PHYSICAL REVIEW B VOLUME 20, NUMBER 12 15 DECEMBER 1979

Electronic structure of ScH_2

D. J. Peterman and B. N. Harmon
Ames Laboratory-USDOE and Department of Physics, Iowa State University, Ames, Iowa 50011

(Received 11 June 1979; revised manuscript received 5 July 1979)

The self-consistent band structure of ScH_2 has been calculated using an improved potential. The results are compared with experiment and with our previous calculation, which used the standard muffin-tin approximation. The new calculation is in much better agreement with thermomodulation and photoemission data and demonstrates the size and character of changes caused by corrections to the standard muffin-tin approximation. Charge-density distributions are also shown which graphically indicate the charge transfer toward the hydrogen position.

I. INTRODUCTION

In a previous paper[1] (henceforth referred to as II) we have discussed the results of self-consistent calculations for metal hydrides which form in the CaF_2 structure. These calculations for ScH_2 and YH_2 were compared with the optical measurements presented in a paper by Weaver, Rosei, and Peterson[2] (henceforth referred to as I). Although good agreement was found between theory and experiment for the onset of interband transitions and features in the thermomodulation spectra, there was a systematic difference with the theoretical transitions occurring at slightly higher energies. In this paper we present the results of an improved calculation for ScH_2, which confirms our earlier interpretation of the optical spectra and yields transition energies in better agreement with experiment. In addition, the new results agree well with the recent photoemission measurements discussed by Weaver, Peterson, and Benbow[3] in the companion paper (henceforth referred to as III). The improved calculation includes a correction to the standard muffin-tin potential by placing an extra muffin-tin sphere at the unoccupied octahedral site in the lattice. The details of this calculation, along with a comparison to the experiments, are given in the next section. The third section is concerned with charge transfer, and the last section contains our conclusions.

II. CALCULATIONAL DETAILS AND RESULTS

The structure reported for ScH_2 is that of CaF_2 with the metal atoms forming an fcc lattice and the hydrogen atoms occupying the tetrahedral sites located one-quarter of the way up the body diagonal (see Fig. 1 of I). In our previous calculations for this tructure, the muffin-tin approximation was used. The muffin-tin sphere radii were chosen so that the sphere surrounding the metal site extended 65% of the way to the hydrogen position. With this arrangement 47% of the unit-cell volume was contained within the muffin-tin spheres. In other words, the crystal potential was taken as constant over 53% of the unit-cell volume. This was a rather drastic simplification of the potential and led us to question the validity of the muffin-tin approximation. Since with the Korringa-Kohn-Rostoker (KKR) method the potential inside the muffin-tin spheres is treated accurately, the problems caused by approximating the potential as a constant in a large region can be alleviated by including more of the unit-cell volume inside spheres. This is accomplished by considering more nonoverlapping spheres. The benefits of including additional spheres are offset by the increased complexity of the wave-function expansion and greater size of the KKR matrix. In our new calculation one additional sphere was included at the unoccupied octahedral site (one-half of the way up the body diagonal and between the metal atoms along the edge of the fcc lattice). The size of this sphere was taken to be as large as possible without changing the other spheres. The radii of the metal, hydrogen, and octahedral spheres were, respectively, 2.47, 1.41, and 1.93 a.u., where the fcc lattice constant was 9.038 a.u. (4.783 Å). The large octahedral sphere increased the amount of unit-cell volume enclosed within muffin-tin spheres to 74%. Although no nucleus was positioned at the center of the new sphere, it was large enough to contain 0.80 electrons, initially, compared to the 0.71 electrons within the smaller hydrogen spheres. The fractions of volume and charge within muffin-tin spheres for the new calculation are now similar to those for close-packed transition-metal elements where the muffin-tin approximation is frequently adequate.

The band-structure calculation was performed using the standard KKR method, the details of which were discussed in II. The new self-consistent energy bands for ScH_2 are shown in Fig. 1.

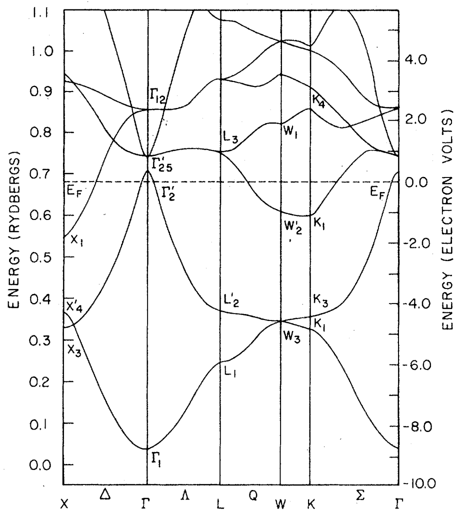

FIG. 1. Self-consistent energy bands of $\mathrm{ScH}_2\square$ calculated with Hedin-Lundqvist exchange and including a muffin-tin sphere (denoted by □) at the unoccupied octahedral site. The lower two bands are largely hydrogen derived and are referred to as the bonding bands in this paper.

In comparison with the previous calculation the hydrogen-derived bonding bands (the two lowest bands, which are largely hydrogen s-like but also have some metal s-, p- and d-like character) are generally lower in energy with respect to the Fermi level, and the d-like complex along Q, W-K, and Σ is narrower. More quantitatively, the difference between our new results and our previous calculation is illustrated by comparing the densities of states (DOS) in Fig. 2. We have labeled the new calculation $\mathrm{ScH}_2\square$ with the □ representing the interstitial sphere.

There are several comparisons to be made with experiments. The optical results of I showed an M_2-type critical-point transition at ~2.95 eV, while our old and new calculated values for this W_2'-W_1 transition are 3.30 and 2.85 eV, respectively. The small underestimation of 0.10 eV in the new calculation is about the best that can be expected, since self-energy corrections were not included in our evaluation of transition energies.[4] The better agreement with experiment results from the narrowing of the splitting between bands 3 and 4 along Q, W-K, and Σ. Another optical feature which is affected by this narrowing is the energy for the onset of interband transitions within the d-band complex. This occurs along the direction Q between band 4 and the states of band 3 near the Fermi level and is reduced from 1.7 to 1.4 eV in the new calculation. In I, Fermi surface transitions were observed in thermoreflectance measurements at 1.3 ± 0.1 eV. The corresponding interband transitions are also evident in the ϵ_2 plots shown in I. The improved agreement for transitions within this d-band complex confirms our original interpretation of the optical spectra and indicates the importance of non-muffin-tin corrections.

The recent photoemission experiments described in III were a prime motivation of our new calculation. A comparison of our old DOS [convolved with a 0.5 eV full width at half maximum (FWHM) Gaussian] and the photoemission experiments for ScH_2 are shown in Fig. 1 of the companion paper (III). Experimentally, the large peak from the hydrogen-derived bonding bands is positioned at 5.1 eV below the Fermi energy, while our original calculation placed this peak at 4.2 eV.

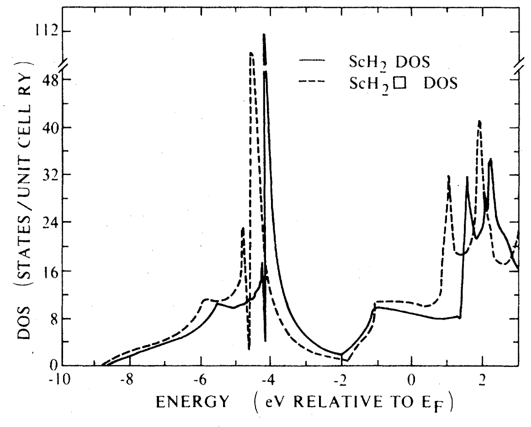

FIG. 2. The electronic density of states (DOS) for the first five self-consistent energy bands of ScH_2 (solid line) and $\mathrm{ScH}_2\square$ (dashed line). The effect of including the new sphere is to lower the bonding bands and narrow the d-like bands.

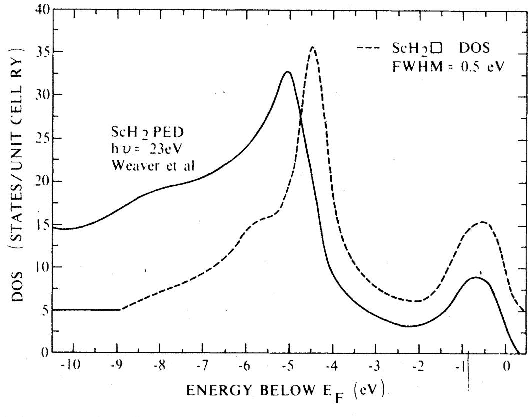

FIG. 3. The $\mathrm{ScH}_2\square$ DOS convolved with a 0.5-eV Gaussian is compared to one of the photoelectron energy distribution (PED) curves of Weaver *et al.*, as was shown in III, compared to our earlier calculation. The PED is shown with arbitrary units with the DOS offset for clarity.

The results of the new calculation along with the experimental spectra (for 23-eV incident energy photons) are shown in Fig. 3. The calculated peak in the bonding bands is shifted downward relative to our previous result by 0.4 eV and is in better agreement with experiment. Also the d-band peak at 1 eV is narrowed and agrees well with experiment. The remaining difference of 0.5 eV between experiment and theory for the position of the peak near 5 eV is probably caused by relaxation. There are other minor considerations, which could also affect the position of this peak. Theoretically, further corrections to the muffin-tin potential (particularly a nonspherical potential within the Sc sphere) may have some effect, as could the vibrational motion of the light hydrogen atoms.

III. CHARGE TRANSFER

In our self-consistent calculations, charge is transferred from the metal site to the hydrogen site. Evidence that charge is transferred toward hydrogen in other metal hydrides is provided by Mössbauer measurements on DyH_2 (Ref. 5) as well as by core-level shifts in $ZrH_{1.65}$,[6] ScH_2,[7] and in other dihydrides studied by Weaver *et al.*[8] Such charge redistribution is also seen in the self-consistent electronic structure calculations of PdH,[9] Pd_6H,[10] and Zr_4H (Ref. 11) as well as in the YH_2 and ScH_2 calculations of II.

To better illustrate the size and nature of the charge transfer in ScH_2, we have plotted the valence-electron charge density along the [100] and [111] directions in Figs. 4 and 5. In these figures the initial valence charge distribution obtained by overlapping the $4s^2$ and $3d^1$ atomic charge densities of the neutral Sc atoms with the $1s^1$ hydrogen densities is shown as a solid curve. The final self-consistent valence-band charge density is shown as the dashed curve. Two trends are immediately obvious: First, charge is transferred to the hydrogen site, and second, the metal d-like charge is quite anisotropic. The charge transfer shown for H in Fig. 4 is very similar to that for H in the Zr_4H calculation of Jena *et al.*[11] shown in Fig. 10 of Ref. 6. The closest peak to the metal site in either of Figs. 4 or 5 is due to the 4s electrons, while the second broader peak is due to the 3d states. The large difference between the two charge densities near the metal nucleus in both figures is caused by the small amount of p character present in the band wave functions. In the [100] direction the d peak near 0.7 a.u. increases as a result of solid-state effects, while in the [111] direction it decreases.

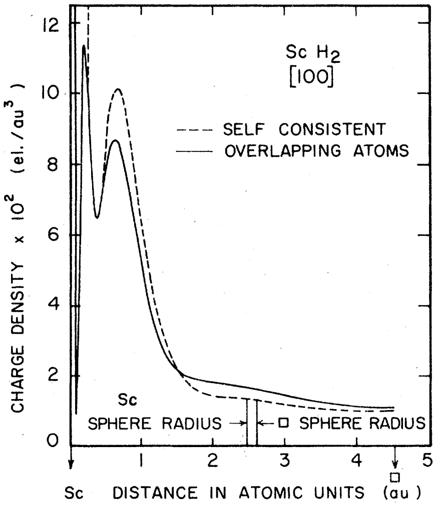

FIG. 4. Charge density in the [100] direction from overlapping the atomic electrons ($3d^14s^2$ and $1s^1$) and from the self-consistent band charge.

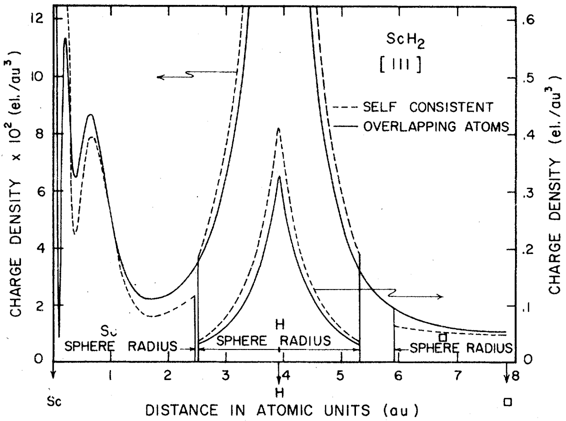

FIG. 5. Charge density in the [111] direction from overlapping atomic electrons ($3d^14s^2$ and $1s^1$) and from the self-consistent band charge.

These changes in charge distribution indicate the lack of d bonding along the [100] direction. Obviously there is some covalent bonding between hydrogen and those metal d-like states with wave functions directed along the [111] direction. This covalency coupled with the ionic bonding is the major reason these compounds are so stable. Hydrogen cannot be viewed as a small perturbation in this lattice.

The amount of charge transferred between the spheres is summarized in Table I for both the old and new calculations. As can be seen, less charge is transferred to the hydrogen sphere from the metal sphere in the new calculations, reflecting the effect of including the octahedral muffin-tin sphere, which has a more repulsive potential than the interstitial average. The actual numbers

TABLE I. Charge inside muffin-tin spheres for the new and old calculation of ScH_2.

	ScH_2 $a = 4.783$ Å						
	New				Old		
	Sc	H	Octahedral	Interstitial	Sc	H	Interstitial
Atomic charge	19.019	0.536	0	0	19.019	0.536	0
Overlapping atoms	19.532	0.707	0.798	1.256	19.532	0.707	2.055
Charge after final interaction	19.336	0.820	0.613	1.411	19.323	0.844	1.989

quoted in Table I should not be taken as a precise quantitative measure of the charge transfer, since these values depend on the chosen muffin-tin radii.

The charge transfer away from the metal site causes the core levels to shift to deeper energy, and this can be observed using various spectroscopies. While an x-ray photoemission spectroscopy (XPS) core-level shift has been reported for the $2p$ cores in ScH_2,[7] the shift was considerably less than that reported in a study of the $2p$ cores in Ti (Ref. 12) (0.2 eV vs 1.1 eV). In both cases however, the metal was simply exposed to hydrogen, so the surface characterization was far from certain. For $ZrH_{1.65}$, a shift of 1.0 eV for the $4p$ levels was reported.[6] In all cases the shift has been to higher binding energy, as expected for charge transfer away from the metal site.

IV. DISCUSSION AND CONCLUSIONS

The trends and conclusions derived from our ScH_2 calculations are applicable to YH_2 and other metallic hydrides with similar structures. In II we were able to relate certain features of the optical spectra with specific transitions within the calculated bands. Although the calculated energies for these transitions were systematically too high, a fairly reliable identification could be made since the experimental trends between ScH_2 and YH_2 were accurately reproduced. The calculations on ScH_2 presented in this paper confirmed our original identifications and showed that the overestimation of the transition energies was caused by the shortcomings of the muffin-tin approximation. One may safely assume that a self-consistent calculation for YH_2 with muffin-tin corrections would yield results in excellent agreement with experiment.

The good agreement between theory and experiment discussed above involves transitions within the d-like bands near the Fermi level. In I no features in the optical spectra could be identified with interband transitions involving the two lowest, largely hydrogen derived, bands. This was partly due to experimental limitations on the photon energy available and perhaps because optical matrix elements for transitions between states primarily located on the H sites to states on the metal sites are small. To study, experimentally, the position of bands 1 and 2, the photoemission measurements in III were undertaken. The comparison of these results for ScH_2 with our convolved DOS in Fig. 3 shows very good agreement and, together with the optical spectra, indicates that the calculated bands are quite accurate. Thus the picture of charge transfer to the hydrogen site (Figs. 4 and 5) is strongly supported.

Finally, the complementary nature of our work with that of Weaver *et al.* and the agreement which we now have with the various experiments allows us to make meaningful observations about the various calculational schemes currently being used for metal dihydrides. In II we discussed the differences observed between the non-self-consistent formalism using full Slater ($\alpha = 1$) exchange that is used by many groups and the self-consistent KKR method using Hedin-Lundqvist exchange-approximation parameters.[4] In the present work we have discussed the changes caused by adding an interstitial sphere to the self-consistent calculations. Although this effect would not be as large if, as is the case with recent non-self-consistent calculations of TiH_2, ErH_2, and TbH_2,[13] a warped muffin-tin potential is used, it does indicate the sensitivity of the bands to various calculational schemes. This sensitivity is especially important when interpreting optical spectra. However, there are other features in the bands that are not affected by different calculational methods, and this can be equally important. For example, Gupta has related a peak in the DOS of TiH_2 at E_F to an electronically driven tetragonal distortion.[13] Though this was a non-self-consistent calculation, she surmised, based on her calculations of TbH_2 and ErH_2, that the presence of this peak at E_F was sensitive neither to the initial atomic configuration nor to the use of a self-consistent potential. We have found this to be the case for all our calculations of ScH$_2$ and YH$_2$. That is, if we rigidly move the Fermi level to account for an added electron for TiH$_2$ or ZrH$_2$, we find that it occurs in the same peak (the first one above E_F in Fig. 2) of the DOS. This is true both for our nonself-consistent (d^1s^2 or d^2s^1) and our self-consistent (with or without the interstitial sphere) results.

ACKNOWLEDGMENTS

This work was supported by the U. S. Department of Energy, Contract No. W-7405-ENG-82, Division of Materials Sciences budget code AK-01-02-02-2. The authors wish to thank D. T. Peterson, D. W. Lynch, R. G. Barnes, D. Torgeson, and, especially, J. H. Weaver for their continuing encouragement and helpful discussions.

---

[1] D. J. Peterman, B. N. Harmon, J. Marchiando, and J. H. Weaver, Phys. Rev. B 19, 4867 (1979), termed II herein.

[2] J. H. Weaver, R. Rosei, and D. T. Peterson, Phys. Rev. B 19, 4855 (1979), termed I herein.

[3] J. H. Weaver, D. T. Peterson, and R. L. Benbow, preceding paper, Phys. Rev. B 20, 5301 (1979), companion paper termed III herein.

[4] L. Hedin and B. I. Lundqvist, J. Phys. C. 4, 2064 (1971).

[5] J. M. Freidt, G. K. Shenoy, B. D. Dunlap, D. G. Westlake, and A. T. Aldred, Phys. Rev. B 20, 251 (1979).

[6] B. W. Veal, D. J. Lam and D. G. Westlake, Phys. Rev. B 19, 2856 (1979).

[7] J. K. Gimzewski, D. J. Fabian, L. W. Watson, and S. Affrossman, J. Phys. F 7, L305 (1977).

[8] J. H. Weaver (private communication).

[9] D. A. Papaconstantopoulos, B. M. Klein, E. C. Economou, and L. L. Boyer, Phys. Rev. B 17, 141 (1978).

[10] P. Jena, C. L. Wiley, and F. Y. Fradin, Phys. Rev. Lett. 40, 578 (1978). Further results discussed in Ref. 6.

[11] P. Jena, F. Y. Fradin, and D. E. Ellis (unpublished), results discussed in Ref. 6.

[12] R. L. Park and J. E. Houston, Adv. X Ray Anal. 15, 462 (1972).

[13] M. Gupta, Solid State Commun. 29, 47 (1979).