PHYSICAL REVIEW B VOLUME 6, NUMBER 12 15 DECEMBER 1972

Temperature-Dependent Electronic Transition in Cerium Hydride

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(Received 23 June 1972)

Resistivity measurements of single crystals of cerium hydride as a function of temperature revealed resistivity anomalies at about 250 °K, which may be associated with a previously reported compositional metal-to-semiconductor transition. Precise x-ray diffractometry disclosed that the cubic fluorite type structure of cerium hydride becomes slightly tetragonal below 250 °K. Neutron-diffraction investigations showed no apparent ordering of excess hydrogen atoms in octahedral interstices and magnetic-susceptibility measurements showed no magnetic ordering. Results of thermoelectric-power measurements are in agreement with a model involving the formation of a defect band to explain the metallic behavior of cerium hydride.

INTRODUCTION

Cerium reacts with hydrogen to form a dihydride CeH_2 which has the cubic fluorite structure, and which exhibits wide deviations from stoichiometry with compositions ranging from $CeH_{1.9}$ to CeH_3.[1] It has been shown[2–4] that for samples whose atomic ratio H/Ce exceeds 2, the excess hydrogen atoms enter the octahedral interstices of the fluorite-type lattice such that all the interstices are occupied at the limiting composition CeH_3 with no apparent change in structure. A recent neutron-diffraction study[5] has indicated that the interstitial hydrogen atoms are slightly displaced from the center of the octahedral sites.

Previous electrical-resistivity studies[6,7] on cerium hydride have established that this compound undergoes a composition-dependent metal-to-semiconductor transition at a composition corresponding to an H/Ce ratio of about 2.8. Resistivity measurements as a function of temperature on samples whose H/Ce ratio is less than 2.7 showed metallic conductivity in that resistivity increased monotonically with temperature in the range 150–310 °K. At the composition $CeH_{2.85}$, there was an exponential increase in resistivity with reciprocal temperature characteristic of a semiconductor (ρ was 0.3 Ω cm at 300 °K and 500 Ω cm at 160 °K).[7]

In the investigation described in this paper, the properties of cerium hydride samples with compositions in the vicinity of the compositional transition ($CeH_{2.7}$-$CeH_{2.8}$) were examined as a function of temperature.

RESISTIVITY MEASUREMENTS

Resistivities of cerium hydride single crystals were measured as a function of temperature using a four-point probe. Since the samples are extremely reactive with air and moisture, all measurements were carried out in an inert-atmosphere glove box. The growth of the crystals[8] and the details of the experimental technique have been described previously.[9] The results of measurements on samples of $CeH_{2.71}$, $CeH_{2.74}$, and $CeH_{2.77}$ are shown in Figs. 1–3. In every case there is a sharp rise in resistivity indicative of a transition at about 245 °K as the temperature of the sample is lowered. Further cooling leads to an apparent decrease in resistivity, although there is a great deal of experimental scatter at low temperatures. We believe that the nonreproducibility at the lower temperatures is due to poor contact between probe points and the crystal, since it was observed that the spring tension in the probe had a tendency to become weaker at low temperatures. The decrease

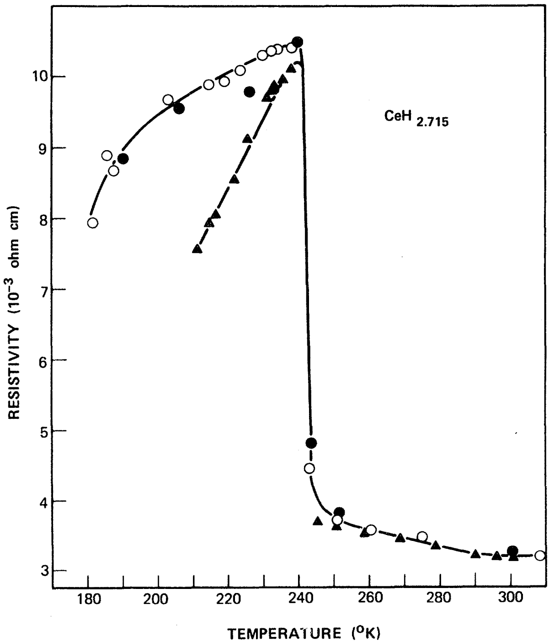

FIG. 1. Resistivity of a single crystal of $CeH_{2.715}$ as a function of temperature.

in resistivity at lower temperatures is probably real, although its magnitude is uncertain. However, the transition at 245 °K is quite reproducible, with no evidence of hysteresis.

Measurements on a $CeH_{2.81}$ sample also indicated a sharp transition at a somewhat lower temperature (~ 234 °K). In this case, however, the resistivity continued to increase below the transition. Figure 4 shows the logarithmic variation of resistivity as a function of reciprocal temperature for this sample. There is a linear dependence below the transition temperature indicating that $CeH_{2.81}$ is a semiconductor at the lower temperature. The activation energy for conduction is 0.10 eV as compared to 0.15 eV for the $CeH_{2.85}$ composition.[7] The reproducibility of the measurements for the $CeH_{2.81}$ sample over the course of four separate runs was excellent.

An electrical-resistivity study of cerium deuteride of composition $CeD_{2.15}$ yielded data which were identical to that of the corresponding hydride (metallic region). The results on $CeD_{2.75}$ were similar to the data for the hydrides shown in Figs. 1–3 except that the transition temperature was shifted from about 245 to 250 °K.

NEUTRON DIFFRACTION

At H/Ce = 2.75, 75% of the octahedral interstices in the cerium hydride lattice are occupied by hydrogen and 25% are vacant. Room-temperature neutron-diffraction studies[2] indicated that the excess hydrogen atoms (above H/Ce = 2.0) are essentially randomly distributed over the octahedral interstices. Consequently, the possibility exists that the electronic transition observed at 245–250 °K may be due to ordering of the hydrogen atoms in the octahedral interstices at low temperatures. In order to determine if this were the case, neutron-diffraction studies of cerium deuteride $CeD_{2.75}$ were carried out. The deuteride was used rather than the hydride because the neutron back-

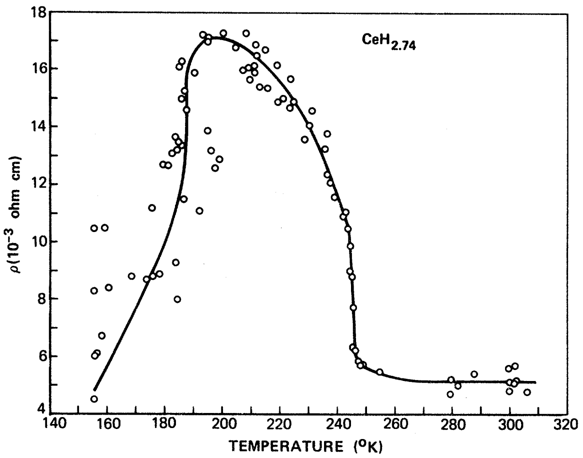

FIG. 2. Resistivity of a single crystal of $CeH_{2.74}$ as a function of temperature.

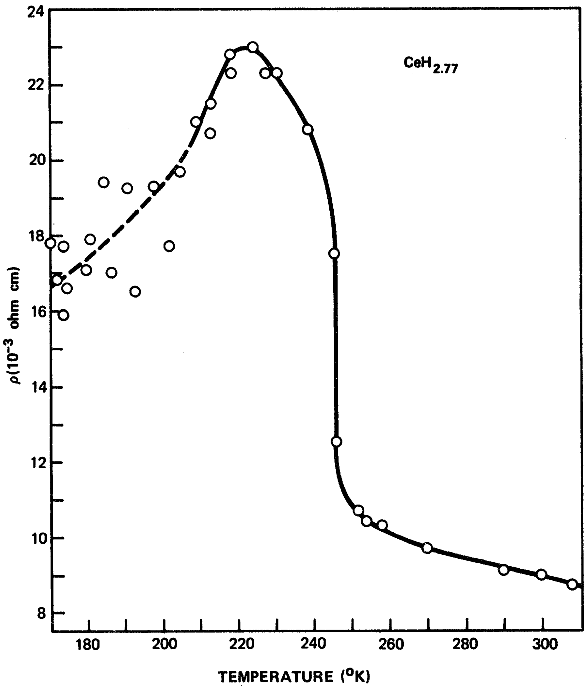

FIG. 3. Resistivity of a single crystal of $CeH_{2.77}$ as a function of temperature.

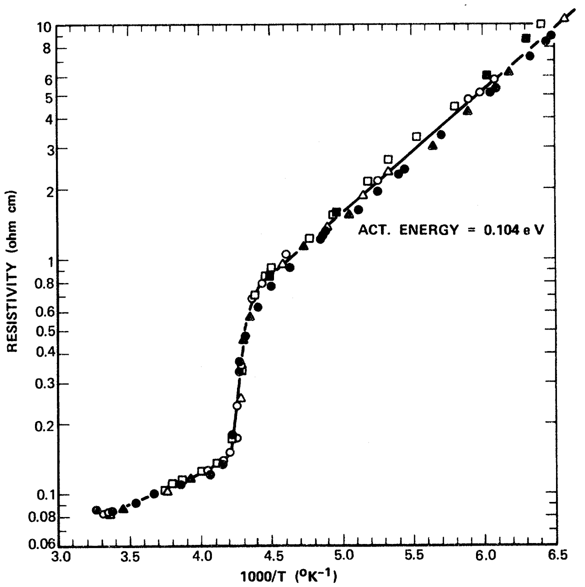

FIG. 4. Logarithmic variation in resistivity with reciprocal temperature for a single crystal of $CeH_{2.81}$.

ground scattering of deuterium is considerably less than that of hydrogen thus making it easier to determine the deuterium (or hydrogen) positions in the lattice.

Polycrystalline $CeD_{2.75}$ was prepared by direct reaction of cerium metal and deuterium gas. The sample was pulverized under inert atmosphere in a glove box[10] and loaded into a cell designed to handle air-sensitive materials at low temperatures. The cell unit consists of an aluminum cell block containing a sample cavity, cover plate, and cadmium neutron shield. The cell was cooled with cold nitrogen gas (obtained by gasifying liquid nitrogen) which is directed by a thin stainless-steel shroud across the front and back sides of the cell. Temperature control was achieved by a gas preheater or by mixing warm dry nitrogen gas with the cold-nitrogen-gas stream. A copper-constantan thermocouple located in the cell wall was used to monitor the temperature of the cell, which was usually stable to about ± 2 °C. During a run it was sometimes necessary to remove frost particles with an occasional sweep of a long-handled brush. The entire cell assembly was fitted to the neutron spectrometer and the cell window was aligned with the neutron beam and counter.

The neutron spectrometer designed by Dr. Chang Choi at the Army Material and Mechanics Research Laboratory at Watertown, Mass. was used in these investigations. The wavelength of the thermal neutrons was 0.985 Å and counts were taken at intervals of 0.2° in 2θ. Runs were made at room temperature and at 210 °K. The resulting diffraction patterns are illustrated in Fig. 5.

Although the 210 °K run is well below the transition observed in the resistivity measurements, it can be seen that the two sets of patterns are identical and they contain only the peaks to be expected for the fluorite lattice with randomly occupied octahedral interstices. Thus, there does not appear to be any ordering of the deuterium at the lower temperature within the detectability of this investigation. However, the possibility was considered that any superlattice peaks due to ordering of the hydrogen (deuterium) atoms may be too weak to be observed. The two most likely cases of hydrogen ordering are assumed to be (i) one in which the body-centered position in the unit cell is regularly vacant leading to a primitive cubic lattice or (ii) a layered structure in which the body-centered position is occupied by hydrogen, but the other octahedral sites on the cube edge in that layer are vacant, leading to tetragonal symmetry. Theoretical intensities were computed for each of these cases, and it was found that some of the peaks in each ordered structure should be of sufficient intensity to have been observed in the present investigation.

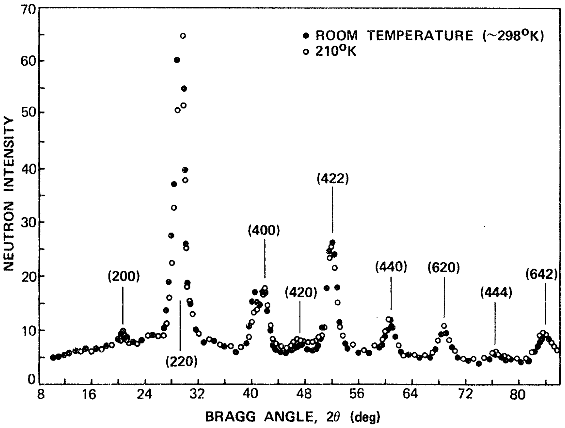

FIG. 5. Neutron diffraction pattern of a polycrystalline sample of cerium deuteride $CeD_{2.75}$.

It should be mentioned that the recent investigation by Cheetham and Fender[5] using a more intense neutron source indicates long-range ordering of hydrogen atoms in some hydrogen-rich samples, particularly at lower temperatures. Although the sample of $CeD_{2.75}$ showed no long range ordering at room temperature, superlattice peaks appear at 90 and 4.2 °K. The nature of the ordering giving rise to these extra peaks has not yet been established, and it is not clear whether this apparent ordering is related to the anomaly at 250 °K.

MAGNETIC SUSCEPTIBILITY

Magnetic-susceptibility measurements on a sample of $CeH_{2.75}$ were performed by Wold, Catalano, and Nahigian at Brown University. The measurements were made with a Faraday balance using a field strength of 6600 G, and the results as a function of temperature are shown in Fig. 6. It can be seen that the hydride exhibits Curie–Weiss behavior. Although there is a slight change in slope at about 255 °K, the temperature at which the electronic transition occurs, there does not appear to be a magnetic transition. The Weiss and Curie constants for the data below 250 °K were − 7 °K and 0.76, respectively, which is in excellent agreement with Stalinski's[6] values of − 11 °K and 0.76 for a sample of $CeH_{2.78}$. However, Stalinski reports no break in the $1/\chi$-vs-T curve in the range 80–290 °K.

X-RAY DIFFRACTION STUDIES

Although neutron-diffraction studies showed no apparent change in diffraction pattern between samples above and below the transition temperature, the possibility existed that a subtle change in structure beyond the resolution of the neutron spectrometer may be occurring at the transition temperature. Consequently, precise x-ray diffractometer

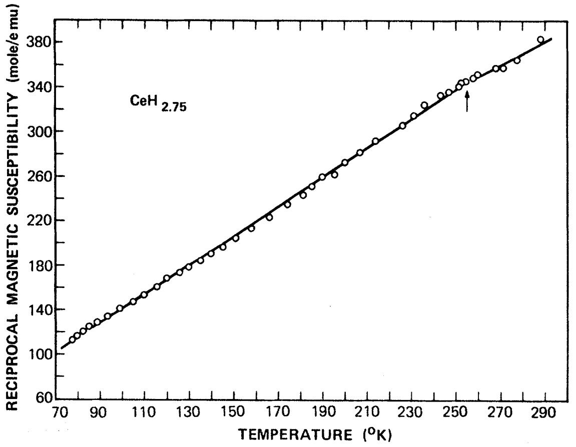

FIG. 6. Magnetic susceptibility of $CeH_{2.75}$ as a function of temperature.

studies with slow scan speeds of $\frac{1}{8}$ °/min or $\frac{1}{4}$ °/min in 2θ were carried out as a function of temperature. The investigation was performed on the same sample of cerium deuteride $CeD_{2.75}$ as was used for the neutron-diffraction measurements.

The low-temperature cell used to hold the sample is similar to one described by Calhoun and Abrahams[11] with some modifications. The cell was constructed from solid aluminum. Cooling was provided by circulating liquid nitrogen through a cryogenic well containing a baffle for more uniform cooling. The liquid nitrogen was fed to the cell through a cryogenic metering valve permitting controlled temperatures of ± 2 °C for runs down to − 100 °C. In order to prevent reaction of the sample with air and moisture, the sample cavity was provided with a hermetically sealed beryllium window. The sample was loaded into the cell in an inert-atmosphere glove box.[10] A thermocouple well under the sample cavity contained a copper-constantan thermocouple which permitted the temperature to be monitored during a run. The whole unit was attached directly to the goniometer shaft of a Norelco high-angle x-ray spectrometer, and thermal insulation between the two was provided by mica spacers.

In order to prevent the formation of frost on the unit during cooling, a polyethylene bag was fitted over the entire assembly and attached with tape to the goniometer shaft. The bag was kept inflated by flowing helium gas into it, and a stream of warm dry nitrogen was directed on the outside of the bag. This procedure prevented formation of frost on the cell, the top of the plastic bag, and the goniometer shaft.

At room temperature, a lattice parameter of 5.5253 ± 0.0010 Å was determined for the $CeD_{2.75}$ sample. As the sample was cooled, this value decreased linearly to 5.5223 at 255 °K. Somewhere between 255 and 248 °K selective broadening of the diffraction peaks occurred and the extent of broadening increased with decreasing temperature below 248 °K. The (111) and (222) peaks remained sharp at low temperatures, but the (200), (331), and (422) peaks broadened and the (531) and (442), (600) peaks showed slight splitting. This behavior is indicative of a cubic to tetragonal phase transition in which the (200), (331), and (422) peaks split into two peaks each, (200) and (002), (331) and (313), and (422) and (224), respectively. Similarly, the (531) peak splits into three peaks, (531), (153), and (315), and the (600), (442) peak splits into four peaks, (600), (006), (442), and (424). Since the crystal axes remain orthogonal as the crystal becomes tetragonal, the (111) and (222) peaks would remain unsplit which is in agreement with the observation that these peaks did not broaden. It was also observed that the broadening of the (200) and (331) peaks was asymmetric, with the (200) peak tailing toward lower 2θ values and the (331) peak towards higher 2θ values. This is consistent with a c/a ratio greater than unity in the tetragonal phase.

Lattice parameters of the tetragonal phase were calculated from the (331), (313), (422), (111), (200), and/or (002) peaks. Results are shown in Fig. 7 along with the calculated variations in c/a ratios and unit cell volumes. Errors shown are the minimum estimated errors. It can be seen that the x-ray transition from cubic to tetragonal structure occurs at about the same temperature (~ 252 °K) as the resistivity transition.

It should be mentioned that a similar crystallographic transition occurs in titanium dihydride[12,13] which also has the cubic fluorite structure. As the dihydride (or dideuteride) is cooled below 310 °K, the cubic phase becomes tetragonal. In this case, however, the c/a ratio is less than unity. As in the case of the cerium hydride, the degree of tetragonality increases with decreasing temperature. However, the extent of the change is much lower in cerium hydride. For example, at 150 °K below the transition temperature, the c/a ratio of titanium dideuteride differs from unity by about 5%. With cerium hydride, there is only a 0.7% change in c/a ratio. It is probably because of this very small change that the effect was not observed in our neutron diffraction investigation, since the neutron spectrometer did not have the resolution of the x-ray spectrometer. For example, the (200) peak width at half-height was 0.25 ° in the x-ray work and 1.5 ° in the neutron diffraction patterns.

Since the temperature-dependent electronic transition at about 250 °K is associated with the onset of tetragonality, x-ray studies were carried out on a hydrogen-rich sample of cerium hydride to deter-

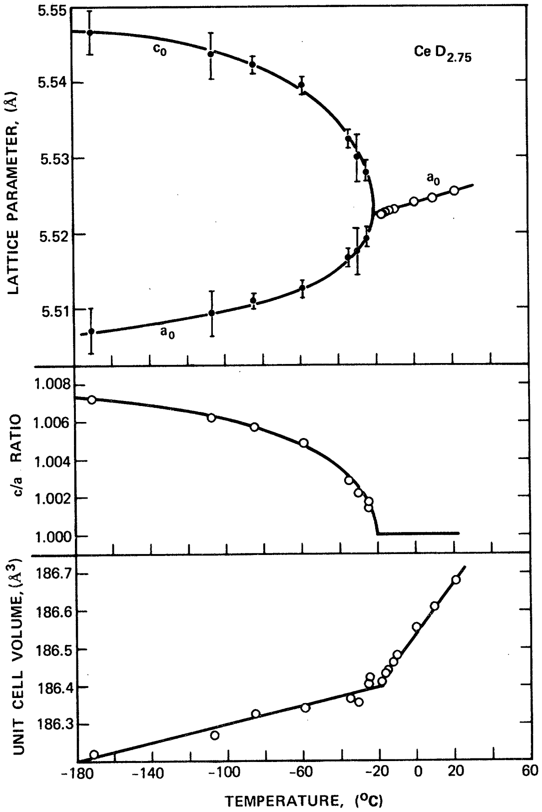

FIG. 7. Variations of lattice parameters, *c/a* ratio, and cell volume of cerium deuteride $CeD_{2.75}$ as a function of temperature.

mine if the composition dependent metal-to-semiconductor transition has a corresponding structural change. X-ray patterns of a polycrystalline sample of $CeH_{2.96}$ taken in a symmetrical focusing back reflection camera revealed no line broadening or splitting. Some extra lines were observed in the patterns but these were attributed to one or more of the many cerium oxides[14] caused by slight oxidation of the very reactive sample. Therefore, it appears that cerium hydride does not undergo a structural change during its compositional transition from metal to semiconductor with increasing hydrogen content.

THERMOELECTRIC POWER

Thermoelectric-power measurements were carried out on several crystals of cerium hydride using the following procedure. A crystal (3–5 mm thick) was placed on a cold stage inside an inert-atmosphere glove box (see Ref. 9). Temperatures were measured by placing the junction of one copper-constantan thermocouple at the bottom of the crystal in contact with both the crystal and the cold stage, and the junction of another thermocouple on the surface of the crystal. The copper lead of each thermocouple was also connected to a Keithly 153 microvoltmeter.

Seeback coefficients as a function of temperature for four different samples are shown in Fig. 8. Temperatures shown are the average temperature between the bottom and top of the crystal. Because of the relatively crude measurements, these Seebeck coefficients are probably not quantitatively significant. However, the purpose of these measurements was merely to determine signs and trends with temperature. It can be seen that for a sample of $CeH_{2.38}$ (which is well within the metallic region) the Seebeck coefficient is positive and independent of temperature as would be expect from metallic behavior. On the other hand, for the $CeH_{2.85}$ crystal, the Seebeck coefficient is negative and the absolute value increases with decreasing temperature, which is characteristic of semiconductor behavior.

DISCUSSION

Since the bonding in rare earth hydrides is essentially ionic,[15] the lattice of cerium hydride consists of Ce^{+3} cations and H^- anions. The experimental results described above can be explained with the following model.[7] At the composition CeH_3 when all the octahedral interstices are occupied, the +3 oxidation state of the cations are completely balanced by the three hydrogen anions

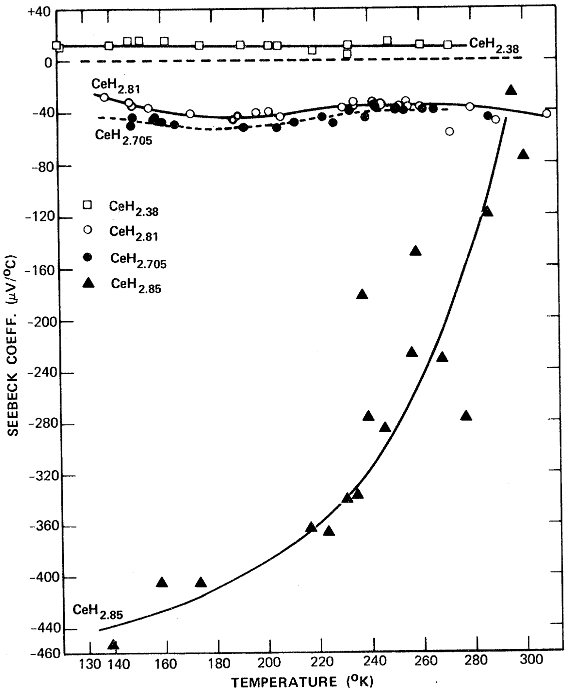

FIG. 8. Seebeck coefficients of single crystals of cerium hydride as a function of temperature.

per Ce^{+3} ion and the hydride should be an insulator with the 1*s* valence band of hydrogen completely filled and the 5*d* (or 5*d*-6*s*) conduction band of cerium completely empty. As hydrogen is removed from the CeH_3 composition, vacancies are formed creating donor levels in the band structure as shown in Fig. 9(a), and the hydride should act as an *n*-type semiconductor. The concentration of donor levels increases with further decrease in hydrogen content until the composition $CeH_{2.8}$ is reached (about 20% of the octahedral positions vacant), at which point overlap of the vacancy orbitals occurs, and there is a transition from a localized electron situation to a narrow defect band (analogous to an impurity band in semiconductors) as shown in Fig. 9(b). The formation of the defect band corresponds to a Mott-type[16] semiconductor-to-metal transition at $H/Ce \simeq 2.8$.

Since the defect band is half filled, the type of conductivity (*n* type or *p* type) would depend upon the density of states distribution in the band. Hall-effect measurements[17] of samples in the metallic range (CeH_2 to $CeH_{2.7}$) showed *p*-type conductivity, in agreement with the positive values for Seebeck coefficients shown in Fig. 8 for the $CeH_{2.38}$ sample. However, the model used here requires that in the semiconductor range ($H/Ce > 2.8$) the sample be *n* type. Although, Hall-effect measurements were not carried out in this region, it can be seen in Fig. 8 that the semiconductor sample $CeH_{2.85}$ does indeed show negative Seebeck coefficients.

In addition to the temperature-dependent resistivity anomaly observed in the range $CeH_{2.7}$ to $CeH_{2.8}$, NMR studies as a function of temperature by Howling[18] show a sharp decrease in the amplitude of the hydrogen resonance peak at 250 °K for a sample of $CeH_{2.75}$. On the other hand, no significant changes in peak amplitudes were observed in samples of $CeH_{2.50}$ (metallic) and $CeH_{2.92}$ (semiconductor). Specific-heat measurements[19] as a function of temperature of cerium hydride at compositions close to the semiconductor region showed a definite anomaly at 255 °K. The fact that the resistivity, NMR, and specific-heat anomalies occur near the composition where the compositional metal-to-semiconductor transition takes place ($CeH_{2.8}$), indicates that they are associated with this transition, and that they may correspond to a temperature-dependent metal-to-semiconductor transition.

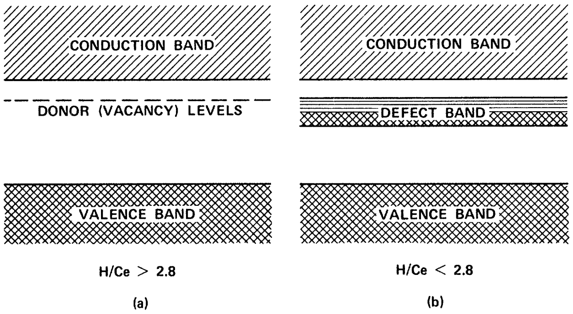

FIG. 9. Proposed band structure of cerium hydride.

In order for a metal-to-semiconductor transition to occur as a sample of $CeH_{2.7-2.8}$ is cooled, the narrow defect band shown in Fig. 9(b) must somehow break up into localized states at the transition temperature of 250 °K. Adler and Brooks[20] have shown that a material with a narrow partially filled conduction band can reduce its total energy by distorting to a lower symmetry with a corresponding splitting of the band due to higher order terms in the crystalline field, thus leading to semiconduction. This could be the situation in $CeH_{2.7-2.8}$ below 250 °K when the crystal becomes tetragonal. As the temperature is raised, the band gap vanishes at 250 °K, due to excitation of free carriers, and the hydride becomes a metal.

ACKNOWLEDGMENT

The authors would like to thank Dr. Chang Choi of Picatinny Arsenal for assistance in the neutron diffraction work, Professor Aaron Wold and associates of Brown University for performing the magnetic-susceptibility studies, Dr. D. H. Howling of this laboratory for making his NMR results available to us, and Professor Gabor Kemeny of Michigan State University for many valuable discussions on theories of the metal-to-semiconductor transition.

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Relation between Elastic Tensors of Wurtzite and Zinc-Blende Structure Materials

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(Received 17 April 1972)

A transformation is derived which relates the fourth-rank elastic tensors of the two common modifications of tetrahedrally coordinated compounds, cubic zinc blende (ZB), and hexagonal wurtzite (Wz). The basic assumptions are that the local tetrahedra extending to second neighbors about each atom are rotated but otherwise identical in the two structures, and that differences between ZB and Wz for third and more distant neighbors are negligible. The procedure involves Robinson's rotations which apply to any tensorial property, to which is added internal strain between the two inequivalently oriented tetrahedra in the Wz structure. Good agreement is found with empirical constants of ZnS which have been measured in both structures. The transformation permits a simple derivation of "effective" cubic constants for Wz compounds, which are sufficient to extract the most important information on average tetrahedral forces. Effective constants are compared with measured ZB constants for the entire range of tetrahedrally coordinated compounds.

I. INTRODUCTION

It has long been recognized that crystals having the wurtzite (Wz) or sphalerite (zinc blende or ZB) structures are fundamentally similar despite differences between the two structures. ZB crystals are fcc (T_d) with two atoms per primitive cell, whereas Wz crystals are hexagonal (C_{6v}) with four atoms per cell. The fundamental relation between the two structures is that the local environment of any atom in either ZB or ideal Wz ($c/a = 1.633$) is exactly the same through the second neighbor. The two lattices differ only in the arrangement of third and more distant neighbors. Robinson[1] has expressed the relation between ZB and ideal Wz succinctly: Each lattice can be constructed from tetrahedral building blocks. In ZB all tetrahedra are equivalent, but in Wz there are two inequivalently oriented tetrahedra each of which can be related to the standard orientation of ZB tetrahedra by a simple rotation. Thus we expect that a given chemical compound is basically the same, independent of the structure in which it crystallizes, and that, to a good approximation, the tensorial representations of any physical property in the two systems are related by simple rotations.

The fundamental correctness of this comparison of Wz and ZB crystals is most clearly seen by comparing empirical data for compounds (such as ZnS) which can crystallize in either form. For a large range of materials, both modifications have essentially the same first- and second-neighbor separations.[2,3] Furthermore, the lattice constants for Wz crystals reveal only small deviations from the ideal c/a ratio[2,3] so the ideal approximation is justified for many properties. Close correspondence between Wz and ZB crystals may be seen in the total energies,[3–5] Raman frequencies,[6] electronic bands,[7,8] dielectric constants,[4] as well as other properties.

The close correspondence of Wz and ZB crystals has been documented by Phillips[4] and Van Vechten[4] in terms of a "universal semiconductor model." They have shown that many properties of the entire range of tetrahedrally coordinated compounds are continuous functions of two variables, lattice constant and ionicity, independent of the structure Wz or ZB. Similar conclusions may be drawn from chemical bond analyses, such as that of Pauling,[9] who implicitly ignores the difference between the structures in his molecular approach. The common feature of the above analyses[4,9] is