There is, therefore, no extensive spin–orbit coupling in this system.

Two recent studies of esr on niobium(IV) complexes have been reported. Rasmussen, *et al.*,[12] have studied $NbCl_5(OCH_3)^{2-}$ and find an average (both the hyperfine interaction and g tenson are anisotropic) hyperfine interaction constant $a = 178 \pm 3$ gauss with $g = 1.861 \pm 0.002$. Lardon and Gunthard[13] have examined what is presumed to be $NbCl_6^{2-}$ and find $a = 177.4 \pm 0.1$ gauss and $g = 1.892 \pm 0.001$. The former complex has niobium(IV) in an approximately tetragonal (C_{4v}) environment. This corresponds to the same local symmetry about a niobium atom in our complexes.

Our value of the hyperfine interaction constant of 20.6 ± 0.5 gauss is slightly less than *one-sixth* of both the constants reported above (29.7 gauss). It supports strongly the use of niobium d orbitals as the basis for the metal–metal bonding within the octahedron. An orbital which can potentially be effective in bonding together the metal octahedron is an a_{2u} (representation of the group O_h) orbital which has been shown by Cotton and Haas[14] to arise from the metal d_{xy} orbitals. Kettle[15] has pointed out that this orbital can be considered to be of a three-center (maximum density above the octahedral faces) type, and we propose that the a_{2u} orbital is in fact the only reasonable choice for the top filled level in the $Nb_6Cl_{12}^{2+,3+}$ species. This is consistent with the bonding scheme given by Cotton and Haas[14] for values of $p \geq 8.3$.[16] It further suggests that the scheme of Robin and Kuebler[7] does not explain the magnetic properties without a substantial reordering of levels.

This work then supports the general principles and assumptions used by Cotton and Haas in their molecular orbital treatment of the M_6X_{12} unit and suggests that proper inclusion of the effects of the chlorine atoms (both bridging and terminal) may well produce an energy level scheme of more than qualitative significance.

We wish to mention further that we have looked for both niobium and chlorine nuclear quadrupole resonance in these compounds. We have searched the region from 10 to 40 Mc at both 24 and −196° with a superegenerative spectrometer incorporating coherence control of the type described by Peterson and Bridenbaugh[17] with no success. We have also searched the region from 2 to 16 Mc at 24° with a Varian Model V-4210 broad-line nmr spectrometer and probes, again without success. The sharpness of the hyperfine components of the esr absorption suggests that the field gradient at niobium is relatively small so that a niobium quadrupole resonance could be expected to fall in the range which we have investigated. The chlorine resonance should certainly fall in this region. The lack of observation of any resonances whatever may be attributable to broadening by the large number of protons due to the tetraethylammonium cation.

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[12] P. G. Rasmussen, H. A. Kuska, and C. H. Brubaker, Jr., *Inorg. Chem.*, **4**, 343 (1965).

[13] M. Lardon and H. S. H. Gunthard, *J. Chem. Phys.*, **44**, 2010 (1966).

[14] F. A. Cotton and T. E. Haas, *Inorg. Chem.*, **3**, 10 (1964).

[15] S. F. A. Kettle, *Theoret. Chim. Acta* (Berlin), **3**, 211 (1965).

[16] p is defined in ref 15 as the product of the metal atom Slater orbital exponent and the metal–metal internuclear separation.

[17] G. E. Peterson and P. M. Bridenbaugh, *Rev. Sci. Inst.*, **35**, 698 (1964).

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Magnetic Properties and Electronic Structure of Lanthanum Hydrides[1]

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Previously, the nuclear magnetic properties of the lanthanum hydrides have been interpreted in terms of a protonic model while the bulk susceptibilities have been attributed to a hydridic structure. The experimental results and their theoretical relation to the electronic structure are discussed. A simple band model is used to show that the hydridic structure also can account for the magnetic resonance results. Application of the band model to other metallic hydrides is considered briefly.

Three different models have been used to describe the bonding in metallic hydrides: the protonic model, the atomic model, and the hydridic model. In the protonic model the hydrogen is supposed to exist as an essentially bare proton, the hydrogen electrons having been lost to the conduction band of the metal. In the hydridic model, on the other hand, the hydrogen species is pictured as carrying a full negative charge. The atomic model is an intermediate version; it considers these hydrides to be alloylike in character with a partial charge, either positive or negative, on the hydrogen. The general arguments for and against each of these models have been reviewed by Gibb[3] and by Libowitz.[4]

Nuclear magnetic resonance shifts, similar to the Knight shifts observed in metals, have been observed

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[1] Presented at the 18th Southeastern Regional Meeting of the American Chemical Society, Louisville, Ky., Oct 1966.

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[3] (a) T. R. P. Gibb, Jr., Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 99; (b) *Progr. Inorg. Chem.*, **3**, 315 (1962), see especially pp 335–372.

[4] G. G. Libowitz, "Solid State Chemistry of Binary Metal Hydrides," W. A. Benjamin, Inc., New York, N. Y., 1965.

for both the hydrogen and metal species in metallic hydrides.[5-10] The shifts K and the closely related spin-lattice relaxation times T_1 have generally been interpreted in terms of a protonic model or an atomic model involving a partial positive charge on hydrogen. In contrast, the large amount of magnetic susceptibility data which has been accumulated for rare earth hydrides[11-17] has been interpreted in terms of the hydridic model. Reconciliation of these divergent interpretations is desirable. As a limited step in this direction, we consider here the magnetic properties and electronic structure of lanthanum hydride in terms of a band model. In the course of the discussion, two points of a more general nature are developed: (1) there is an intrinsic ambiguity in the interpretation of the magnetic properties; and (2) there are significant differences between the hydrides of lanthanum (and other rare earth metals) and those of transition metals of groups IVb and Vb.

The magnetic properties reported for lanthanum and lanthanum hydrides[6,11,18,19] are summarized in Table I.

TABLE I

MAGNETIC SUSCEPTIBILITIES, La AND H KNIGHT SHIFTS, AND La SPIN-LATTICE RELAXATION TIMES FOR LANTHANUM METAL AND LANTHANUM HYDRIDES

	$10^6\chi$, emu g^{-1}	K_{La}, %	K_H, %	$1/T_1T$ for La, sec^{-1} deg^{-1}
La	0.69[a]	0.63[b]	...	5,[b] 20[c]
LaH_2	0.40[a]	0.23[d]	*ca.* 0[d]	0.09[d]
LaH_3	−0.17[a]	*ca.* 0[d]	*ca.* 0[d]	...

[a] Measured at 290°K.[11] [b] At 300°K, T_1 by saturation methods.[18] [c] From ref 19, by radiofrequency pulse methods. [d] At 673°K.[6]

We center our attention on the susceptibility χ (on a gram or per atom basis) and on the lanthanum resonance data. Between LaH_2 and LaH_3 χ decreases linearly with increasing hydrogen content; K_{La} also decreases but the decrease becomes progressively more rapid at higher hydrogen content. The very pronounced decrease in $1/T_1T$ for the La nuclear resonance in going from La to LaH_2 is particularly noteworthy. For compositions above LaH_2, χ is independent of temperature. K_{La} is also independent of temperature, at least above 400° where quadrupolar effects are averaged out by hydrogen diffusion and the La resonance was observed.[6]

Theoretical Background

In our analysis of such data we assume distinct s-spin, d-spin, and d-orbital contributions to the paramagnetic susceptibility, the Knight shift, and spin-lattice relaxation. While the electrons in the band cannot be distinguished as being s or d, this formulation provides a convenient method of recognizing the contributions of the various atomic orbitals to the character of the conduction band. On a per atom basis and neglecting diamagnetic contributions, we write therefore

$$\chi = \chi_s + \chi_d + \chi_o \tag{1}$$

$$K = K_s + K_d + K_o \tag{2}$$

$$\frac{1}{T_1} = \frac{1}{T_{1s}} + \frac{1}{T_{1d}} + \frac{1}{T_{1o}} \tag{3}$$

For χ_s we make the usual approximation

$$\chi_s = 2\beta^2 N_s(E_F) \tag{4}$$

where β is the Bohr magneton and $N_s(E_F)$ is the density of s states for one direction of spin at the Fermi energy. The s contributions to the Knight shift[20] and to the relaxation[21] are well known and may be written as

$$K_s = \frac{8\pi}{3}\langle|\psi_s(0)|^2\rangle_{E_F}\chi_s \tag{5}$$

and

$$\frac{1}{T_{1s}T} = \frac{4\pi k}{\hbar}[\beta\gamma_n\hbar\frac{8\pi}{3}\langle|\psi_s(0)|^2\rangle_{E_F}]^2 N_s^2(E_F) \tag{6}$$

Here $\langle|\psi_s(0)|^2\rangle_{E_F}$ represents the density of s states with the Fermi energy, evaluated at the site of the nucleus in question. The relationship among K_s, T_{1s}, and the absolute temperature T was first derived by Korringa.[21] By combining eq 4 and 5, one finds the relation to be

$$1/T_{1s}T = (4\pi k/\hbar)(\gamma_n^2/\gamma_e^2)K_s^2 \tag{7}$$

The d contributions to χ, K, and T_1 have been the subject of extensive discussion in the context of nmr studies of transition metals and their alloys.[22-25] For χ_d we make the approximation

$$\chi_d = 2\beta^2 N_d(E_F) \tag{8}$$

This approximation cannot be expected to be as good as eq 4, but it is sufficiently accurate for the qualitative arguments which follow. For K_d and T_{1d} we write

$$K_d = \frac{8\pi}{3}\langle\rho(0)\rangle\chi_d \tag{9}$$

and

$$\frac{1}{T_{1d}T} = \frac{4\pi k}{\hbar}[\beta\gamma_n\hbar\frac{8\pi}{3}\langle\rho(0)\rangle]^2 N_d^2(E_F)q \tag{10}$$

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(5) D. S. Schreiber, *Phys. Rev.*, **137**, A860 (1965).
(6) D. S. Schreiber and R. M. Cotts, *ibid.*, **131**, 1118 (1963).
(7) D. Zamir, *ibid.*, **140**, A271 (1965); D. Zamir and R. M. Cotts, *ibid.*, **134**, A666 (1964).
(8) R. A. Oriani, E. McCliment, and J. F. Youngblood, *J. Chem. Phys.*, **27**, 330 (1957).
(9) B. Stalinski, C. K. Coogan, and H. S. Gutowsky, *ibid.*, **34**, 1191 (1961).
(10) R. E. Norberg, *Phys. Rev.*, **86**, 745 (1952).
(11) B. Stalinski, *Bull. Acad. Polon. Sci., Classe III*, **5**, 997 (1957).
(12) B. Stalinski, *ibid.*, **7**, 269 (1959).
(13) Y. Kubota and W. E. Wallace, *J. Appl. Phys.*, **34**, 1348 (1963).
(14) R. L. Zanowick and W. E. Wallace, *Phys. Rev.*, **126**, 537 (1962).
(15) W. E. Wallace, Y. Kubota, and R. L. Zanowick, Advances in Chemistry Series, No. 39, American Chemical Society, Washington, D. C., 1963, p 122.
(16) Y. Kubota and W. E. Wallace, *J. Chem. Phys.*, **39**, 1285 (1963).
(17) Y. Kubota and W. E. Wallace, *J. Appl. Phys. Suppl.*, **33**, 1348 (1962).
(18) W. E. Blumberg, J. Eisinger, V. Jaccarino, and T. B. Matthias, *Phys. Rev. Letters*, **5**, 52 (1960).
(19) Y. Masuda, *J. Phys. Soc. Japan*, **19**, 239 (1964).
(20) C. H. Townes, C. Herring, and W. D. Knight, *Phys. Rev.*, **77**, 852 (1950).
(21) J. Korringa, *Physica*, **16**, 601 (1950).
(22) J. Butterworth, *Proc. Phys. Soc.* (London), **83**, 71 (1964).
(23) Y. Yafet and V. Jaccarino, *Phys. Rev.*, **133**, A1630 (1964).
(24) A. M. Clogston, V. Jaccarino, and Y. Yafet, *ibid.*, **134**, A650 (1964).
(25) J. A. Seitchik, A. C. Gossard, and V. Jaccarino, *ibid.*, **136**, A1119 (1964).

where $\langle \rho(0) \rangle$ represents the average s spin density at the nucleus, produced *via* core polarization by the d electrons with energy near E_F. Equation 10 differs from eq 6 primarily in the presence of the reduction factor q, defined by $q = {}^1/_3 f + {}^1/_2(1 - f)^2$, where f is the relative weight of Γ_5 orbitals at the Fermi surface. Thus, q varies between 0.2 and 0.5, depending on the relative amounts of Γ_3 and Γ_5 character at E_F.[23] By virtue of the sensitivity of $N_d(E_F)$ to temperature, the d contributions are expected to exhibit a greater temperature dependence than do the s components. As in the case of the s components, a relation exists between K_d and T_1

$$1/T_{1d}T = (4\pi k/\hbar)(\gamma_n^2/\gamma_e^2)K_d^2 q \qquad (11)$$

The orbital contribution to the paramagnetic susceptibility of conduction electrons has been treated rigorously by Kubo and Obata.[26] We employ an approximation used by Marshall and Johnson[27]

$$\chi_o = (2\beta^2/5\Delta)n(10 - n) \qquad (12)$$

where Δ is an energy parameter approximately equal to the band width and n is the number of d electrons per atom. For K_o and T_{1o} the appropriate relations are[23]

$$K_o = 2\langle r^{-3} \rangle_D \chi_o \qquad (13)$$

and

$$\frac{1}{T_{1o}T} = \frac{4\pi k}{\hbar}[2\beta\gamma_n\hbar\langle r^{-3}\rangle_d]^2 N_d^2(E_F)p \qquad (14)$$

where $p = {}^2/_3 f(2 - {}^5/_3 f)$ and varies between zero and 0.4 depending on the relative weights of Γ_3 and Γ_5 at E_F. The subscripts D and d refer, respectively, to all of the d electrons in the band and those at the Fermi surface only. Because of this difference in the states over which r^{-3} is averaged, it is not possible to write a Korringa-type relation between K_o and T_{1o}.

Application to Lanthanum Hydrides

Several important considerations are apparent upon examining the expressions given above for the three contributions to χ, K, and $1/T_1T$. Each contains a term which will approach zero for either a nearly filled or a nearly empty band: $n(10 - n)$ for χ_o and K_o, and $N(E_F)$ for each of the others. Thus, the decreases observed in χ and in K and $1/T_1T$ for lanthanum upon increasing the hydrogen content are insufficient to distinguish between a conduction band being filled with electrons from hydrogen or a conduction band being depopulated by donation of electrons to the hydrogen species.

The former approach has been taken by Schreiber.[5] He assumed the conduction band to be split in such a way as to have a capacity of six electrons and interpreted the data to indicate a protonic structure. As he noted,[5] the data indicate that the density of states at E_F for LaH_2 must be low compared to that for the metal. A decrease in the orbital contributions is also likely. However, at the composition of LaH_2 metallic character still persists. In LaH_2 as well as at higher hydrogen contents, the hydrogen resonance is observed to be unshifted. The density of conduction electrons must, therefore, be zero or nearly so at the hydrogen nuclei. Schreiber interprets this to mean that each hydrogen has lost its electron to the conduction band and exists as a proton.

Nonetheless, the formation of hydride ions is also consistent with the experimental results. The zero Knight shift found for the protons could be attributed to the shielding effect of filled 1s orbitals on the hydrogens and the absence of any appreciable exchange interactions of the conduction electrons with the hydrogen 1s electrons. The observed decreases in χ and in K and $1/T_1T$ for lanthanum would then be ascribed to depopulation of the conduction band. Either model is capable of direct extension to higher compositions, including nonmetallic LaH_3. A simple band diagram for the hydridic model is shown in Figure 1. It is, in effect, a mirror image of that proposed for the protonic model[28] except that it does not require a split conduction band. The exact shape of the conduction band cannot be determined without an accurate knowledge of all of the parameters appearing in eq 4–14, so this diagram is not intended to be more than qualitative.

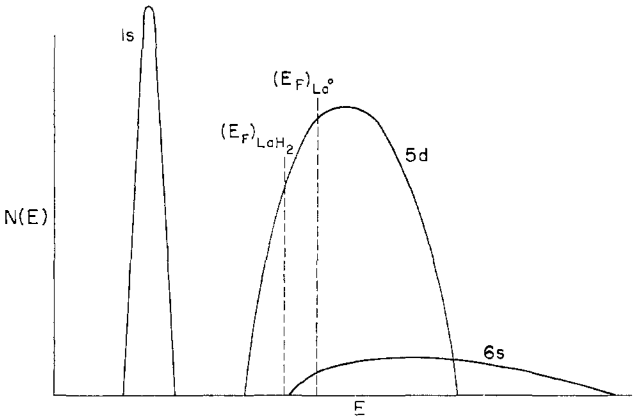

Figure 1.—Possible band structure for lanthanum dihydride (schematic). *For each hydrogen atom entering the lattice, an* electron is assumed to be transferred from the conduction band to a localized hydrogen 1s orbital. Formation of LaH_3 would correspond to an essentially empty conduction band.

To support the choice of the protonic model for the interpretation of the magnetic properties of lanthanum hydrides, Schreiber[5] cites the similarity of K and T_1 for vanadium and for niobium, whether the metal is alloyed with hydrogen or with other metals of a type expected to donate electrons to the conduction band. Indeed, a remarkably close similarity does exist for the properties of these systems.[7] It has been suggested[5] that for the metals of groups IIIb, IVb, Vb, and VIb the conduction band has a nominal capacity of six electrons per metal atom. It would then follow that the capacities of the metals of these groups for hydrogen

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(26) R. Kubo and Y. Obata, *J. Phys. Soc. Japan*, **11**, 547 (1956).

(27) W. Marshall and C. E. Johnson, *J. Phys. Radium*, **23**, 733 (1962).

(28) M. F. Merriam and D. S. Schreiber, *J. Phys. Chem. Solids*, **24**, 1375 (1963).

would be 3, 2, 1, and 0 atoms per metal atom. The limitation on the capacity of the conduction band must be attributed to a minimum in the density of states, so a pronounced decrease in metallic character is predicted for hydrides of compositions approaching their limit. For the hydrides of lanthanum and other IIIb metals such a decrease is observed. There is some evidence[7] that the same is true for the hydrides of group Vb. The properties of group IVb hydrides deviate from this prediction to such a large extent that no definite regularities are apparent. Zirconium hydrides of compositions approaching ZrH_2 are better electrical conductors than zirconium metal[29] and are reported to have magnetic susceptibilities of the same order of magnitude as the metal.[30] The magnetic susceptibility of $TiH_{1.98}$ is half again as large as that of titanium metal.[31]

In terms of a generalized band scheme, a more consistent picture can be developed for the hydrides of groups Ia, IIa, and IIIb, making use of the hydridic model. In this case the limiting composition would be governed by the number of electrons per metal atom available for transfer to the hydrogen species from the conduction band. This model is of course generally accepted for groups Ia and IIa. Although there is not an obvious extension of the scheme to groups IVb and Vb, the extension to group IIIb is not unreasonable. With respect to several properties closely related to electronic structure, LaH_3 resembles the ionic hydrides. The stoichiometry of the metal when saturated with hydrogen is that predicted by the normal maximum positive valence. Upon reaching this composition, the compound has such typically nonmetallic properties as diamagnetism and poor electrical conductivity.

The existence of a dihydride in the lanthanum–hydrogen system can be reconciled with this scheme in a simple manner. There is a decrease in metallic character of the hydride from that of the metal but LaH_2 is still metallic, so it is reasonable to suppose that one electron per metal atom remains in the conduction band at this composition. As a result there would exist residual metal–metal bonding and metallic character. Lower valence state compounds of the rare earth metals are by no means limited to the hydrides. For example, rare earth monosulfides[32] and diiodides[33] have been prepared, and these compounds exhibit metallic character.

Changes in the properties of yttrium and scandium upon hydride formation are closely parallel to those of lanthanum,[5] and the electronic structures of the hydrides may be assumed to be similar. While nuclear magnetic resonance data are not available for other rare earth hydrides, their other properties[34] indicate a close similarity to lanthanum hydrides. The hydrides of other periodic groups appear to differ somewhat. The absence of a proton resonance shift for lanthanum hydrides may be taken as an indication of a large energy separation between the hydrogen 1s orbitals and the conduction band, as assumed in Figure 1. It may be that, for the hydrides of groups IVb and Vb, the energy gap is sufficiently small to permit exchange interactions. Such an explanation is consistent with the observation of the relatively large hydrogen resonance shifts observed in titanium hydrides.[9] That is to say, while either a protonic or hydridic model may be used to account for the nonmetallic character of LaH_3 and for the absence of a hydrogen resonance shift in LaH_2, some modification of either model seems necessary to explain the properties of the hydrides of groups IVb and Vb. A somewhat different approach has been used by Gibb in the interpretation of the magnetic susceptibility data for vanadium[35] and also palladium[36] hydrides. He suggests that the primary effect of hydrogen entering the metallic lattice is due to changes in the metal–metal interactions as a result of the distension of the lattice. Still another approach to the problem of transition metal hydrides is illustrated by a band scheme proposed for the tetragonal-to-cubic phase transition of TiH_2.[37] This compound is treated as a semimetal with an overlap of the valence and conduction bands in the vicinity of the Fermi level. Changes in physical properties on going from one structure to another are attributed to a change in the shape of the bands.

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(29) P. W. Bickel, NAA-SR-4173, Jan 1960.

(30) J. Fitzwilliam, A. Kaufman, and C. Squire, *J. Chem. Phys.*, **9**, 678 (1941); see also ref 3b, pp 416, 424, and ref 4, p 104.

(31) W. Trzebiatowski and B. Stalinski, *Bull. Acad. Polon. Sci., Classe III*, **1**, 131 (1953).

(32) R. Didchenko and F. P. Gortsema, *J. Phys. Chem. Solids*, **24**, 863 (1963).

(33) J. E. Mee and J. D. Corbett, *Inorg. Chem.*, **4**, 88 (1965).

(34) W. G. Bos and K. H. Gayer, *J. Nucl. Mater.*, **18**, 1 (1966).

(35) T. R. P. Gibb, Jr., J. MacMillan, and R. J. Roy, *J. Phys. Chem.*, **70**, 3024 (1966).

(36) T. R. P. Gibb, Jr., and W. A. Norder, *Inorg. Chem.*, **5**, 1947 (1966).

(37) K. Gesi, Y. Takagi, T. Takeuchi, and S. Nuguchi, *Met. Soc. Am. Inst. Mining, Met. Petrol. Engrs., Inst. Metals Div., Spec. Rept. Ser.*, **13**, 45 (1964).