APPENDIX: RELATIONSHIP BETWEEN ACTUAL CHARGE AND EFFECTIVE CHARGE PER PARTICLE OF A SPECIES DIFFUSING IN A POLARIZABLE AND PARTIALLY COVALENT MEDIUM

In the limit of equilibrium, the relationship between the areal densities of charged particles in adjacent potential minima is given by the Boltzmann factor, so that

$$n_k = n_{k-1}\exp(-\Delta U_{k-1}/k_BT)\,, \tag{A1}$$

where ΔU_{k-1} is the difference in potential energy between the two positions. The energy ΔU_{k-1} is simply the product of the *actual* charge per particle of the diffusing species and the electrostatic potential difference ΔV_{k-1} between the two positions,

$$\Delta U_k = q\Delta V_{k-1} = -2qaE_k\,, \tag{A2}$$

where Eq. (2.6) has been utilized.

In addition, at equilibrium the particle current J_k is zero, in which case Eq. (2.12) [i.e., Eq. (2.5) of Ref. 17] yields

$$n_k = n_{k-1}\exp(2ZeE_ka/k_BT)\,. \tag{A3}$$

Comparison of (A3) with (A1) shows that

$$\Delta U_k = -2ZeE_ka\,. \tag{A4}$$

Comparing (A2) with (A4) yields the result $Ze = q$.

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Electron-Spin Susceptibilities of the Liquid Binary Alkali Metal Alloys*

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We report measurements of the Knight shifts of the liquid binary alkali metal alloys over the entire range of concentration of constituents for the alloys Na-Cs, K-Rb, K-Cs, and Rb-Cs. We interpret all existing measurements of the Knight shift in the binary alloys of Na, K, Rb, and Cs to give the electron-spin susceptibility χ_e of those pure alkalis not previously measured. Our interpretation uses the assumption that $\langle|\psi(0)|^2\rangle_{E_F}$ for a particular constituent of a particular alloy remains constant, equal to that for the pure metal, over the entire concentration range in that alloy. In previous work on the alkali alloys, the changes in the Knight shift in dilute alloys were attributed solely to changes in $\langle|\psi|^2\rangle_{E_F}$ due to scattering by impurity atoms, whereas we attribute the changes primarily to changes in χ_e and the atomic volume. New results for pure metals, in cgs volume units, are $\chi_e = (0.84\pm0.08)\times10^{-6}$ for potassium and $\chi_e = (0.80\pm0.08)\times10^{-6}$ for both rubidium and cesium. Our values are based upon the measured value $\chi_e = 1.13\times10^{-6}$ for sodium as a calibration point. The inferred susceptibilities are consistent with values of the parameter ξ of 0.69 ± 0.07, 0.72 ± 0.07, and 0.79 ± 0.08 for potassium, rubidium, and cesium, respectively, where ξ is the ratio of electron wave function density at the nucleus in the metal to the same quantity in the free atom. We compare the inferred susceptibilities with the calculations of Silverstein. We also make comparisons via the measured total susceptibilities for the alkalis with some existing calculations of the diamagnetic and ionic susceptibilities for these metals.

I. INTRODUCTION

A QUANTITY of considerable interest in the modern theory of metals is the conduction-electron-spin susceptibility χ_e of the simple metals. There exist in the literature direct measurements of values of χ_e of Li and Na.[1–3] The measurement technique used to obtain the value of χ_e is that of Schumacher and Slichter.[1] The experiment consists of the comparison of the integrated conduction-electron spin-resonance (CESR) absorption to the integrated nuclear magnetic resonance (NMR) absorption at constant frequency. The technique has not yet been applied to simple metals other than Li or Na because of unfavorably large CESR linewidths of the other metals.[4,5]

We present a technique by which we obtain values of χ_e for K, Rb, and Cs by means of an indirect measurement of χ_e in the liquid binary alkali alloys. Our technique uses the Knight shifts[6] of the liquid binary alkali alloys of Na, K, Rb, and Cs. We use the results

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[1] R. T. Schumacher and C. P. Slichter, Phys. Rev. **101**, 58 (1956).

[2] R. T. Schumacher and W. E. Vehse, J. Phys. Chem. Solids **24**, 297 (1963).

[3] R. Hecht, Phys. Rev. **132**, 966 (1963).

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

[5] Sheldon Schultz and M. R. Shanabarger, Phys. Rev. Letters **16**, 178 (1966); W. M. Walsh, Jr., L. W. Rupp, Jr., and P. H. Schmidt, *ibid.* **16**, 181 (1966).

[6] W. D. Knight, Phys. Rev. **76**, 1259 (1949).

of Rimai and Bloembergen[7] for the Knight shifts of Na^{23} in Na-K and of Na^{23} and Rb^{87} in Na-Rb. We have obtained experimental results for the rest with the exception of the Knight shifts of K in the potassium alloys. Our model employs the Knight shifts in the alloys, the Knight shifts in the pure metals Na, K, Rb, and Cs, and the Schumacher-Vehse measurement[2] of the χ_e of Na to obtain the values of χ_e. The principal features of the model are as follows:

(i) We assume the usual expression for the Knight shift,[6]

$$K=(8\pi/3)\chi_e\Omega_0\langle|\psi(0)|^2\rangle_{E_F}, \tag{1}$$

to be valid as a proper description of the Knight shift in the pure metals and the liquid binary alloys. Ω_0 is the atomic volume and $\langle|\psi(0)|^2\rangle_{E_F}$ is the conduction-electron wave-function density at the nucleus, averaged over the Fermi surface. The conduction-electron wave functions are normalized so that the integral of the wave-function density over the atomic volume is unity.

(ii) We assume that the value of $\langle|\psi(0)|^2\rangle_{E_F}$ for a particular atomic constituent of an alloy is equal to a constant, independent of the concentration of atomic constituents and of the particular alloy.

(iii) Interpolation between values of Ω_0 for pure materials to obtain values of Ω_0 for the alloys is made via Vegard's rule, using the room-temperature lattice constants of the pure metals. (Vegard's rule asserts that the lattice constant is linearly proportional to the concentration of a constituent.) Using these assumptions, the measured Knight shifts of the alloys allow us to obtain values of χ_e for the alloys by means of Eq. (1). Extrapolation of the resulting plot of χ_e for the alloy yields values of χ_e for the pure metals. Section III discusses in detail the model and the values of χ_e obtained by its use.

The relatively large changes of the Knight shifts in the alkali alloys have been a puzzle for many years. Previous interpretations of existing data[7] have attributed these changes entirely to changes in the wave-function density at the nucleus resulting from the scattering of electrons at the Fermi surface by the nonuniformity of the potential due to mixture of different kinds of atoms. Our model, to the contrary, focuses on changes in χ_e and the atomic volume as being the major contributions to the Knight-shift changes. In the context of our model, the relatively large changes in the Knight shifts in the alkali alloys may thus be accounted for primarily on the basis of relatively large changes in the electron density in the alkali alloys.

II. EXPERIMENTAL DETAILS

The samples were prepared form quantities of the bulk pure metals; Cs and Rb were obtained from MSA Research Corporation and K and Na from local supplies. The alloys were prepared from weighed quantities of the bulk materials. These were melted together and then whipped into a dispersion in mineral oil with a small amount of oleic acid added. The phase diagrams of the alloys[8] dictate the temperature at which the mixing and whipping processes take place. The technique is similar to that described in an earlier report from this laboratory.[9]

The Knight shifts were measured using a Varian wideline rf unit Model 4210A stabilized by a crystal oscillator. The Na alloys, while continuously soluble in the liquid state, form a eutectic, whereas the others are continuously soluble in the solid state.[8] However, the solid solutions of the latter are not homogeneous because of the existence of a distinct solidus and liquidus. Because of the large changes in the Knight shift with concentration of constituents in these materials, the solids have large linewidths. Hence the experiments were performed in the liquid state. We employed an oven which consisted of an L-shaped Dewar which fit into the Varian probe. The magnetic field was measured with a Harvey Wells gaussmeter. The Knight shifts of the constituents of the alloys were measured with respect to the resonance frequency of the pure metals of the respective constituents at 25°C.

III. χ_e OF THE ALLOYS

A. Preliminary Discussion

It is convenient to characterize simple metals by a parameter which is a function of the electron density. It will be seen that this is a particularly satisfactory means of cataloging the properties of the alloys. We follow the usual procedure of making the specification via the parameter r_s defined by the equation

$$\Omega_0=\tfrac{4}{3}\pi a_0^3 r_s^3\equiv 1/N, \tag{2}$$

where a_0 is the Bohr radius and N is the electron density. In Table I we list values for r_s for the various alkali metals. As can be seen in this table, there is a rather substantial increase in the atomic volume as one progresses from Li to Cs.

As one dilutes Na with Cs, for example, there is a smooth change of the atomic volume from that of pure Na to that of pure Cs. The accompanying expansion of the average distance between atoms has important consequences for the properties of the electron gas. The Fermi energy and Fermi wave vector uniformly decrease as the electron density decreases. Important changes also take place in the conduction-electron wave functions. These changes are most usefully examined by focusing on the question of wave-function normalization.

TABLE I. Values of r_s for the alkali metals.

	Li	Na	K	Rb	Cs
r_s	3.22	3.96	4.87	5.18	5.57

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[7] L. Rimai and N. Bloembergen, J. Phys. Chem. Solids **13**, 257 (1960).

We digress briefly to discuss common normalizations of conduction-electron wave functions. The two common normalization volumes used are unit volume and atomic volume. Normalization in the atomic volume is useful in comparing the wave functions of bulk metals to the wave functions of the free metal atom. Comparison is made through the factor ξ:

$$\xi = \langle|\psi(0)|^2\rangle_{E_F} / |\psi_A(0)|^2 , \qquad (3)$$

where $\psi_A(\mathbf{r})$ is the valence electron wave function of the free atom. For the alkalis and many other metals, ξ is of order unity. This fact is an important one which we shall use later. It tells us that in spite of the drastic change in exterior environment as the atom changes from the free state to metallic state, $|\psi(0)|^2$ is not substantially altered. Its value is determined primarily by the inner core potential of the atom. On the other hand, normalization to unit volume in a metal naturally gives the factor by which the electron density at the nucleus is enhanced over the value appropriate to uniform density of electrons.

The following relation obtains for the wave-function densities for the two normalization procedures:

$$\langle|\psi'(0)|^2\rangle = \langle|\psi(0)|^2\rangle / N . \qquad (4)$$

The prime indicates unit volume normalization. The fact that ξ is of order unity suggests that it may be reasonable to assume that ξ is constant, independent of concentration, for a given atomic constituent in any alloy in which it is a constituent. Then Eq. (4) implies that $\langle|\psi'(0)|^2\rangle$ is inversely proportional to N.

Equation (1) reveals the dependence of the Knight shift on N for the free-electron model. The Pauli susceptibility is proportional to $N^{1/3}$. We assume ξ is independent of N. Thus Eq. (2) combined with Eq. (1) shows that the Knight shift is proportional to $N^{-2/3}$. We shall see that the prediction that the Knight shift should be proportional to $N^{-2/3}$ qualitatively gives the dependence of the Knight shifts in the liquid alkali metal alloys where the changes in lattice constant, and hence N, are large.

The assumed constancy of ξ or equivalently, of $\langle|\psi(0)|^2\rangle$, as N varies has another consequence. As the lattice constant decreases, $|\psi|^2$ must increase proportionally with N in the region *between the atoms*; this result follows from the normalization condition.[10]

Another interesting fact about the alkali metals (and certain other metals) is that, upon melting, only very small changes are observed in the total susceptibility χ_t,[11] the Knight shift,[12,13] χ_e,[14] the nuclear spin-lattice relaxation time,[15] and the electron spin-lattice relaxation time.[16] Although the evidence cited is not complete, it suggests that many properties of the electron system are unchanged upon melting. The Knight shift presumably measures the product $\Omega_0\chi_e\xi$. Since, at least for Li,[14] Ω_0 and χ_e change little upon melting, the small change of the Knight shift indicates that ξ is nearly constant through the melting point. We shall exploit this feature in using our model. Both the nuclear and electron spin-lattice relaxation rates presumably measure the density of states at the Fermi surface, and the evidence suggests that this quantity is also essentially unchanged. We refer the reader to papers by Ziman[17] and Knight *et al.*[18] for discussion concerning the implications of these interesting results in the theory of liquid metals.

Finally, it should be emphasized that different values of $\langle|\psi(0)|^2\rangle$ for different constituents has another consequence in determining the nature of the binary alkali alloys. It destroys the symmetry that the conduction-electron wave functions possess for a perfect crystal of the pure metal. However, the symmetry properties of the pure metal are also destroyed upon melting. We expect no drastic changes in the equilibrium properties of the electron system to follow as a result of the former cause of symmetry breakdown, just as they do not for the latter.

It is important to take cognizance of the phenomenon of "charging," that is, nonuniform distribution of the electronic charge density in an alloy. There is one case for which there is apparently clear evidence for charging, namely, alloys of gold and silver. These alloys are interesting because gold and silver have the same valence, lattice constant, and crystal structure, and the lattice constant of the alloys is almost unchanged throughout the whole concentration range of constit-

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[8] M. Hansen, *Constitution of Binary Alloys* (McGraw-Hill Book Co., New York, 1958).

[9] D. F. Holcomb, J. A. Kaeck, and J. H. Strange, Phys. Rev. **150**, 306 (1966).

[10] In actual metals, one is usually permitted to experimentally observe only $\langle|\psi(0)|^2\rangle$. However, in the case of heavily doped metallic semiconductors, it is possible to observe $|\psi|^2$ in the "region between the atoms." In particular, we discuss the case of Si heavily doped with P [see R. K. Sundfors and D. F. Holcomb, Phys. Rev. **136**, A810 (1964)]. The wave function of the impurity band conduction electrons may be described as a linear combination of Si conduction band minimum orbitals modulated by a shape function determined by the P atoms. As in the case of more usual metals, $|\psi|^2$ is large at the P sites and small at the Si sites, the ratio being 26. If the assumption that $|\psi|^2$ at the P sites is constant as the density of conduction electrons changes holds, then $|\psi|^2$ at the Si^{29} sites should increase in proportion to N. Instead of the Si^{29} Knight shift being proportional to $\mathrm{N}^{-2/3}$, as should be the case for the P^{31} Knight shift, it should be proportional to $\mathrm{N}^{1/3}$. This is, in fact, observed for the Si^{29} Knight shift in Si:P. A similar effect is observed in heavily nitrogen-doped SiC [see M. N. Alexander, Phys. Rev. (to be published); M. N. Alexander and D. F. Holcomb, Solid State Commun. **6**, 355 (1968)].

[11] E. W. Collings, Physik Kondensierten Materie **3**, 335 (1965).

[12] B. R. McGarvey and H. S. Gutowsky, J. Chem. Phys. **21**, 2114 (1953).

[13] W. van der Lugt and J. S. Knol, Phys. Status Solidi **23**, K83 (1967).

[14] J. E. Enderby, J. M. Titman, and G. D. Wignal, Phil. Mag. **10**, 663 (1964).

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[16] C. E. W. Hahn and J. E. Enderby, Proc. Phys. Soc. (London) **92**, 418 (1967).

[17] J. M. Ziman, Advan. Phys. **16**, 421 (1967).

[18] W. D. Knight, A. G. Berger, and V. Heine, Ann. Phys. (N. Y.) **8**, 173 (1959).

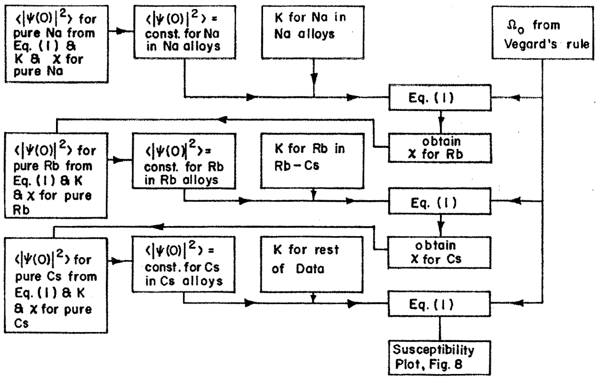

FIG. 1. Flow diagram summarizing the procedure used to obtain the susceptibilities for the liquid alkali metal alloys.

uents of the alloy.[19] However, as can be seen from Table II, the ionization energies for Ag and Au are different, Au having the larger value. Hence, Mott[20] some years ago suggested that extra charge would, on the average, pile up on the Au atoms. Measurements of the Knight shifts of Ag in Ag-Au by Narath[21] bear this suggestion out, since the Knight shift of Ag continuously decreases until for dilute Ag it is about 70% of its value for pure Ag. Since the lattice constant remains unchanged, the effects of electron-electron interactions, which are presumed to be a function only of r_s, should remain unchanged. (Narath reached this conclusion about the effects of electron-electron interactions on a somewhat different basis.) The ratio of the electronic specific heat of silver to that of gold is 0.89, which indicates that the effective mass of the electrons changes little. The implied change in effective mass is both too small and in the wrong direction to explain changes in the silver Knight shift. Hence, it seems likely that charging is responsible for the Knight-shift changes. To qualitatively assess the possible importance of this effect on alkali alloys, we refer again to Table II. Table II suggests that the effects of charging would be most prominent for Na alloys, especially Na-Cs, but would be particularly small for K-Rb and Rb-Cs.

The differences in Table II suggest a simple model with which to describe the effects of charging on the Knight shift in dilute alloys.[7,22] Changes in the charge density and hence Knight shift have been obtained in dilute alloys by use of scattering phase shifts for spherical potential wells or barriers located at the sites of the solute atoms. The scattering phase shifts are generally calculated by use of experimental resistivities and Friedel's sum rule. We refer the reader to criticism of this model by Faber.[23] One must take care in applying it or any similar theory to Knight shifts in the alkali alloys. The large variation in lattice constant in these alloys (Table I) implies large changes in the atomic volume Ω_0 as well as in χ_e. These give rise to substantial direct changes in the Knight shift [see Eq. (1)], as well as altering the scattering phase shifts through changes in the Fermi energy and Fermi wave vector.[24] Our model, which neglects charging, assumes that the changes in Ω_0 and χ_e largely determine the Knight-shift changes in the alkalis.

TABLE II. Ionization energies (eV) for the alkali and noble metals.

Li	Na	K	Rb	Cs	Cu	Ag	Au
5.37	5.12	4.32	4.16	3.87	7.68	7.54	9.20

Finally, we comment that the rigid band model is not applicable to the alkali alloys because of the large, continuous changes in the lattice constant in the alloys.

B. Model

Figure 1 is a flow diagram showing the steps we followed to infer χ_e from the Knight shifts of the liquid binary alkali alloys. We normalize the wave function in the atomic volume and assume Eq. (1) to be valid throughout. We assume the atomic volume in Eq. (1) is the same for both solute and solvent; this is essentialy a free-electron specification of the normalization which neglects any local size effects. Vegard's rule is then used to interpolate Ω_0 between the Ω_0 for the pure metals of a particular alloy at 20°C.

We start the analysis by obtaining $\langle|\psi(0)|^2\rangle$ for pure sodium from the Schumacher-Vehse value[2] for χ_e and the experimental Knight shift for pure Na.[12] We then invoke the assumption that the value of ξ thus determined for Na is constant for Na in all alloys in which Na is a constituent. That is, we use this one value of $\langle|\psi(0)|^2\rangle$ for the interpretation of all Na Knight shifts in Na alloys. We note that this assump-

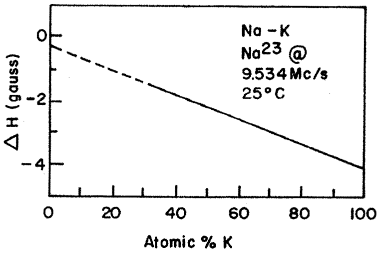

FIG. 2. Shift of resonance position from pure metal resonance for Na^{23} in Na-K; the solid line is the smoothed data taken from Ref. 7. No data were taken in the region of the dashed curve; note that the dashed curve extrapolated to 0 at.% K results, as pointed out in Ref. 7, is the shift of the Knight shift of pure molten Na relative to solid Na.

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[19] W. B. Pearson, *Handbook of Lattice Spacings and Structures of Metals* (The McMillan Co., New York, 1958).

[20] N. F. Mott, Proc. Cambridge Phil. Soc. **32**, 281 (1936).

[21] A. Narath, Phys. Rev. **163**, 232 (1967).

[22] A. Blandin and E. Daniel, J. Phys. Chem. Solids **10**, 126 (1959).

[23] T. E. Faber, Advan. Phys. **16**, 637 (1967).

[24] A. Meyer, C. W. Nestor, Jr., and W. H. Young, Advan. Phys. **16**, 581 (1967).

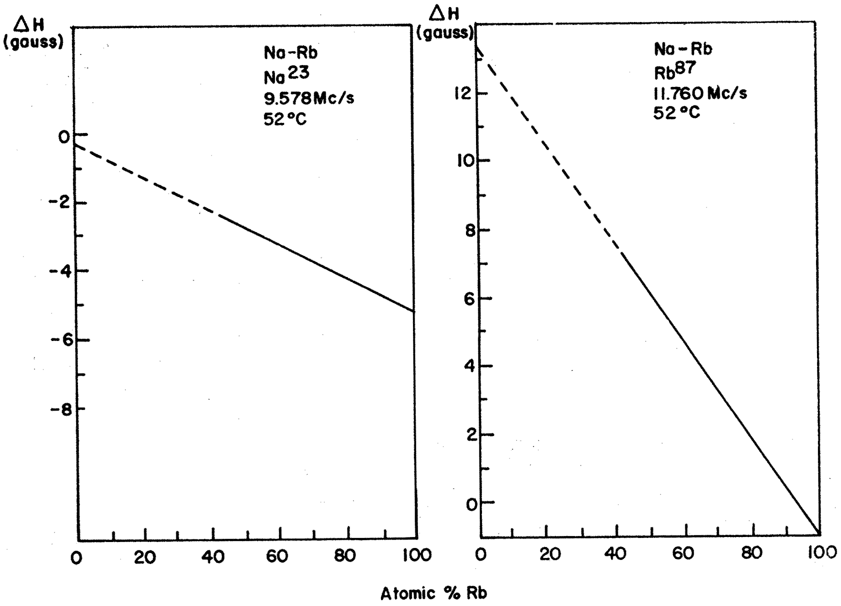

FIG. 3. Shift of resonance position from pure metal resonance for (a) Na^{23} in Na-Rb and (b) Rb^{87} in Na-Rb; data taken from Ref. 7 is solid line. The nature of the dashed and solid curves is the same as that in Fig. 2; as in the case of Fig. 2, the results are those from Ref. 7.

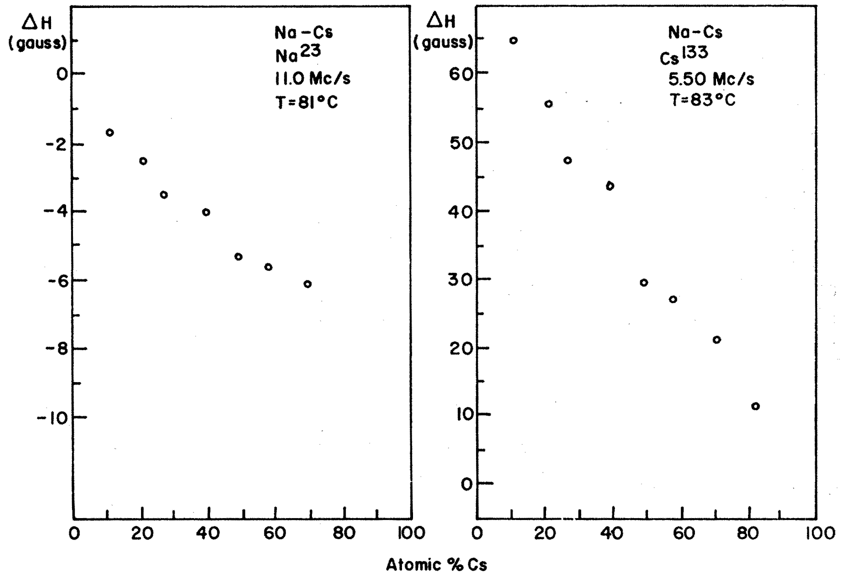

FIG. 4. Shift of resonance position from pure metal resonance for (a) Na^{23} in Na-Cs and (b) Cs^{133} in Na-Cs.

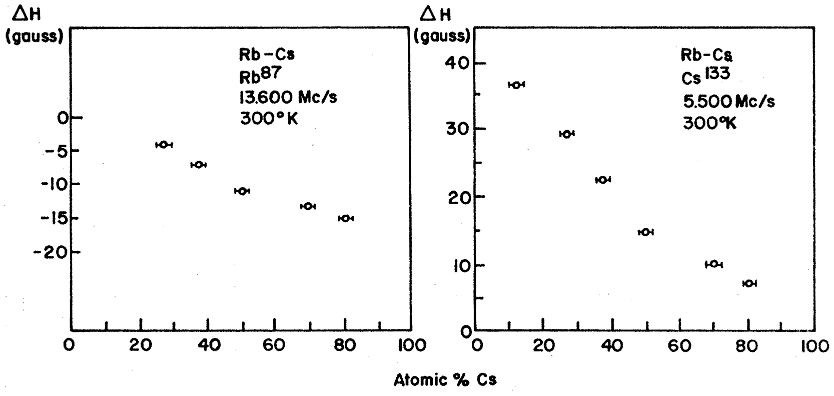

FIG. 5. Shift of resonance position from pure metal resonance for (a) Rb^{87} in Rb-Cs and (b) Cs^{133} in Rb-Cs.

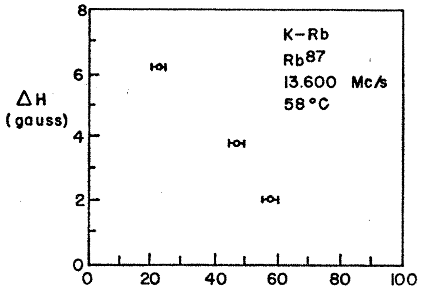

FIG. 6. Shift of resonance position from pure metal resonance for Rb^{87} in K-Rb.

tion neglects all effects of scattering arising from differences in local potential from solute to solvent sites. We then use the Knight shift of Na in Na-Rb and Eq. (1) to infer values of χ_e appropriate to that alloy. We then extrapolate these from the last experimental point at 10% Na to pure Rb. We then use this value of χ_e for Rb, along with the measured Knight shift for Rb^{87},[12] to obtain the value of $\langle|\psi(0)|^2\rangle$ for Rb from Eq. (1). We then repeat this process for the Rb^{87} Knight shifts in Rb-Cs and extrapolate to obtain χ_e for Cs. Again, we obtain $\langle|\psi(0)|^2\rangle$ for Cs. χ_e for K is obtained from the Knight shift of Na in Na-K by the procedure identical to that used to obtain χ_e for Rb from the Na-Rb data. Note that we have obtained the six quantities, χ_e and $\langle|\psi(0)|^2\rangle$ for K, Rb, and Cs, with just three sets of alloy Knight-shift data. All the remaining Knight-shift data were then interpreted in a similar manner (using only the appropriate $\langle|\psi(0)|^2\rangle$ already obtained above) to obtain the χ_e appropriate to the respective alloy compositions.

C. Experimental Results

Figures 2–7 show the Knight shifts in the alkali alloys except for K in the K alloys. The data in Figs. 2 and 3 are taken from the paper of Rimai and Bloembergen.[7] The data all approximately fulfill the prediction of free-electron theory that the Knight shift is proportional to $N^{-2/3}$.

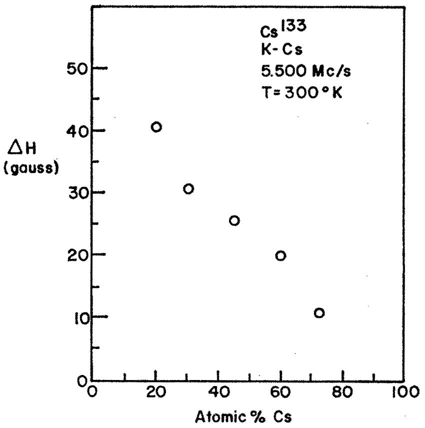

FIG. 7. Shift of resonance position from pure metal resonance for Cs^{133} in K-Cs.

Figure 8 shows the χ_e inferred from the data of Figs. 2–7 by means of the procedure described in Sec. III B. In general, self-consistency of the inferred values of χ_e is fairly good, and we take this feature to lend support to our model. The largest deviations from self-consistency are for Na in Na-Cs, for Cs in Na-Cs and in Rb-Cs, and for Rb in Na-Rb. It is encouraging to note that even though the inferred values of χ_e in the alloy Na-Cs depart from the other values of χ_e in the middle range of r_s, the χ_e inferred from the *cesium* Knight shifts for the case of dilute Cs tend toward the experimental value of χ_e for pure Na, and the inferred χ_e from the *sodium* Knight shifts for the case of dilute Na tend toward the value of χ_e for pure Cs obtained from the independent chain Na → Rb → Cs. Thus, the basic assumption that $\langle|\psi(0)|^2\rangle_{E_F}$ has a single value for any

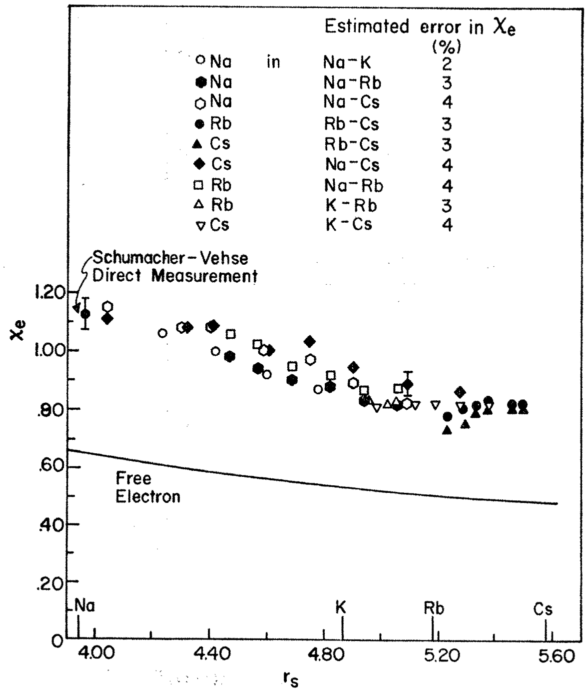

FIG. 8. Susceptibilities of the alkali alloys as a function of r_s as obtained through the procedure outlined in the text. The vertical errors are indicated in the table in the figure. These errors, as explained in the text, include experimental errors in the measured Knight shifts, the measured concentrations of the alloys which are reflected into the atomic volume, and the errors propagated via the analysis procedure. The errors for r_s in % for the alloys are 0.4 for Na-K, 0.5 for Na-Rb, 0.6 for Na-Cs, 0.2 for K-Rb, 0.5 for K-Cs, and 0.1 for Rb-Cs. A typical vertical error is indicated for an inferred susceptibility from a Cs Knight shift in Na-Cs. The value of r_s for the pure metals is indicated in the figure. All points except for those inferred from the Knight shifts of Na-K and Na-Rb are taken directly from the experimental points in Figs. 4–7. Extrapolations of χ_e to pure metals were made directly in this figure, according to the procedure outlined in the text.

TABLE III. Experimental, experimentally inferred, and theoretical predictions of χ_e and ξ for the alkali metals.

	χ_e(10^{-6} cgs volume units)				ξ		
	Expt.	H	N-P	F	Expt.		Theory
Li	2.08 ± 0.10[a]	2.28[b]	2.10[c]	0.81	0.45 ± 0.04[d]	0.442 ± 0.015[e]	0.49[f]
Na	1.13 ± 0.05[g]	0.96[b]	0.86[c]	0.65	0.60 ± 0.03[d]	0.635 ± 0.030[h]	0.64[i]
K	0.84 ± 0.08[j]		0.73[k]	0.53	0.69 ± 0.07[j]		
Rb	0.80 ± 0.08[j]		0.78[k]	0.51	0.72 ± 0.07[j]		
Cs	0.80 ± 0.08[j]		1.15[k]	0.47	0.79 ± 0.08[j]		

[a] Reference 1.
[b] Reference 26.
[c] D. Pines and P. Nozière, *The Theory of Quantum Liquids* (W. A. Benjamin, Inc., New York, 1966), p. 340, Table 5.6.
[d] From experimental Knight shift and χ_e.
[e] Reference 29.
[f] Reference 31.
[g] Reference 2.
[h] Reference 30.
[i] Reference 32.
[j] Inferred χ_e from this work.
[k] Reference 27.

given nucleus in all alloys gains some credence. We feel that this result is significant since Na-Cs presents the most severe test of this model. [Differences in ion size, ionization energy, and values of $|\psi_A(0)|^2$ are all large.] In view of the Cs data from K-Cs it is not clear what significance to attach to the bump in the values of χ_e inferred from Rb-Cs. We also comment that it is impossible at this point to determine the exact sources of the spread in values of χ_e at a given value of r_s; the spread may arise from charging, from band structure effects in the alloys or from local susceptibilities at the sites of individual species. It is hoped that calculations of $\langle|\psi(0)|^2\rangle$ along the lines suggested by Faber[23] may become available. At such time, the model used here could easily be upgraded in sophistication.

The experimental errors on the susceptibilities directly inferred from the Knight-shift measurements are indicated in Fig. 8. (The susceptibilities extrapolated for the pure metals are *not* plotted in Fig. 8; their errors are more involved and are discussed shortly.) There are three sources of error. Two are experimental in nature and one arises from the analysis:

(1) error in the measurement of the Knight shifts;

(2) error in the measurements of concentration of constituents in the alloy;

(3) error in the analysis through extrapolation of the inferred susceptibilities to the susceptibility of a pure metal.

This last error is propagated to susceptibilities inferred from Knight shifts as one follows the prescription outlined in Sec. III B, above. Errors in concentration have two consequences: first they lead to errors in specification of r_s; these errors generally turned out to be smaller than the width of the points shown on Fig. 8. Second, errors in concentration and hence r_s lead to errors in the atomic volume as calculated from Eq. (2); these were generally non-negligible. The errors quoted in Fig. 8 represent the combination of all three sources of error quoted above. We note that all the inferred susceptibilities share the 5% error of the Schumacher-Vehse determination of χ_e for Na (this error is *not* included in those specified in Fig. 8). Our error estimates clearly show that the small systematic deviations from the model are real.

The values of the χ_e extrapolated to the pure metals K, Rb, and Cs are shown in Table III. The errors on these χ_e are different from those shown in Fig. 8 due to the necessity of including a measure of the systematic deviations from the model evident upon inspection of Fig. 8. As mentioned above, some of the systematic differences are undoubtedly due to the breakdown of the assumption that ξ is constant. Also, Vegard's rule may not always be strictly true, particularly in liquid metals. Density measurements in Na-K in the liquid state at 100°C indicate slight deviation from Vegard's rule[25]; however, Vegard's rule is well satisfied for the solid alloys K-Cs and Rb-Cs.[8,19] Density measurements as a function of temperature in all the alloys would be helpful in providing proper values of the atomic volume in the alloys. (For our analysis, the case for which our specification of atomic volume is probably the worst is Na-Cs, since the Knight shifts were measured at about 80°C; we expect that the actual atomic volumes are somewhat larger than the ones we used and would bring the inferred χ_e from the Na and Cs Knight shifts in Na-Cs closer to the others.) To incorporate the effects of the breakdown of our model, we calculated the root-mean-square deviation of the inferred χ_e from the smooth curve generated by the coincident inferred χ_e obtained from the Na Knight shifts in Na-K and Na-Rb and the assumption that χ_e is constant from Rb to Cs; the result was 6%. We combined this with the two other independent errors—the error of the measured χ_e in Na of 5% and the largest error stated in Fig. 8 of 4%. These combined to give a confidence interval of 9% for the inferred-extrapolated χ_e for the pure metals; this is the error which is quoted in Table III.

We next make a comparison of the various theoretical estimates of the enhancement of χ_e over the Pauli susceptibility due to band structure and electron

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[25] G. Abowitz and R. B. Gordon, J. Chem. Phys. 37, 125 (1962).

TABLE IV. Comparison of experimentally inferred $\chi_{\text{ion}}+\chi_d$ with some theoretical calculations (all 10^{-6} cgs volume units).

		Expt.			Theory[a]	
	χ_t[b]	χ_e	$\chi_{\text{ion}}+\chi_d$	χ_{ion}	χ_d	$\chi_{\text{ion}}+\chi_d$
Li	1.78±0.06	2.08±0.10[c]	−0.30±0.16	−0.05	−0.20	−0.25
Na	0.59±0.01	1.13±0.05[d]	−0.54±0.06	−0.29	−0.25	−0.54
K	0.39±0.03	0.84±0.08[e]	−0.45±0.11	−0.38	−0.21	−0.59
Rb	0.34	0.80±0.08[e]	−0.46	−0.41	−0.21	−0.62
Cs	0.39±0.04	0.80±0.08[e]	−0.41±0.12	−0.49	−0.21	−0.70

[a] Quoted in Ref. 33.
[b] Reference 33.
[c] Reference 1.
[d] Reference 2.
[e] Inferred from this work.

many-body effects with our inferred values of χ_e for K, Rb, and Cs. The results are given in Table III. The values in the first column (Expt) are from Refs. 1 and 2 and this work. The second column (H) is taken from the calculations of Rice[26] using the Hubbard model and the third column (N-P) is taken from the work of Silverstein[27] using the Pines-Nozière model. Rice made small corrections to Silverstein's results for Li and Na, and we used these. Rice's result for Li was obtained using a band mass $(m^*/m)_{\text{BS}}=1.33$. Silverstein used the band mass of Ham.[28] The column (F) is the free-electron value. The results of Silverstein suggest that Ham's band mass for Cs is too large. It would be interesting to see the Rice calculations extended to $r_s=5.5$. We also include in Table III the experimental values of ξ from direct determinations by Ryter[29,30] for Li and Na and from this work for K, Rb, and Cs, along with the theoretical values of Kjeldaas and Kohn[31] for Li and of Taylor *et al.*[32] for Na. The trend of the experimental values for ξ certainly does not suggest any spectacular decrease in s character of the conduction-electron wave functions as one progresses to the heavier alkalis.

We conclude this section with a comparison of our inferred values of χ_e as well as those of Schumacher and co-workers with measurements of the total susceptibility χ_t.[33] The results are given in Table IV. The third column in Table IV is obtained by the usual relation among the various susceptibilities,

$$\chi_t=\chi_e+\chi_{\text{ion}}+\chi_d\,, \tag{5}$$

where χ_{ion} and χ_d are the ionic and electronic diamagnetic susceptibilities, respectively. The last three columns are theoretical calculations quoted in Ref. 33. The experimental and theoretical results for the sum of χ_{ion} and χ_d compare reasonably well for Li and Na, but less so for K, Rb, and Cs. For Li and Na, the data indicate that χ_d does not coincide with $-\frac{1}{3}\chi_e$.

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