

THE FEATURES OF THE ELECTRONIC STRUCTURE OF LANTHANIDES

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Abstract. In the presented work, is given an analysis of rare earth elements based on their electronic structure. It is shown that the most stable states of lanthanides are f^0 , f^7 and f^{14} - configurations. It was found that most likely f^0 - configuration and characteristic valence +3. When passing to cerium, the probability f^0 - states decreases, but remains quite high. At the same time, a certain probability of formation of f^7 configurations causes an increase in the valence of cerium, which usually ranges from +3 to +4. An increase in the statistical weights of f^7 configurations when approaching europium leads to an admixture of +2 valence. It was found, also in accordance with the change in the statistical weight of the stable f^7 configurations that the donor demand for lanthanide atoms decreases when going from lanthanum to europium and from gadolinium to ytterbium. It is shown that the change in the adsorption energy of lanthanides occurs in the same sequences.

Keywords: lanthanides, electronic configuration, f^0 , f^7 and f^{14} - configurations, electron shell, statistical weight.

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1. Introduction

At present, there is no doubt that the change in various properties in the lanthanide series is determined by the peculiarity of their electronic structure, which consists in filling deep-lying $4f$ - shells and the presence of vacant $5d$ -levels in most of them.

Theoretically rigorous from the point of view of quantum mechanics is the band theory of solids. However, despite certain successes, this theory can only be considered as a qualitative picture of the electronic processes in a solid, reflecting only some features of the crystalline state. But this is not enough to interpret the various properties of solids; moreover, the simplification of the general problem of the interaction of particles in a solid, which leads to the band model, causes that the band theory does not consider the state of heavy particles. At the same time, when considering the change in properties in the series of lanthanides, atomic radii are put forward as the determining factors, radius ratio $4f$ – electrons to atomic radius, etc. It is assumed that the change in the properties of lanthanides is due to the participation in the formation of a chemical bond on s -electrons, and d, f, p – electrons. However, the use of the proposed mechanisms and these parameters when discussing a wide range of properties of lanthanides encounters a number of regularities in the electronic structure of lanthanides (Table 1).

The most general approach to explaining the diversity properties of lanthanides is the application of the configurational model of matter (Samsonov *et al.*, 1965). This model bridges the gap between the methods of molecular orbitals and valence bonds, i.e. between the individuality of the element, which is emphasized in chemistry, and the band

nature of the energy spectrum, which forms the basis for considering most physical properties.

Table 1. Configurations, basic states and parameters of ions of rare earth elements

No	Element	Z	R	R^{3+}	Radius of 4f shell, Å	Main state, R^{3+}	Ionic radius, Å	Melting temperature, K	Boiling temperature, K
1	La	57	$5d^16s^2$	$5s^25p^6$	0.610	1S_0	1.061	1193	3742
2	Ce	58	$4f^26s^2$	$4f^15s^25p^6$	0.578	$^2F_{5/2}$	1.034	1068	3740
3	Pr	59	$4f^36s^2$	$4f^25s^25p^6$	0.550	3H_4	1.013	1208	3300
4	Nd	60	$4f^46s^2$	$4f^35s^25p^6$	0.528	$^4I_{9/2}$	0.995	1297	3300
5	Pm	61	$4f^56s^2$	$4f^45s^25p^6$	0.511	5I_4	0.979		
6	Sm	62	$4f^66s^2$	$4f^55s^25p^6$	0.496	$^6H_{5/2}$	0.964	1345	2077
7	I	63	$4f^76s^2$	$4f^65s^25p^6$	0.480	7F_0	0.950	1029	1712
8	Gd	64	$4f^75d^1$	$4f^75s^25p^6$	0.468	$^8S_{7/2}$	0.938	1585	3270
9	Tb	65	$4f^96s^2$	$4f^85s^25p^6$	0.458	7F_6	0.923	1629	3070
10	Dy	66	$4f^{10}6s^2$	$4f^95s^25p^6$	0.450	$^6H_{15/2}$	0.908	1680	2870
11	Ho	67	$4f^{11}6s^2$	$4f^{10}5s^25p^6$	0.440	5I_8	0.894	1734	2870
12	Is	68	$4f^{12}6s^2$	$4f^{11}5s^25p^6$	0.431	$^4I_{15/2}$	0.881	1823	2923
13	Tm	69	$4f^{13}6s^2$	$4f^{12}5s^25p^6$	0.421	3H_6	0.869	1818	2000
14	Yb	70	$4f^{14}6s^2$	$4f^{13}5s^25p^6$	0.413	$^2F_{7/2}$	0.858	1101	1700

Compounds formed by rare earth elements are widely studied. It was found that materials have different physical properties depending on the electronic structure of these elements (Zhong *et al.*, 2015; Leanea *et al.*, 2017; Khan *et al.*, 2020; Tanaka *et al.*, 1991). Rare earth elements that are part of semiconductor matrices form optically active centers (Smet *et al.*, 2010; Barthou *et al.*, 2006; Tagiev *et al.*, 2022; Korthout *et al.*, 2011; Hidaka & Takizawa, 2002). Therefore, they are widely used in modern optical devices. To accurately explain the results obtained in studies in this direction, it is important to study the electronic structures of rare earth elements and create a unified model for these elements.

2. Model of the electronic structure of lanthanides

It is usually assumed that the f - electrons of the lanthanides do not directly participate in the formation of a chemical bond, however, through $4f \rightarrow 4f^{n-1}5d$ - transitions, they are able to pass into the d - state and participate in the formation of a chemical bond (Table 2). This allows, in the first approximation, to consider part of the f -electrons that have passed into the d -state as valence. The statistical nature of the transitions requires that these f - electrons be assigned to the localized part of the valence electrons. According to the configuration model of a solid, the localized fraction of lanthanide valence electrons forms a statistical set of different configurations with the largest weights in this set of the most energetically stable f^0 , f^7 and f^{14} - configurations.

Information about the fraction of itinerant electrons and statistical weights of stable configurations corresponding to the minimum free energy of a crystal is, from the standpoint of the configuration model, a sufficient condition for obtaining qualitative information about its diverse properties.

The basis for calculating the statistical weight of stable configurations of lanthanides can be, in the first approximation, energy characteristics $4f^n \rightarrow 4f^{n-1}5d$ -transitions calculated for isolated ions Ln^{+2} (Giftopoulos & Hyspoulos, 1969).

The use of these energy characteristics, known for the entire series of lanthanides, is justified by the fact that the crystalline field subsequently has relatively small orbital radii of f -electrons and strong electron-electron interaction has little effect on the energy state of f -electrons (Marchenko & Samsonov, 1965; Elyashevich, 1953; Yarembash, Eliseev, 1975).

The energy of $4f^n \rightarrow 4f^{n-1}5d$ - transitions can be considered as the sum of energy costs associated with the violation of stable configurations characteristic of a given number of f - electrons (Vasilyeva *et al.*, 1979; Samsonov, 1970; Samsonov, 1973, Edison, 1966; Samsonov, 1964).

Since the implementation of the method of stable configurations for any n occurs with a probability of 100%, then by equating to this value the sum of the energy contributions of stable configurations characteristic of a given n , one can determine the statistical weight of any of the components. The results of such calculations are presented in Table 2.

Table 2. Energy $f \rightarrow d$ transitions and statistical weight of stable configurations of lanthanides

Lanthanides	Energy $4f^n \rightarrow 4f^{n-1}5d$ - transition, (J/mol.)	Statistical weight of configurations, %		
		f^0	f^7	f^{14}
La	-191483	93.3	8.4	0.3
Ce	-72487	79.4	19.8	0.8
Pr	-23883	51.2	47.0	1.8
Nd	48185	22.3	74.9	2.8
Sm	167600	2.1	94.3	3.8
Eu	275702	0.8	95.8	3.6
Gd	-95532	0.5	86.1	13.4
Tb	36034	0.4	61.1	48.5
Dy	131566	0.2	28.1	71.7
Ho	131566	0.1	8.8	91.1
Er	119834	0.02	2.3	97.7
Tm	215785	0.01	0.6	99.4
Yb	34770	0.00	0.3	99.7

f^0 configuration is most probable and the valence +3 is typical. On going to cerium, the probability of f^0 configurations decreases, but remains sufficiently high. This leads to the preferential valence of cerium +4. At the same time, a certain probability of formation f^7 configuration causes an increase in the cerium valency, which is usually +3 to +4. Comparable statistical weights f^0 and f^7 configurations in praseodymium cause, along with the ground valence state +3, the ability to higher valence. This ability decreases with the transition to neodymium and promethium. An increase in the statistical weight of f^7 configurations as it approaches europium leads to a predominant valency of +2.

Comparison of the statistical weights f^0 and f^7 of the configurations of the elements of the cerium subgroup of the lanthanides f^7 and f^{14} of the configurations of

the elements of the yttrium subgroup shows that ytterbium is similar to europium, dysprosium more similar to neodymium than praseodymium, while terbium is similar to cerium. The latter is due to the fact that the electronic configuration of the terbium atom is $4f^85d$, and this lanthanide, like cerium, is characterized by the formation of compounds in which it exhibits a +4 valence.

The authors of the works Samsonov, (1964, 1965); Dorenbos, (2012); Gschneidner, (1971) the probability of participation of f electrons due to $f \rightarrow d$ transitions in the formation of chemical bonds in lanthanides was estimated. Accounting for $f \rightarrow d$ transitions in lanthanides is the first approximation to the real distribution of electrons. The presence of unfilled $5d$ levels significantly complicates the phenomenon of electronic transitions and leads to the need to take into account $s \rightarrow d$ transitions, which, like $f \rightarrow d$ transitions, are aimed at the formation of energetically maximally stable d configurations. Presence of $s \rightarrow d$ transitions is well illustrated by the change melting points of the lanthanides. The temperature increase of the fused from cerium to samarium occurs in accordance with an increase in the statistical weight of f^7 -configurations, the maximum statistical weight of which is achieved in the case of europium. It is for europium due to the completion of the formation of the f^7 -configuration and the complete transition $6s^2$ -electrons into a non-localized state is characterized by a sharp decrease in the melting temperature. The increase in the melting point of gadolinium compared to europium is due to the fact that in this lanthanide, as well as for all subsequent ones, not only $f \rightarrow d$, but also $s \rightarrow d$ transitions that enhance the localization of electrons in stable configurations. In the case of ytterbium, achieving the maximum statistical weight of the configuration f^{14} leads to a significant decrease in the melting temperature.

3. Results and discussions

The prevailing role of f^7 configuration compared to f^{14} can be clearly seen in the change in the coefficient of thermal expansion of the lanthanides. In accordance with the increase in the statistical weight of f^7 configurations in the lanthanum \rightarrow samarium series, an increase in the thermal expansion coefficient is observed, while an increase in the statistical weight of f^{14} -configuration of gadolinium to ytterbium does not cause a noticeable change in the coefficient of thermal expansion. At the same time, the delocalization of $6s$ electrons at completely filled stable configurations f^7 and f^{14} causes an increase in the thermal expansion coefficient of europium and ytterbium. In accordance with this model, the most densely packed structures and structures with the highest symmetry are formed on the basis of a high statistical weight of stable configurations of localized electrons under the condition of a small loosening action of itinerant electrons. As the temperature rises, the least energetically stable configurations are excited and destroyed, and the statistical weight of the most stable configurations increases due to them, i.e., an increase in the localization of valence electrons. The localization of electrons in the case of lanthanides occurs in stable f^0 , f^7 , f^{14} configurations.

Since the d^5 configuration is energetically more stable f^7 configurations, then it should be assumed that the structure should be determined by the statistical weight of d^5 configurations arising due to $f \rightarrow d$ transitions. At the same time, with an increase in the statistical weight of f^7 -configurations, the probability $f \rightarrow d$ transitions decreases, the formation of d^5 configurations, on which the body-centered cubic lattice is based, becomes more difficult, and as a result, the temperatures of polymorphic transformations

increase. From these positions, the absence of polymorphic transformations in europium, which has the maximum statistical weight of the stable f^7 configuration and the practical impossibility of $f \rightarrow d$ transition. With a further transition to gadolinium, the probability of the formation of d^5 configuration, the high energy stability of which determines the high temperature of the transition from lower to high symmetry. The same is observed for terbium. Starting from dysprosium and up to and including thulium, no polymorphic transformations were found, and these metals are known only in a modification that has a face-centered lattice, which is deformed due to the high concentration of itinerant electrons. Obviously, high-temperature modifications must also exist for these metals, with the $\alpha \rightarrow \beta$ transition temperatures naturally decreasing from dysprosium to thulium. However, the thermal excitation temperatures of the f^7 and f^{14} configurations seem to lie above the melting temperatures of these metals, which explains the absence of polymorphic transformations. Monomorphism is interrupted in ytterbium, for which, with increasing temperature, a transformation of a low-temperature - face-centered cubic lattice structure based on a high statistical weight is observed f^{14} - configurations, in body-centered cubic structures.

From a comparison of the atomic radii of the lanthanides, it follows that europium and ytterbium, whose properties are in some respects not typical of the lanthanides, resemble the alkaline earth elements. Under normal conditions, both have a cubic structure. The properties of cerium also differ from the properties of other lanthanides. The melting points of these three elements are lower than the melting points of the other lanthanides.

For europium and ytterbium, due to completion f^7 and f^{14} -configurations and complete transition $6s^2$ electrons into a nonlocalized state, a strong electron-electron interaction occurs, weakening the lattice, as a result of which the value of their atomic radii increases sharply in comparison with other lanthanides.

The heat of sublimation is a quantitative characteristic of the strength of the chemical bond of metals. The type chemical bond is determined by the nature of the participation and distribution of valence electrons over single bonds. For lanthanides, the determining factor in the formation of a chemical bond is the stabilization of f^7 and f^{14} -configurations $4f$ - shell, the electrons of which through $f \rightarrow d$ and $s \rightarrow d \rightarrow f$ transitions are involved in chemical bonds. Increasing the statistical weight f^7 and f^{14} - configurations, as it approaches europium and ytterbium, respectively, and as a consequence, a decrease in the number of electrons participating in bonds leads to a decrease in the heat of sublimation of lanthanides.

This is the reason why lanthanum, gadolinium and lutetium, whose atoms in an isolated state have $5d$ electrons are characterized by the highest heats of sublimation, and europium and ytterbium, which have f^7 and f^{14} configurations with small statistical weights, have the lowest heats of sublimation.

As another example, consider the adsorption of lanthanides on tungsten. According to modern quantum theory, the adsorbed atom is in a state of continuous electronic exchange with the adsorbent. It is obvious that the stronger the interaction, the greater the difference in the donor-acceptor properties of the components of the adsorption system. In accordance with the change in the statistical weight of the stable configurations f^7 and f^{14} , the donor ability of lanthanide atoms decreases on passing from lanthanum to europium and from gadolinium to ytterbium.

It is in the same sequence that change in the adsorption energy. The presence of a local extremum in the case of cerium is due to the fact that this element is characterized by the ability to exhibit a +4 valence.

4. Conclusion

In the presented work is given the analysis based on the electronic structures of lanthanides, which differ in the characteristics of the periodic table of elements and are called rare earth elements. It is shown that among the mentioned elements, the elements with the outer electron shells f^0 , f^7 , f^{14} electronic structure usually behave trivalently. The reasons for the variable valence of the layers with different outer electron shells are analyzed and some properties of the mentioned elements are classified according to their electronic structures.

References

- Barthou, C., Jabbarov, R.B., Benalloul, P., Chartier, C., Musayeva, N.N., Tagiev, B.G., Tagiev, O.B. (2006). Radiative properties of the blue $\text{BaAl}_2\text{S}_4:\text{Eu}^{2+}$ phosphor. *Journal of the Electrochemical Society*, 153, 3, G253.
- Dorenbos, P. (2012). Electronic structure engineering of lanthanide activated materials. *Journal of Materials Chemistry*, 42, 22344-22349.
- Edison, W. (1966). *Allotropy of Chemical Elements*. Mir. Moscow, 265.
- Elyashevich, M.A. (1953). *Spectra of rare earths*. GST. Moscow, 206.
- Giftopoulos, E., Hyspoulos, G. (1969). *Direct conversion of thermal energy into electrical and fuel cells*. VINITI, Moscow
- Gschneidner, K.A. (1971). On the nature of $4f$ bonding in the lanthanide elements and their compounds. *Journal of the Less Common Metals*, 25(4), 405-422
- Hidaka, C., Takizawa, T. (2002). Single-crystal growth and optical properties of undoped and Ce^{3+} doped CaGa_2S_4 . *Journal of Crystal Growth*, 3, 237-239.
- Khan, D.T., Dang, N.T., Jabarov, S.H., Naghiyev, T.G., Rzayev, R.M., Nguyen, T.Q., Tuyen, H.V., Thanh, N.T., Son, L.V.T. (2020). Study on luminescent properties of Tb^{3+} and Sm^{3+} co-doped CaSiO_3 phosphors for white light emitting diodes. *Materials Research Express*, 7(1), 016507.
- Korthout, K., Smet, P.F., Poelman, D. (2011). Rare earth doped core-shell particles as phosphor for warm-white light-emitting diodes. *Applied Physics Letters*, 98, 261919.
- Leanenia, M.S., Lutsenko, E.V., Rzhetski, M.V., Pavlovskii, V.N., Yablonskii, G.P., Naghiyev, T.G., Tagiev, B.G., Abushev, S.A., Tagiev, O.B. (2017). Photoluminescence of $\text{Ca}_x\text{Ba}_{1-x}\text{Ga}_2\text{S}_4:\text{Eu}^{2+}$ solid solutions in wide excitation intensity and temperature intervals. *Journal of Luminescence*, 181, 121-127.
- Marchenko, V.I., Samsonov, G.V. (1965). Chemical bond in sulfides of rare earth metals. In *Chemical Bonding in Semiconductors and Solids. Science and Technology*, 216-223.
- Samsonov, G.V. (1964). *Refractory compounds of rare earth metals with nonmetals*. Metallurgy, Kiev, 110.
- Samsonov, G.V. (1970). *On Sat. Rare earth metals and their compounds*. Naukova thought, Kiev, 24.
- Samsonov, G.V. et al. (1965). *Physical and chemical properties of elements*. Naukova Dumka, Kyiv.
- Samsonov, G.V., Ristik, M.M. (1973). *On the generalized theory of sintering*. ITST, Belgrade, 361.
- Smet, P.F., Moreels, I., Hens, Z., Poelman, D. (2010). Luminescence in sulfides: A rich history and a bright future. *Materials*, 3(4), 2834-2883.

- Tagiev, O.B., Asadov, E.G., Tagiev, K.O., Gadzhieva, G.S., Naghiyev, T.G. (2022). Influence of external factors on photoluminescence of $\text{Ca}(\text{Al}_x\text{Ga}_{1-x})_2\text{S}_4:\text{Eu}^{2+}$ solid solutions. *Solid State Communications*, 342, 114587.
- Tanaka, Sh., Yoshiyama, H., Nakamura, K., Wada, S., Morita, H.M.H., Kobayashi, H.K.H. (1991). Photo-induced transferred charge in rare-earth-doped alkaline-earth sulfide electroluminescent thin films. *Japanese Journal Applied Physics*, 30(6A), L1021.
- Vasilyeva, I.G., Mironov, K.E., Sokolov, V.V., Kamarzin, A.A. (1979). *Prospects for the study of diagrams of rare-earth metal-sulfur systems. Refractory connections rare earth metals*. Nauka, Novosibirsk, 183-186.
- Yarembash, E.I., Eliseev, A.A. (1975). *Chalcogenides of rare earth elements*. Nauka. Moscow, 258.
- Zhong, T., Kindem, J.M., Miyazono, E., Faraon, A. (2015). Interfacing broadband photonic qubits to on-chip cavity-protected rare-earth ensembles. *Nature Communications*, 8, 14107.