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E. E. Vainshtein, M. N. Bril, I. B. Staryi, M. E. Kost

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Abstract

Full Text

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On Some Results of an X-ray Spectral Study of Cerium and Lanthanum Hydrides

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Recently there has been great interest in the hydrides of transition and, in particular, rare-earth elements (REE). This is connected primarily with the possibilities for their broad practical application in metallurgy, vacuum technology, the practice of inorganic synthesis, and a number of other fields. At the same time, a comprehensive study of these compounds, which belong to phases of variable composition with very distinctive properties, is also of independent scientific interest, since it opens up broad possibilities for investigating questions connected with the nature of the chemical bond in berthollide phases. Attention was drawn to this latter circumstance already by N. S. Kurnakov ([1]).

Fig. 1. Schematic representation of the apparatus for working with REE hydrides.

In recent years a considerable number of studies have been carried out devoted to the investigation of the conditions of preparation, composition, and properties of the hydrides of various REE ([2]). The Ce–H system has been studied especially thoroughly. Phase relations in the Me–H system, the crystal structures of the dihydrides of various REE, the thermal stability and regions of existence of the compounds established in these systems have been studied; dissociation isotherms and the conditions of hydrolysis of hydrides at various temperatures have been investigated; and, finally, for some systems data have been obtained on the electrical conductivity and magnetic properties of phases with different hydrogen contents. All this has considerably enriched our knowledge of the properties of REE hydrides and has made it possible to formulate certain general conclusions regarding the nature of interatomic interaction in these compounds, the range of applicability and significance of which sometimes go beyond the limits of the group of substances investigated. The most important of these

conclusions concern the question of the presumed ([3]) valence state of REE atoms in hydrides and the nature of the chemical bond within the single-phase berthollide region (MeH_2—MeH_3), for which, for example in the Ce–H system, a gradual weakening of the degree of metallic bonding and an increase in its ionic character as the trihydride is approached has been experimentally established. In this connection it was suggested that within this solid phase there is an equilibrium coexistence of two forms of cerium valence and a gradual change in the nature of the chemical bond ([2]).

The validity of the conclusions reached has so far not been subject to direct experimental verification.

In the present work such an attempt is made for the first time by using the method of X-ray spectral analysis. The cerium and lanthanum hydrides studied were obtained by the direct action of hydrogen on the metal. Provided that the metal surface is thoroughly cleaned, hydriding can be carried out at room temperature without preliminary heat treatment of the metal. The hydride formed under these conditions is close in composition to the trihydride. By heating with evacuation of the hydrogen evolved, specimens with a lower hydrogen content were obtained. At the same time, as verification showed, holding this hydride at room temperature under vacuum ($\sim 10^{-3}$ mm Hg) does not lead to a change in its composition*.

It was established ([4]) that, as cerium is saturated with hydrogen, a change is observed in the density of the hydrides from the value 6.49 g/cm^3, characteristic of metallic cerium, to the minimum value 5.43 g/cm^3, corresponding to the dihydride. In the single-phase region CeH_2–CeH_3 there is a slight increase in the density of the hydrides, accompanied by a decrease in the period of the cubic face-centered lattice from the value characteristic of the dihydride, 5.55 Å, to 5.53 Å, corresponding to a hydride of composition $CeH_{2.73}$. Accurate determination of the lattice period for a hydride strictly corresponding to the composition CeH_3 proved difficult because of the broadening of the lines on the Debyegrams of this compound.

Bearing in mind the aims of the present investigation, Berthollide phases in the La–H and Ce–H systems were prepared and subjected to X-ray spectral study: three lanthanum hydrides of compositions $LaH_{1.97}$, $LaH_{2.26}$, and $LaH_{2.66}$ and four cerium hydrides–CeH_2; $CeH_{2.24}$; $CeH_{2.59}$, and $CeH_{2.97}$. The hydrogen content in the hydrides was determined volumetrically with an error of $\sim 0.5\%$ ([5]).

When working with rare-earth hydrides, and especially with cerium hydrides, difficulties arise associated with the need to prevent the possibility of their contact and interaction during the investigation with oxygen and water vapor in the air. Cerium hydrides ignite in air. Therefore, in carrying out the X-ray spectral investigations, a special procedure was used. The absorbers were prepared by rubbing the corresponding hydride specimens into the pores of thin silk matter, after which they were sealed into two-layer polyethylene packets and

Figure 2

Figure 2: Figure 2

hermetically sealed by fusing the plastic film along the contour of the absorber with the aid of a special heated stamp. All preparatory operations connected with the preparation of the absorbers were carried out in a special dry chamber in an atmosphere of carbon dioxide (Fig. 1). Under these conditions, as was shown earlier ([5]), passivation of the surface of cerium hydride takes place, not, however, leading to a change in its composition. The hydrides to be investigated were also stored, in order to avoid their change with time, in carefully sealed test tubes in an atmosphere of carbon dioxide. After preparation, the absorbers were immediately placed in a special holder–

Fig. 2. LIII absorption spectra of cerium in the dioxide (5) and in CeH_n hydrides with different relative hydrogen contents. 1 –n = 2.97; 2 –2.59; 3 – 2.24; 4 –2.00

* The latter circumstance is very important, since it makes it possible to carry out X-ray spectral investigation of hydrides in a vacuum spectrograph without special precautions.

body in vacuum and remained there throughout the entire exposure time. As a check showed, with this technique for carrying out the experiments and storing the specimens before investigation, the invariability of their composition and their preservation during the experiment can be fully ensured. Cerium hydrides, for example, did not lose even their pyrophoric properties. The additional absorption of X-rays in the foil of the protective plastic packet proved to be insignificant.

The X-ray $LIII$-absorption spectra of rare-earth elements in the hydrides of lanthanum and cerium were obtained with a focusing vacuum tube spectrograph in the second order of reflection from the $(10\bar{1}1)$ plane of a bent quartz crystal. The radius of curvature of the crystal was 330 mm. The dispersion was $\sim 6'$/mm. The resolving power of the instrument was 7500. The spectra were photographed on a flat cassette positioned perpendicular to the direction of the incident X-rays. The operating conditions of the X-ray tube were 10–12 kV, 50 mA. The exposure was 2–3 hours. The anode was copper. The optimal absorber density was 4–5 mg/cm^2. The spectra of each of the rare-earth elements in the hydrides were photometered and, after averaging over 5 independent films, recalculated on an electron-volt scale. As comparison lines in the study of the cerium spectrum, Sm$L\alpha_1$ and Mn$K\alpha_1$ were used; in the study of the lanthanum hydrides, Sm$L\alpha_1$ and Cr$K\alpha_1$ in the second order of reflection were used. The accuracy in determining the energies of individual points of the absorption edge was 0.2 eV.

Fig. 3. $LIII$-absorption spectra of lanthanum in the oxide (4) and in the hydrides LaH_n: 1 –n = 2.96; 2 –2.26; 3 –1.97.

Fig. 4. Comparison of the absorption spectra of cerium in CeH_2 and CeB_6

Figure 3: Fig. 4. Comparison of the absorption spectra of cerium in CeH_2 and CeB_6

The experimental results relating to the hydrides of cerium and lanthanum are compared in Figs. 2 and 3. For comparison, the absorption spectra of the corresponding metals in cerium dioxide and lanthanum oxide, obtained under identical conditions, are also shown there. As was to be expected, the fine structure of the absorption spectra of the metals in the hydrides is practically absent or is manifested very weakly. This is explained by the extremely small scattering power of the hydrogen surrounding the atoms of the rare-earth elements in the hydride lattice. Nevertheless, consideration of the data obtained and comparison of them with the absorption spectra of the same metals in oxides and some other compounds (see, for example, Fig. 4) make it possible to arrive at certain conclusions that supplement or support modern ideas about the nature of the chemical bond and the valence state of rare-earth atoms in hydrides in the region of berthollide phases.

The spectra shown in Figs. 2–4 fully confirm the proposition that cerium and lanthanum are trivalent in hydrides, advanced at one time by Libowitz and Gibb (3). Moreover, another supposition of the same authors is also consistent with the experimental facts: namely, that of the three electrons made available for bonding by rare-earth atoms in dihydrides and phases with a higher hydrogen content, only a part is used to organize the ionic bond with hydrogen,* while the remainder take part in the metallic bond. It is precisely the latter electrons that should exert

* In favor of the supposition of the ionic character of the bonds of rare-earth elements with hydrogen in hydrides, there are, in particular, the data of Bills' s work (7).

has a decisive influence on the magnitude of the electrical conductivity of these compounds, which, as is known ([8a]), does indeed decrease regularly and progressively in the berthollide region as the relative hydrogen content in the hydride increases and as its composition approaches that of the trihydride. For the dihydrides of cerium and lanthanum, the hypothesis of Libowitz and Gibb is confirmed by the complete identity of the energy position and long-wavelength structure of the X-ray spectra in these compounds and of the spectra of the same metals in the hexaborides (Fig. 4), for which an analogous character of the participation of the electrons in the chemical bond in the compound had been demonstrated experimentally earlier ([6]).

Fig. 4. Comparison of the absorption spectra of cerium in CeH_2 and CeB_6

As for the berthollide phases in the region MeH_2–MeH_3, then, as the data of the present investigation show, on passing from the dihydride to phases with a higher hydrogen content no changes whatever are observed in the structure

and energy position of the X-ray L-absorption spectra of the rare-earth atoms. This indicates that in these phases there is no change in the valence state of the rare-earth metal and, all the more, no coexistence of several forms of its valence that are in equilibrium. As experience shows ([8]), the magnitude of the magnetic susceptibility of cerium and lanthanum atoms also remains unchanged in the corresponding hydrides. Thus, the total number of electrons supplied by the rare-earth ion for the organization of the chemical bond in berthollides of different composition remains unchanged. As the specific hydrogen content in the hydride increases and its composition approaches that of the trihydride, evidently only the participation of the electrons of the rare-earth atoms in the ionic bond with hydrogen atoms gradually increases, and correspondingly the number of current carriers responsible for the metallic conductivity of these compounds decreases. Such phenomena observed in the berthollide region as, for example, the regular decrease in interatomic distance and the increase in the density of the hydrides ([4]), the sharp decrease in the electrical conductivity of these phases and the characteristic change in its temperature dependence ([8,b,c]), must inevitably be associated with this process. At the same time, such a course of change in the chemical bond in the group of berthollides under consideration also explains the data on the chemical activity of rare-earth hydrides and many other chemical properties of these substances ([2]).

Institute of Inorganic Chemistry,
Siberian Branch of the Academy of Sciences of the USSR
Institute of Inorganic Chemistry named after N. S. Kurnakov,
Academy of Sciences of the USSR
Odessa Pedagogical Institute
named after K. D. Ushinskii

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Note: Figure translations are in progress. See original paper for figures.