_1 d^3 x_2 e^{i \vec{q} \cdot (\vec{x}_1 - \vec{x}_2)} v_{\rm eff}(\vec{x}_1, \vec{x}_2) \\ &= 4\pi e^2 / q^2 [\epsilon^L(q) + 4\pi\alpha] , \end{aligned}$$

where $\epsilon^{L}(q)$ is the familiar Lindhard dielectric function. Since the Fermi liquid parameters are, roughly speaking, moments of $N(E_F)v_{\text{eff}}(\vec{q})$, where $N(E_F)$ is the Fermi-level density of states, one finds that they depend upon $r_s^* = r_s/(1 + 4\pi\alpha)$.

The values of r_s^* for the liquid alkali metals from semiempirical ionic polarizabilities³⁸ are as follows: Li, 3.28; Na, 3.85; K, 4.44; Rb, 4.49; Cs, 4.63. The range of r_s^* is narrower than that of r_s because the heavier ions are more polarizable. When the susceptibility enhancements given in Table I are plotted versus r_s^* (assuming a linear dependence of α upon alloy concentration), one obtains again a weak and nearly unique dependence upon the electron-gas parameter. However, under the r_s^* analysis the present calculation becomes less useful for discrminating between various electron-gas theories, since the range of the electrongas parameter over the alkali alloys is reduced.

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Optical Properties of Excitons Bound to Copper-Complex Centers in Gallium Arsenide

F. Willmann, D. Bimberg, * and M. Blätte

Max-Planck-Institut für Festkörperforschung, 7 Stuttgart, Germany

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The photoluminescence of copper-doped high-purity epitaxial GaAs in the near-gap region is investigated as a function of excitation intensity, temperature, and an external magnetic field up to 5.7 T. Sharp emission lines are identified as originating from the recombination of excitons bound to neutral-copper-complex centers of $C_{3\nu}$ and $C_{2\nu}$ symmetry with ionization energies of 156 and about 450 meV, respectively. The spectrum exhibits replicas of these lines, which are due to the simultaneous excitation of resonant modes of 3.6- and 6.1-meV energy. The relative intensities obey a Poisson distribution law. The dissociation of the bound excitons takes place in a two-step process: First a free single particle is liberated, whereas at higher temperatures free-electron-hole pairs are created. The linear dependence of the luminescence on the excitation intensity leads to the conclusion that photocreated coupled electron-hole pairs are trapped directly by the binding center. A group-theoretical analysis of the Zeeman pattern attributes the different lines to the appropriate electronic transitions between states of the double groups $C_{3\nu}$ and $C_{2\nu}$. The crystal field is sufficiently strong to completely decouple the $|m_j|=1/2$ and 3/2 levels of the acceptor ground state. The $|m_j|=3/2$ state is degenerate with the valence-band continuum.

I. INTRODUCTION

Photoluminescence, absorption, and reflection measurements of copper-doped GaAs crystals have first been performed in the near-gap energy range by Gross et al.¹ The luminescence of this relatively impure bulk material was dominated by an unresolved recombination band labeled B. In highpurity epitaxial GaAs this band was later identified as arising from conduction-band-acceptor (e, A^0) and donor-acceptor (D^0, A^0) recombination.² The luminescence spectra of Gross showed two additional lines at the high-energy tail $(C_0 \text{ and } C_1)$ and two lines at the low-energy tail $(F_0 \text{ and } F_1)$ of the B band with a half-width of about 1 meV at 4.2 K. These lines C_0 and F_0 were interpreted to be caused by the recombination of excitons bound to copper centers. Piezospectroscopic and reaction-kinetic studies led to the assumption that the copper centers are anisotropic and have trigonal (C_0 line) and orthorhombic symmetry (F_0 line). A comparison of the luminescence and absorption spectra showed that the C_1 and F_1 lines are electronic transitions accompanied by the simultaneous excitation of a vibrational quantum.

In this paper, we present the results of a systematic study of the luminescence of the copper-induced bound-exciton lines and of the multivibrational-mode emission processes. The investigations were performed with an epitaxial material of much lower impurity content than that used in the earlier mentioned work. The improved technique leads especially to a reduction in the half-widths of the lines by an order of magnitude. The luminescence was measured as a function of (a) the excitation intensity, (b) the sample temperature, and (c) an external magnetic field. The variation of these different parameters leads to an identification of the binding complex centers and to new results on the spectral positions of the lines, the binding energies of the excitons to the complex copper centers, the dissociation processes of the bound excitons arising by an increase of the temperature, and to the electronic structure of the binding center and the bound exciton.

II. EXPERIMENTAL

The samples were mounted in an immersion Dewar for most of the photoluminescence measurements and excited by an Ar⁺ laser (514 nm) at normal incidence. Variation of the excitation intensity was achieved by a set of calibrated neutral density filters. The detecting system consisted of a $\frac{3}{4}$ -m Spex grating monochromator and a photomultiplier (RCA C31000E) cooled by dry nitrogen gas. We used a photon-counting technique, with a storage of spectra which is similar to the multiscaling setup, published recently by Bachrach.³ A multichannel analyzer system (Nuclear Data 4410) for data acquisition was used. It easily provides data manipulation such as background subtraction and integration operations in a given spectral range. Typical darkcount rates were less than 25 pulses/sec.

The temperature-dependent data were measured