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Hyperfine Structure of the Hydrogen Atom in CaF_2 as a Function of Temperature

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We have measured the electron-proton hyperfine constant for interstitial hydrogen atoms in CaF_2 in the temperature range 77–300 K. By introducing the pressure derivative at constant temperature, we are able to compute the temperature dependence of the hyperfine coupling constant at constant volume and compare it with calculations. The effects of the dynamic motion of the hydrogen atom and the lattice are discussed.

I. INTRODUCTION

Atomic hydrogen has been imbedded as a substitutional or interstitial impurity in many solids. The paramagnetic resonance of the atom has been found in rare-gas matrices,[1] glasses,[2,3] frozen solutions,[4] alkali halides,[5–8] and alkaline-earth fluorides.[8–15]

In these studies, one finds a spectrum similar to that of gaseous atomic hydrogen, with the electron-proton hyperfine constant B slightly different from, and usually greater than, free hydrogen. In addition, one finds more or less resolved hyperfine structure attributable to the nearest-neighbor ions. The interaction of the hydrogen with more distant ions has also been measured in a few experiments[9,12,15] employing the electron-nuclear double resonance (ENDOR)[16] technique to unravel the unresolved hyperfine structure.

Attempts to calculate the magnetic resonance parameters have for the most part employed model systems in which the hydrogen and its surroundings are static.[12,17,18] The methods used are essentially those developed by Adrian.[19]

However, some of the properties of the hydrogen-atom system, including the spin-lattice relaxation time[3,14,20,21] and the hyperfine constants,[9,13,22,23] show evidence of important local vibrational modes. In addition, there is a direct verification of the existence of the local mode through the discovery, in the infrared, of absorption lines associated with the impurity.[24]

The similar system, H^- ion in a solid host, also demonstrates the existence of local modes of vibration.[25–29]

The interstitial hydrogen center in calcium fluoride has been studied in some detail. Hall and Schumacher[9] (HS) studied the EPR and ENDOR spectra and were able to describe the geometry and specify a model for this center. HS measured some of the hyperfine coupling constants at two temperatures: 300 and 77 K. They attempted a dynamic calculation of the hyperfine constants but were not able to fit their experimental results using a simple local-mode model. Welber[11] has made similar measurements on the system H : BaF_2. His experimental results give temperature dependences for some of the hyperfine constants in BaF_2 opposite to those found in CaF_2. Blum[13] was able to give an explanation of these results on the basis of a charge-transfer model.[13,30]

The local vibrational mode of the hydrogen has been detected indirectly by Feldman *et al.*[14] in the spin-lattice relaxation time. They found a behavior with temperature indicative of a local vibrational mode with frequency equal to 591 ± 42 cm^{-1}. Other indirect evidence was found by Blum[13] in the investigation of the effects of hydrostatic pressure on the hydrogen center. Shamu *et al.*[24] subsequently observed the infrared absorption line associated with this local mode at 640 ± 0.5 cm^{-1}.

The motion of the lattice is usually not considered. The surrounding ions, being much more massive than the hydrogen atom, are assumed to be stationary. Evidence for the importance of the lattice modes of vibration will be discussed later.

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In this paper the temperature variation of the hydrogen hyperfine coupling constant B is given. This information is related to a simple model which incorporates the local-mode vibrations, the lattice dynamics, and charge transfer.

II. EXPERIMENTAL DETAILS

Hydrogen-ion centers were formed according to the prescription of HS by heating Harshaw CaF_2 in the presence of hydrogen gas and aluminum. Conversion to interstitial hydrogen is accomplished with x irradiation. The deuterium center was made by using deuterium gas instead of hydrogen. Single-crystal samples were powdered for the most accurate measurement of B.

A Varian E-3 EPR spectrometer was employed with a Varian E4540 variable temperature controller to provide sample temperatures from 95 to 300 K. Measurements at liquid-nitrogen temperature were possible with the use of an accessory Dewar. Higher-temperature measurements were not possible because of thermal bleaching of the paramagnetic center. A proton magnetometer was used to calibrate the magnetic field at resonance. The radio frequency necessary to induce NMR transitions in a sample of glycerol was counted on a Hewlett Packard 5245L counter. Temperature calibration of the Varian controller was made with a copper-constantan thermocouple in oil whose mass was equal to that of the powdered H: CaF_2 sample. A Hewlett Packard 2590B microwave frequency converter and 5245L counter with a 5253B plug-in were incorporated to accurately determine the E-3 klystron frequency.

Figure 1 shows the variation of B with temperature at constant pressure (1 bar). In order to compare this result with theory it is necessary to correct the data to constant volume. This is accomplished in the following way: At a given temperature T we can write

$$B(T, V) = B(T, V_0) + \left(\frac{\partial B}{\partial V}\right)_T (V - V_0) \tag{1}$$

and

$$\left(\frac{\partial B}{\partial V}\right)_T = \left(\frac{\partial B}{\partial P}\right)_T \left(\frac{\partial P}{\partial V}\right)_T = -\frac{1}{VK_T}\left(\frac{\partial B}{\partial P}\right)_T , \tag{2}$$

where K_T is the isothermal compressibility. The value of B corrected to constant volume is thus

$$B(T)_{\text{corr}} = B(T)_{\text{meas}} + \frac{1}{K_T}\left(\frac{\partial B}{\partial P}\right)_T \frac{(V - V_0)}{V} . \tag{3}$$

The compressibility[31] and the lattice constant[32] have been measured for pure CaF_2 as a function of temperature. $(\partial B/\partial P)_T$ has been measured[13] at room temperature only. In the correction we assume the pressure derivative is the same at all temperatures. $B(T)$ corrected to the volume at 300 K is also plotted in Fig. 1.

We note that the effect of thermal expansion is quite large, contrasting with the case of Mn^{2+} in a cubic environment[33] in which the thermal expansion produces only a small effect of opposite sign to the observed temperature dependence.

In Fig. 2 we have plotted the measured ratio of the deuterium hyperfine coupling constant C to B as a function of temperature. This is compared to the free deuterium and hydrogen ratio $(C/B)_{\text{free}} = 0.153\,50$.

III. DISCUSSION

B is given by the following expression[9,13,34]:

$$B = \tfrac{8}{3}\,\gamma_p \mu_B \langle \psi | \, \delta(\vec{r}) \, | \psi \rangle , \tag{4}$$

where γ_p is the proton gyromagnetic ratio, μ_B is the Bohr magneton, and ψ is the wave function for the system. In the Heitler-London model ψ is approximated by

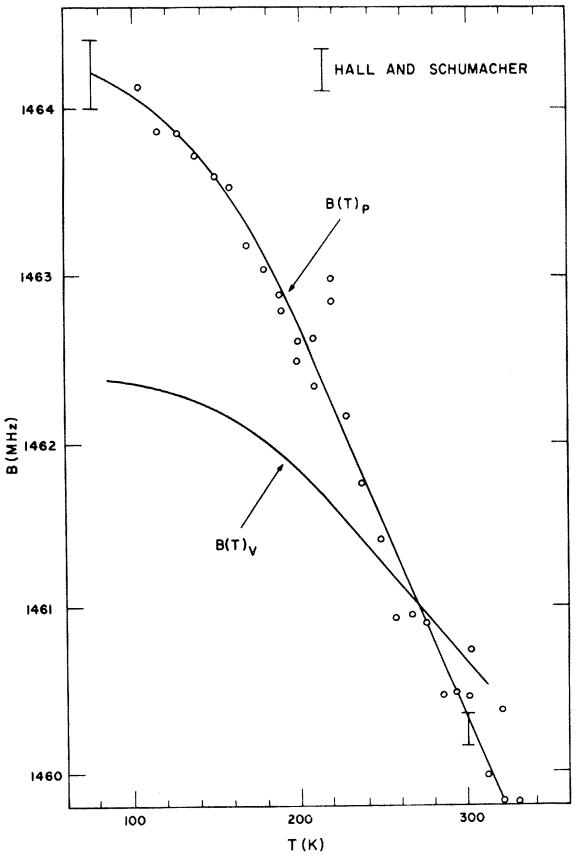

FIG. 1. Experimental variation of B with temperature at constant pressure and B vs T at constant volume corrected according to Eq. (3) in the text. Circles are data points. Error bars are experimental work of Hall and Schumacher (Ref. 9).

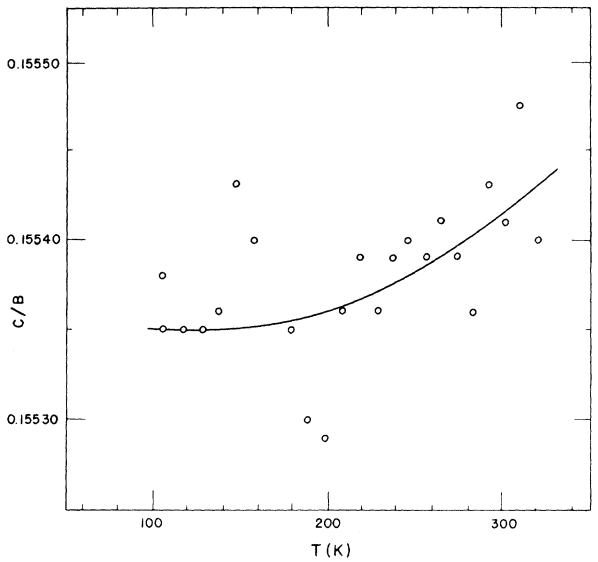

FIG. 2. Ratio of the hyperfine constants, C/B, for deuterium and hydrogen as a function of temperature.

$$\psi = N(\phi - \textstyle\sum_\alpha \lambda_\alpha \chi_\alpha), \quad N = (1 - 2\sum_\alpha \lambda_\alpha S_\alpha + \sum_\alpha \lambda_\alpha^2)^{-1/2}, \tag{5}$$

where ϕ is the hydrogen-atom wave function, χ_α are the neighboring fluorine-ion wave functions, and S_α is equal to $\langle \phi | \chi_\alpha \rangle$. The parameter λ_α determines the degree of charge transfer or configuration mixing.[30] $\lambda_\alpha = S_\alpha$ gives us a purely ionic model. We choose[13] $\lambda_\sigma = S_\sigma + \gamma$, where σ refers to the $2p$ fluorine-ion wave function pointing along the symmetry axis joining the hydrogen and fluorine sites and γ is a measure of the nonionic or charge-transfer nature of the system.

The model as outlined above predicts no temperature variation of B unless γ or S depends on temperature.

There are two dynamic effects which can introduce a temperature variation in B. These are (a) the modification of overlap integrals caused by the localized hydrogen-atom vibration and by the phonon spectrum of the host lattice and (b) the coupling of excited states into the ground state through the orbit-lattice interaction.[35] The latter effect also depends on the phonon spectrum of the host.

We consider first the simpler problem of the effect of the local vibrational mode on the overlap integrals.

A. Local Mode

We assume for the purposes of this calculation that the hydrogen atom moves as an entity in the harmonic-oscillator potential produced by the static lattice. These conditions appear to be satisfied for the similar system of H^- in various host lattices[25] at least at low temperatures where the zero-point motion of the hydrogen predominates.

As the hydrogen atom moves away from its equilibrium position, the instantaneous values of the overlap integrals change. We average S_α over the proton position using the harmonic-oscillator ground-state and excited-state wave functions. Mimura and Uemura[22] and Spaeth[23] have carried out such a calculation for the zero-point vibration. We have extended their results to include the first excited state.

The probability $P(\vec{R})$ for the proton position $\vec{R}$ away from its equilibrium position is

$$P(\vec{R}) = |\varphi(\vec{R})|^2 , \tag{6}$$

where $\varphi(\vec{R})$ is the harmonic-oscillator wave function. The overlap integrals become

$$(S_\alpha)_{\text{dynamic}} = \int P(\vec{R}) \langle \phi(\vec{R}_0 - \vec{R}) | \chi_\alpha \rangle d\vec{R} , \tag{7}$$

where $\vec{R}_0$ is the vector from the proton to the fluorine ion at equilibrium. To a good approximation S_α is proportional to the magntiude of ϕ at $\vec{R}_0$. This allows us to write

$$(S_\alpha)_{\text{dynamic}} = (S_\alpha)_{\text{static}} \rho^{1/2} , \tag{8}$$

where

$$\rho = \frac{|\phi(\vec{R}_0)|^2_{\text{dynamic}}}{|\phi(\vec{R}_0)|^2_{\text{static}}} = \frac{\int P(\vec{R}) |\phi(\vec{R}_0 - \vec{R})|^2 d\vec{R}}{|\phi(\vec{R}_0)|^2} . \tag{9}$$

Using the measured energy[24] of the first excited vibrational states of the hydrogen atom in CaF_2, 640 cm^{-1} or 910 K as an equivalent temperature, the proton mass, and the lattice constant, we find $\rho_0 = 1.15$ for the ground state and $\rho_1 = 1.36$ for the first excited state.

As a function of temperature, if we consider only the ground and first excited states,

$$S_{\text{dynamic}} = S_{\text{static}} \left(\frac{1.15 + 1.36 e^{-910/T}}{1 + e^{-910/T}} \right)^{-1/2} . \tag{10}$$

Figure 3 shows the variation of B with temperature predicted when S_{dynamic} replaces S_{static} in Eqs. (4) and (5) and $\gamma = 0$. The local mode by itself thus predicts an incorrect temperature dependence. In this model it is necessary to have $\gamma > 0$ and $\gamma = \gamma(T)$ in order to have B decrease with increasing temperature. We have solved Eq. (4) for $\gamma(T)$ and plotted the results in Fig. 4. This is the variation in $\gamma(T)$ after the effects of the local-mode vibration are removed. We have assumed[30] that $\gamma \propto S$ so that in Fig. 4 we have plotted $\gamma \rho^{-1/2}$. The problem then is to explain the remaining temperature dependence of $\gamma(T)$.

In the temperature variation of the ratio C/B shown in Fig. 2, we have further evidence for the local-mode vibration. However, the scatter in the data is too great to allow a quantitative discussion at this time.

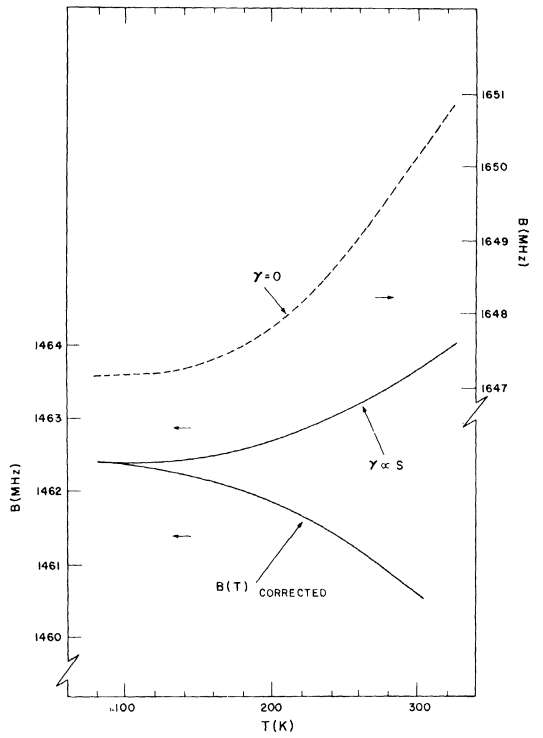

FIG. 3. Comparison of the variation of B at constant volume with temperature to the ionic ($\gamma = 0$) and simple ($\gamma \propto S$) charge-transfer models.

B. Lattice Effect

Šimánek and Orbach[35] were able to describe the temperature dependence of the Mn^{2+} hyperfine coupling constant[33] for Mn in MgO by proposing an orbit-lattice interaction, in which the Mn^{2+} is excited from its $3d^5$ s-like electronic ground-state configuration to $3d^4ns$ configurations. The excited states have different hyperfine coupling constants. The excitation occurs through thermal activation.

Although the initial work assumes a Debye phonon spectrum, this has been later modified to include a more realistic phonon spectrum.[36]

Experimental studies were extended to other cubic hosts[37] with similar results.

At low temperature, the hyperfine constant $A(T)$ for Mn^{2+} can be fit by an expression of the form

$$A(T) = A(0)(1 - CT^n) \ , \tag{11}$$

where $n = 1.5$ experimentally[33] and $n = 4$ on the basis of a Debye model.[37] We find that we can fit our constant volume $B(T)$ with an expression of the form

$$B(T) = B(0)(1 - CT^n) \ , \tag{12}$$

where $n = 4.75$ for temperatures below 200 K. This is close to the Debye prediction.

However, the electronic configuration present in CaF_2: H is quite different from that in Host: Mn. Rather than promote the 1s hydrogen electron to an excited state, an effect of little importance,[34] we can increase the charge transfer of the fluorine electrons; i.e., we can increase γ with temperature.

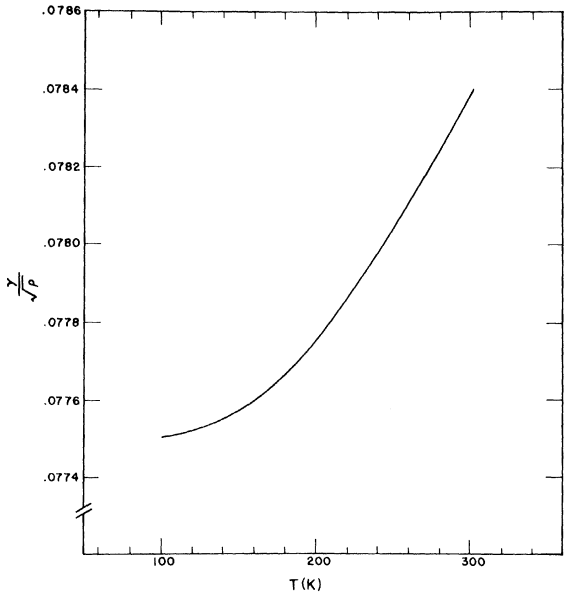

FIG. 4. Computed values of γ versus temperature to fit Eq. (4) in the text.

If we assume the Debye model, we should be able to write[35]

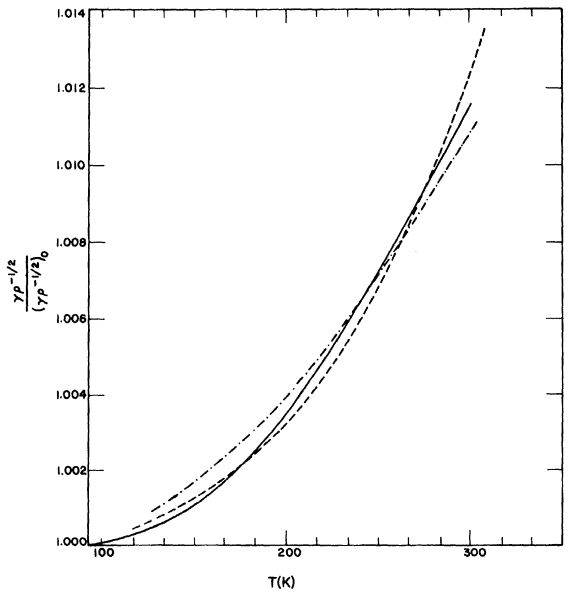

FIG. 5. Comparison between the temperature variation of $(\gamma\rho^{-1/2})/(\gamma\rho^{-1/2})_{T=0}$ chosen to fit the observed temperature dependence of B (solid line), taken from Fig. 4, and the results of applying a Debye model described in the text. Dashed curve, $\Theta = 1500$ K, $C = 35 \times 10^5$ K^{-4}; dotted curve, $\Theta = 1000$ K, $C = 4.7 \times 10^5$ K^{-4}.

$$(\gamma\rho^{-1/2})_T = (\gamma\rho^{-1/2})_{T=0}\left(1 + CT^4\int_0^{\Theta/T}\frac{x^3\,dx}{e^x - 1}\right), \quad (13)$$

where Θ and C are parameters.

In Fig. 5 we have fitted the experimentally determined values of $\gamma\rho^{-1/2}$ (from Fig. 4) with various Θ and C. We see that the fit is moderately good for $\Theta \sim 1500$ K. This seems to be extraordinarily high for CaF_2 whose actual Debye temperature[31] is about 500 K.

An improved agreement between the Šimánek-Orbach model and experiment can be achieved by taking the thermal average in Eq. (13) over the actual phonon distribution. Alternatively, we can limit the application of Eq. (13) to the low-temperature region in which case, as we have already stated, the fit to the Debye model is fairly good. In attempting to fit just the low-temperature region, we can choose $\Theta \sim 500$ K, leaving a large excess experimental temperature dependence for $\gamma\rho^{-1/2}$ at higher temperatures arising from the ignored optical modes.

IV. CONCLUSION

Although we can only offer our analysis as a preliminary step, we believe that we have considered the important interactions in this system. While it is quite clear that the zero-point vibration and local mode are important in calculating the temperature dependence of B, the most important feature is the increase in the charge transfer which is apparently promoted by an orbit-lattice interaction.

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[1]C. K. Jen, S. N. Foner, E. L. Cochran, and V. A. Bowers, Phys. Rev. 104, 846 (1956); E. L. Cochran, V. A. Bowers, S. N. Foner, and C. K. Jen, Phys. Rev. Letters 2, 517 (1959); S. N. Foner, E. L. Cochran, V. A. Bowers, and C. K. Jen, J. Chem. Phys. 32, 963 (1962).

[2]R. A. Week and M. Abraham, J. Chem. Phys. 42, 68 (1965).

[3]D. W. Feldman, J. G. Castle, Jr., and G. R. Wagner, Phys. Rev. 145, 237 (1966).

[4]C. J. Ultee and C. R. Kepford, J. Chem. Phys. 52, 3462 (1970).

[5]F. Kerkhoff, W. Martienssen, and W. Sander, Z. Physik 173, 184 (1963); H. Thomas, Ann. Physik 38, 601 (1940); C. Delbecq, B. Smaller, and P. H. Yuster, Phys. Rev. 104, 599 (1956); E. Duval, J. Serughetti, and R. Lovat, Solid State Commun. 8, 1155 (1970); A. Kazumata, Phys. Status Solidi 25, 563 (1968).

[6]W. Hayes and J. W. Hodby, Proc. Roy. Soc. (London) A294, 359 (1966).

[7]J. M. Spaeth, Z. Physik 192, 106 (1966); G. Lehnert and J. M. Spaeth, Phys. Status Solidi 31, 703 (1969).

[8]R. G. Bessent, W. Hayes, and J. W. Hodby, Phys. Letters 15, 115 (1965).

[9]J. L. Hall and R. T. Schumacher, Phys. Rev. 127, 1892 (1962).

[10]B. Welber, J. Chem. Phys. 43, 3015 (1965); H. A. Atwater, *ibid.* 40, 606 (1964).

[11]B. Welber, Phys. Rev. 136, A1408 (1964).

[12]R. G. Bessent, W. Hayes, and J. W. Hodby, Proc. Roy. Soc. (London) A297, 376 (1967); A309, 53 (1969).

[13]H. Blum, Phys. Rev. 161, 213 (1967); H. Blum and G. B. Benedek, Bull. Am. Phys. Soc. 8, 619 (1963).

[14]D. W. Feldman, J. G. Castle, Jr., and J. Murphy, Phys. Rev. 138, A1208 (1965).

[15]R. Böttcher, A. Frieser, B. Milsch, G. Völkel, S. Wartewig, M. Welter, and W. Windsch, Phys. Status Solidi 38, K97 (1970).

[16]G. Feher, Phys. Rev. 114, 1219 (1959).

[17]F. J. Adrian, J. Chem. Phys. 32, 972 (1960).

[18]K. Cho, H. Kamimura, and Y. Uemura, J. Phys. Soc. Japan 21, 2294 (1966); K. Cho, *ibid.* 23, 1296 (1967); B. Sammel, Phys. Status Solidi 12, K11 (1965); 34, 409 (1969).

[19]B. S. Gourary and F. J. Adrian, *Solid State Physics* (Academic, New York, 1960), Vol. 10, p. 227.

[20]P. G. Klemens, Phys. Rev. 138, A1217 (1965); 125, 1795 (1962); 122, 443 (1961).

[21]J. Murphy, Phys. Rev. 145, 241 (1966).

[22]H. Mimura and Y. Uemura, J. Phys. Soc. Japan 14, 1011 (1959).

[23]J. M. Spaeth, Phys. Status Solidi 34, 171 (1969).

[24]R. E. Shamu, W. M. Hartman, and E. L. Yasaitis, Phys. Rev. 170, 822 (1968); T. L. Gilbert and W. M. Hartmann, Bull. Am. Phys. Soc. 14, 391 (1969); W. M. Hartmann, T. L. Gilbert, K. A. Kaiser, and A. C. Wahl, Phys. Rev. B 2, 1140 (1970).

[25]R. J. Elliott, W. Hayes, H. F. Macdonald, and C. T. Sennett, Proc. Phys. Soc. (London) A289, 1 (1965); W. Hayes, H. F. Macdonald, and R. J. Elliott, Phys. Rev. Letters 15, 961 (1965); W. Hayes and H. F. Macdonald, Proc. Roy. Soc. (London) A297, 503 (1967).

[26]D. Bauerle and B. Fritz, Phys. Status Solidi 24, 207 (1967).

[27]B. Fritz, J. Phys. Chem. Solids 23, 375 (1962); in *Lattice Dynamics*, edited by R. F. Wallis (Pergamon, London, 1965), p. 485.

[28]G. Shaefer, J. Phys. Chem. Solids 12, 233 (1960).

[29]R. E. Shamu and F. O. Bellinger, Bull. Am. Phys. Soc. 12, 393 (1967).

[30]H. Blum, J. Chem. Phys. 46, 650 (1967).

[31]D. R. Huffman and M. H. Norwood, Phys. Rev. 117, 709 (1960).

[32]D. N. Batchelder and R. O. Simmons, J. Chem. Phys. 41, 2324 (1964).

[33]W. M. Walsh, Jr., J. Jeener, and N. Bloembergen, Phys. Rev. 139, A1338 (1965).

[34]Recent papers by W. E. Hagston [Phys. Status Solidi 39, 539 (1970); 39, 551 (1970)] review the theory of the magnetic properties of the hydrogen atom in host lattices.

[35]E. Šimánek and R. Orbach, Phys. Rev. 145, 91 (1966).

[36]T. J. Menne, Phys. Rev. B 1, 4496 (1970); C. Y. Huang, Physics 3, 231 (1967).

[37]J. Rosenthal, L. Yarmus, and R. H. Bartram, Phys. Rev. 153, 407 (1967); R. A. Serway, Phys. Letters 26A, 642 (1968); C. Y. Huang, J. F. Reichert, and J. Gigante, *ibid.* 26A, 219 (1968); R. Calvo and R. Orbach, Phys. Rev. 164, 284 (1967).

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Impurity-Induced g Shift of Conduction Electrons

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A simple theory of the g shift of conduction electrons induced by nonmagnetic impurities embedded in a metal is described. A single impurity atom is placed at the center of a large sphere containing a free-electron gas. The major contribution to the g shift is obtained by calculating the change in the orbital angular momentum due to the spin-orbit interaction. Quite large g shifts obtain when the spin-orbit interaction with the impurities is large, when the scattering phase shifts are not too small, when one or more partial waves go through a narrow resonance, or when the phase shifts change rapidly with energy without becoming large, and when the alloys are concentrated. Application of the theory to very dilute lithium alloys has revealed that the g shifts are too small to be observable by means of conduction-electron spin resonance. This was confirmed by performing spin-resonance experiments on dilute Li-Zn, Li-Ag, and Li-Cd alloys. The theory presented here provides the extension of the theory of the g factor of atomic electrons to the case of electrons in the continuum states.

I. INTRODUCTION AND CONCLUSION

Recently, Slichter and co-workers[1-3] measured and calculated the spin-flip cross section for scattering of conduction electrons from nonmagnetic impurity atoms embedded in lithium and sodium metal. They showed that satisfactory agreement with experimental data can be obtained if it is assumed that the spin-dependent scattering is due to the spin-orbit interaction of the spin of the conduction electron with its orbital motion in the electric field of the impurity atoms. Furthermore, these authors demonstrated that conduction-electron spin-resonance experiments on the alkali metals containing a small concentration of nonmagnetic impurity atoms with a valence different from 1 provide a convenient way to study the electric screening of an excess charge in these metals.

The main purpose of the present paper is to explore the feasibility of obtaining additional knowledge about the electric screening of an excess charge by also measuring and interpreting the g shift of the conduction electrons. Although Slichter *et al.* did not report g-shift measurements, Hahn and Enderby[4] measured the g shift in three dilute lithium alloys. They obtain g shifts of $(-7.8\pm0.6)\times10^{-3}$, $(-2.2\pm0.1)\times10^{-2}$, and $(-3.5\pm0.1)\times10^{-2}$ for the alloys Li–0.05 at.% Zn, Li–12 at.% Mg, and Li–0.032 at.% Ag, respectively. These values should be compared with the very small conduction-electron g shift of pure lithium,[5] which is -6.1×10^{-5}. The present work was motivated by the desire to understand the (seemingly) large g shifts reported in Ref. 4.

In Sec. II we describe the theoretical aspects of this problem. We assume that the difference in g shift of the alloy and the pure host metal is also caused by the spin-orbit interaction of the conduction electrons with the impurity atoms. In order to estimate this impurity-induced g shift we consider a single impurity immersed in a free-electron gas. For simplicity, the impurity potential is taken to be spherical. It turns out that the theory is particularly simple when the impurity is placed at the center of a sufficiently large perfectly reflecting sphere containing the free-electron gas, and use is made of the angular momentum representation. We show that in a conduction-electron spin-resonance experiment transitions take place between a predominantly spin-up state and a predominantly spin-down state. The predominantly spin-up state is the sum of a large spin-up component and a small spin-down component. Similarly, the predominantly spin-down state consists of a large spin-down part and a small spin-up part. The large components are eigenfunctions of L_z, so that the two states are characterized by the orbital angular momentum quantum number l, the magnetic quantum number m, and the wave number k. The small components vanish in the absence of the spin-orbit interaction. The g factor of a conduction electron is associated with the difference in energy of these two states in the presence of a static magnetic field. The impurity-induced g