JOURNAL OF SOLID STATE CHEMISTRY 76, 136–142 (1988)

Relationship between the Crystal Field Splitting of the Nd^{3+} Ion Manifolds and the Ratio of Charge to Radius of Ions *A* and *B* in the ABO_n (n = 2–4)-Type Compounds

Y. Q. JIA

Changchun Institute of Applied Chemistry, Academia Sinica, Changchun, Jilin, People's Republic of China

Received December 21, 1987; in revised form April 4, 1988

A certain simple relationship has been found between the total crystal field splitting ΔE of the Nd^{3+} ion manifolds and the ratio of the charge to radius of ions A and B in the ABO_n ($n = 2$–4)-type compounds. An empirical formula has been proposed to calculate the total crystal field splitting ΔE of the Nd^{3+} ion manifolds in the ABO_n ($n = 2$–4)-type compounds. The results calculated by using the formula for the total crystal field splitting ΔE of the $^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$ manifolds of the Nd^{3+} ion in 22 different ABO_n-type compounds are in agreement with the experimental data. The deviation between the calculated ΔE and the experimental result is less than 10% in three-quarters of the examples. All of the unknown total crystal field splitting ΔE of the Nd^{3+} ion manifolds in these ABO_n-type compounds have been evaluated by means of the formula.

Introduction

The relationship between the physical and chemical properties of materials and their composition and structure has been a significant subject for both experimental and theoretical investigations. When a relationship can be found, it is helpful in the search for new materials with given physical and chemical properties and in the prediction of the properties a new material may possess. Unfortunately, the relationship between the physical and chemical properties and the composition and structure of the materials is often so complicated that it is difficult to establish a quantitative relationship between them. Therefore, as a first stage, it may be useful to establish some simple empirical relationships between the physical or chemical properties and some parameters of the components of the material.

Neodymium is a typical rare-earth element in both rare-earth physics and rare-earth chemistry. In addition, the trivalent positive neodymium ion is the most widely used laser crystal activator, and spectroscopic data about the total crystal field splitting ΔE of the Nd^{3+} ion manifolds in tens of different host crystals have been published in detail. So, we have enough experimental data to check and to establish whether there exists a certain functional relationship between some spectroscopic properties of the Nd^{3+} ion and some chemical and physical parameters of the host crystals.

In this paper, we demonstrate such a relationship for the spectroscopic properties of the neodymium ion in some ABO_n-

0022-4596/88 $3.00

type compounds. Here, only the spectroscopic properties of the Nd^{3+} ion measured at low temperature (77 K) are used. In this case, the effect of the electron–phonon interaction on the total crystal field splitting is small, and can be ignored. We know that the potential at the cation site occupied by the dopant ion depends on the charge distribution in the crystal, whereas the charge distribution in the crystal mainly depends on the chemical bonding between the atoms in the crystal. Therefore, we can expect a certain relationship to exist between the total crystal field splitting ΔE of the dopant ion manifolds and the chemical bond parameters of the atoms composing the crystal. Thus, we have investigated the total crystal field splitting, ΔE, of the Nd^{3+} ion manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$) in some simple ABO_n (n = 2–4)-type compounds, and found that there does exist a certain relationship between the total crystal field splitting ΔE and the ratio of the charge to radius of ions A and B.

Results and Discussion

It has been found that the total crystal field splitting ΔE of the Nd^{3+} ion manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$) in the simple ABO_n (n = 2–4)-type compounds can be evaluated by the following formula

$$\Delta E = a - b(B/A)^c$$

where B, A: the ratio of the charge to radius of ion A and ion B, respectively, and a, b, and c = constants.

For the $^4I_{9/2}$, $a = 818$ cm^{-1}, $b = 71.6$ cm^{-1}, and $c = 1.0$; for the $^4I_{11/2}$, $a = 838$ cm^{-1}, $b = 340$ cm^{-1}, and $c = 1/3$; for the $^4I_{13/2}$, $a = 1021$ cm^{-1}, $b = 433$ cm^{-1}, and $c = 1/3$; for the $^4I_{15/2}$, $a = 2013$ cm^{-1}, $b = 841$ cm^{-1}, and $c = 1/3$, respectively.

In the above described formula, $A = Z_a/R_a$, $B = Z_b/R_b$; Z_a and Z_b are the ionic valence of ion A and ion B; R_a and R_b are the crystal radius of ion A and ion B, respectively. The crystal radii used in the calculations are from Ref. (*1*).

All the total crystal field splitting ΔE of the Nd^{3+} ion manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$) in 22 different ABO_n (n = 2–4) compounds have been evaluated by means of the formula mentioned above. The calculated results are listed in Tables I, II, III, and IV, respectively.

For comparison, corresponding experimental data of the total crystal field splitting ΔE of the Nd^{3+} ion manifolds in these compounds are listed in the tables. For lack of some experimental data, we cite some experimental results that are not the complete splitting ΔE of the ^4I_J manifolds and need further clarification to check whether the calculated total crystal field splitting ΔE is reasonable. Those experimental data in the tables marked by the superscript *a* are not equal to, but less than the total crystal field splitting ΔE.

As the results in Tables I, II, III, and IV show, although the total crystal field splitting ΔE of the Nd^{3+} ion manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$) measured in experiments are over a rather wide energy region (about 300–1000 cm^{-1}), the calculated total crystal field splitting ΔE is very close to the experimental data for most of the ABO_n-type compounds. The deviation is less than 10% in about three-quarters of the examples. It is very interesting that the calculated total crystal field splitting ΔE is larger than or close to the corresponding data marked with superscript *a*. As mentioned above, the latter should be less than the total crystal field splitting ΔE. So, it shows that the calculated total crystal field splitting may be reasonable.

Morozov *et al.* (*4*) have found that the total crystal field splitting ΔE of the Nd^{3+} ion manifolds in some scheelite-type compounds, for example, in the molybdates and the tungstates of calcium, strontium, and barium, monotonously varied with the crystal lattice parameters. We consider that,

TABLE I

THE TOTAL CRYSTAL FIELD SPLITTING ΔE OF THE $^4I_{9/2}$ MANIFOLD OF THE Nd^{3+} ION IN THE ABO_n (n = 2–4)-TYPE COMPOUNDS

Compound	A	B	B/A	ΔE (cal) (cm^{-1})	ΔE (exp) (cm^{-1})	δ (%)	Ref.
$LiYO_2$	1.37	2.885	2.106	667.2	639	4.4	(*2*)
$LiNbO_3$	1.37	6.41	4.679	483	486	−0.6	(*3*)
$CaMoO_4$	1.754	9.375	5.345	435.3	456	−4.5	(*4*)
$CaWO_4$	1.754	9.231	5.263	441.2	472	−6.5	(*4*)
$SrMoO_4$	1.515	9.375	6.188	374.9	377	−0.1	(*4*)
$SrWO_4$	1.515	9.231	6.093	381.7	395	−3.4	(*4*)
$YAlO_3$	2.885	5.66	1.962	677.5	671	1.0	(*6*)^b
$YScO_3$	2.885	3.39	1.175	733.9	709	3.5	(*7*)
YVO_4	2.885	7.353	2.549	635.5	433	46.8	(*8*)
$YNbO_4$	2.885	6.41	2.222	658.9	636	3.6	(*9*)
$YTaO_4$	2.885	6.41	2.222	658.9	650	1.4	(*9*)
$CdMoO_4$	1.835	9.375	5.109	452.2	499	−9.4	(*4*)
$BaMoO_4$	1.342	9.375	6.986	317.8	310	2.5	(*4*)
$BaWO_4$	1.342	9.231	6.879	325.5	313	4.0	(*4*)
$LaAlO_3$	2.56	5.66	2.211	659.7	671	−1.7	(*10*)
$LaNbO_4$	2.56	6.41	2.504	638.7	506	26.2	(*9*)
$LaTaO_4$	2.56	6.41	2.504	638.7	688	−7.2	(*9*)
$GdAlO_3$	2.783	5.66	2.034	672.4	666	1.0	(*11*)
$LuAlO_3$	2.997	5.66	1.889	682.7	662	3.1	(*12*)
$LuScO_3$	2.997	3.39	1.131	737	740	−0.4	(*13*)
$PbMoO_4$	1.504	9.375	6.233	371.7	363	2.4	(*4*)
$PbWO_4$	1.504	9.231	6.138	378.5	385	−1.7	(*4*)

^{b} The experimental data (*6*) are the experimental values at 300 K.

perhaps, the relationship may be suitable only to compounds that possess the same crystal structure. Here, we point out that the ABO_n-type compounds mentioned above possess not only very different chemical composition, but also very different crystal structure. For example, atom A includes 10 elements (Li, Ca, Sr, Ba, Cd, Pb, Y, La, Gd, and Lu); atom B includes 8 elements (Al, Y, V, Nb, Ta, W, Mo, and Sc). Some of these elements are very different from each other both in physical and in chemical properties. In addition, the crystal space groups of the compounds are very different. For example, the molybdates and the tungstates of calcium, strontium, and barium possess a scheelite-type structure and belong to the tetragonal crystal, but the orthoaluminates of yttrium, gadolinium, and lutetium possess a perovskite-type structure and belong to the monoclinic system. The cation site symmetries in these compounds are very different, also. That the calculated total crystal field splittings, ΔE, of the Nd^{3+} ion manifolds in such different host crystals are very close to the experimental data indicates that the approximate formula mentioned above has a rather wide application and is valid for the ABO_n series compounds with different composition and crystal structure. In this way, we can predict the unknown total crystal field splitting ΔE of the Nd^{3+} ion manifolds in the other ABO_n-type compounds. Perhaps it will also be very helpful to determine the positions of some Stark levels. For example, according to the theoretical calculation, there should exist six

TABLE II

The Total Crystal Field Splitting ΔE of the $^4I_{11/2}$ Manifold of the Nd^{3+} Ion in the ABO_n (n = 2–4)-type Compounds

Compound	A	B	B/A	ΔE (cal) (cm^{-1})	ΔE (exp) (cm^{-1})	δ (%)	Ref.
$LiYO_2$	1.37	2.885	2.106	402.2	467	−13.9	(2)
$LiNbO_3$	1.37	6.41	4.679	269.3	276	−2.4	(3)
$CaMoO_4$	1.754	9.375	5.345	243.5	245	−0.6	(4)
$CaWO_4$	1.754	9.231	5.263	246.6	250[a]		(4)
$SrMoO_4$	1.515	9.375	6.188	213.8	184[a]		(4)
$SrWO_4$	1.515	9.231	6.094	217	210[a]		(4)
$YAlO_3$	2.885	5.66	1.962	412.4	355	16.2	(6)[b]
$YScO_3$	2.885	3.39	1.175	479.2	540	−11.3	(7)
YVO_4	2.885	7.353	2.549	373.6	216	73.0	(8)
$YNbO_4$	2.885	6.41	2.222	394.3	345	14.3	(9)
$YTaO_4$	2.885	6.41	2.222	394.3	357	10.4	(9)
$CdMoO_4$	1.835	9.375	5.109	254.2	263[a]		(4)
$BaMoO_4$	1.342	9.375	6.986	188	178	5.6	(4)
$BaWO_4$	1.342	9.231	6.879	191.4	171[a]		(4)
$LaAlO_3$	2.56	5.66	2.211	395.1	255[a]		(10)
$LaNbO_4$	2.56	6.41	2.504	376.3	282	33.4	(9)
$LaTaO_4$	2.56	6.41	2.504	376.3	449	−16.2	(9)
$GdAlO_3$	2.783	5.66	2.034	407.2	347	17.3	(11)
$LuAlO_3$	2.997	5.66	1.889	417.7	358	16.7	(12)
$LuScO_3$	2.997	3.39	1.131	483.8	550	−12.0	(13)
$PbMoO_4$	1.504	9.375	6.233	212.3	199	6.7	(4)
$PbWO_4$	1.504	9.231	6.138	215.5	206[a]		(4)

[b] The experimental data (6) are the experimental values at 300 K.

Stark levels for the $^4I_{11/2}$ manifold. However, only five of these Stark levels of the $^4I_{11/2}$ manifold in the $CaWO_4$ cyrstal have been established experimentally. It cannot be determined whether the Stark level that possesses the highest energy in all five Stark levels is the highest Stark level for the $^4I_{11/2}$ manifold. From the results in Table II, it can be found that the energy gap between the observed highest Stark level and the observed lowest Stark level is 250 cm^{-1}, and that this energy gap is very close to the calculated total crystal field splitting ΔE (246.6 cm^{-1}) of the $^4I_{11/2}$ manifold. Thus, it is very possible that the observed highest Stark level (2226 cm^{-1}) (4), indeed, is the highest Stark level for the $^4I_{11/2}$ manifold in the CaWO4 crystal. Therefore, we can also be sure that the energy of the Stark level, which has not been observed, must be lower than 2226 cm^{-1}. Similarly, we can determine either that the highest level in the observed five Stark levels of the $^4I_{11/2}$ manifold of the Nd^{3+} ion in the $SrMoO_4$ crystal is the true highest Stark level and the lowest Stark level in the observed five Stark levels is not the true lowest Stark level, or that the observed highest Stark level is not the true highest Stark level and the observed lowest Stark level is the true lowest Stark level of the $^4I_{11/2}$ manifold, because the observed splitting ΔE (184 cm^{-1}) is not the true total crystal field splitting ΔE. Thus, we can predict that the unknown Stark level of the $^4I_{11/2}$ manifold should be either higher than the observed highest Stark level, or lower than the observed lowest Stark level.

Auzel (5) has obtained a new parameter

TABLE III

THE TOTAL CRYSTAL FIELD SPLITTING ΔE OF THE $^4I_{13/2}$ MANIFOLD OF THE Nd^{3+} ION IN THE ABO_n (n =3 2–4)-TYPE COMPOUNDS

Compound	A	B	B/A	ΔE (cal) (cm^{-1})	ΔE (exp) (cm^{-1})	δ (%)	Ref.
$LiYO_2$	1.37	2.885	2.106	466	263[a]		(*2*)
$LiNbO_3$	1.37	6.41	4.679	296.8	293	1.3	(*3*)
$CaMoO_4$	1.754	9.375	5.345	263.9	268	−1.5	(*4*)
$CaWO_4$	1.754	9.231	5.263	267.8	276	−3.0	(*4*)
$SrMoO_4$	1.515	9.375	6.188	226.1	235	−3.8	(*4*)
$SrWO_4$	1.515	9.231	6.093	230.1	245	−6.1	(*4*)
$YAlO_3$	2.885	5.66	1.962	478.9	495	−3.3	(*6*)[b]
$YScO_3$	2.885	3.39	1.175	564.1	563	0.2	(*7*)
YVO_4	2.885	7.353	2.549	429.5	260	65.2	(*8*)
$YNbO_4$	2.885	6.41	2.222	456	387	17.8	(*9*)
$YTaO_4$	2.885	6.41	2.222	456	409	11.5	(*9*)
$CdMoO_4$	1.835	9.375	5.109	275.2	281	−2.1	(*4*)
$BaMoO_4$	1.342	9.375	6.986	193.3	215	−10.1	(*4*)
$BaWO_4$	1.342	9.231	6.879	197.5	219	9.8	(*4*)
$LaAlO_3$	2.56	5.66	2.211	456.9			(*10*)
$LaNbO_4$	2.56	6.41	2.504	433	322	34.5	(*9*)
$LaTaO_4$	2.56	6.41	2.504	433	507	−14.6	(*9*)
$GdAlO_3$	2.783	5.66	2.034	472.4	492	−4.0	(*11*)
$LuAlO_3$	2.997	5.66	1.889	485.7	486	−0.1	(*12*)
$LuScO_3$	2.997	3.39	1.131	569.9	584	−2.4	(*13*)
$PbMoO_4$	1.504	9.375	6.233	224.1	221	1.4	(*4*)
$PbWO_4$	1.504	9.231	6.138	228.2	234	−2.5	(*4*)

[b] The experimental data (*6*) are the experimental values at 300 K.

N_v from the crystal field parameters B^k_q, and found that there is a linear relationship between the parameter N_v and the largest splitting of the $^4I_{9/2}$, $^4I_{15/2}$, and $^4F_{3/2}$ manifolds of the Nd^{3+} ion in some host crystals. It is known that the crystal field parameters mainly depend on the arrangement of atoms and charge distribution in crystal. In the ABO_n-type compounds, the oxygen atom bonds both with atom A and with atom B. Because the electronegativity of the oxygen atom is larger than that of atoms A or B, the oxygen atom will possess more negative charge, and atoms A and B will possess more positive charge. If atom A and atom B are the same, it can be expected that the center of the charge distribution in the A–O–B link should be at the oxygen atom, and that the potentials at atoms A and B, created by the oxygen anion, should be same. However, if atoms A and B are different, the center of the charge distribution in the A–O–B link should be either between atom A and the oxygen atom, or between atom B and the oxygen atom. Therefore, we consider that the potential at atom A is relative not only to the chemical bonding of atom A with the oxygen atom, but also to the chemical bonding of atom B with the oyxgen atom. The total crystal field splitting ΔE of the activator ion manifolds in the host crystal mainly depends on the potential at the position of the atom replaced by the dopant ion; perhaps, this is why there exists a certain relationship between the total crystal field splitting ΔE of the activator ion manifolds and the ratio of the charge to radius of atoms A and B.

TABLE IV

THE TOTAL CRYSTAL FIELD SPLITTING ΔE OF THE $^4I_{15/2}$ MANIFOLD OF THE Nd^{3+} ION IN THE ABO_n (n =3 2–4)-TYPE COMPOUNDS

Compound	A	B	B/A	ΔE (cal) (cm^{-1})	ΔE (exp) (cm^{-1})	δ (%)	Ref.
$LiYO_2$	1.37	2.885	2.106	935			(*2*)
$LiNbO_3$	1.37	6.41	4.679	606.4	672	−9.8	(*3*)
$CaMoO_4$	1.754	9.375	5.345	542.6	504^a		(*4*)
$CaWO_4$	1.754	9.231	5.263	550.1	529^a		(*4*)
$SrMoO_4$	1.515	9.375	6.188	469			(*4*)
$SrWO_4$	1.515	9.231	6.093	476.9	375^a		(*4*)
$YAlO_3$	2.885	5.66	1.962	960.2	990	−3.0	(*6*)[b]
$YScO_3$	2.885	3.39	1.175	1125.6			(*7*)
YVO_4	2.885	7.375	2.549	864.2	544^a		(*8*)
$YNbO_4$	2.885	6.41	2.222	915.6	713^a		(*9*)
$YTaO_4$	2.885	6.41	2.222	915.6	741^a		(*9*)
$CdMoO_4$	1.835	9.375	5.109	564.5	560^a		(*4*)
$BaMoO_4$	1.342	9.375	6.986	405.3	356^a		(*4*)
$BaWO_4$	1.342	9.231	6.879	413.5	379^a		(*4*)
$LaAlO_3$	2.56	5.66	2.211	917.4			(*10*)
$LaNbO_4$	2.56	6.41	2.504	871	555^a		(*9*)
$LaTaO_4$	2.56	6.41	2.504	871	834	4.4	(*9*)
$GdAlO_3$	2.783	5.66	2.034	947.4			(*11*)
$LuAlO_3$	2.997	5.66	1.889	973.4	975	−0.2	(*12*)
$LuScO_3$	2.997	3.39	1.131	1136.8	864^a		(*13*)
$PbMoO_4$	1.504	9.375	6.233	465.3	408^a		(*4*)
$PbWO_4$	1.504	9.231	6.138	473.2			(*4*)

[b] The experimental data (*6*) are the experimental values at 300 K.

Here, we must emphasize that we never expected to establish the accurate potential value at atom A; we just expected to establish the effect of relative change in the potential at the A or B ion, due to the difference between A and B, on the total crystal field splitting ΔE of the Nd^{3+} ion manifolds in the ABO_n series compounds.

In addition, we have also noted that the deviations for several compounds, for example, the YVO_4 crystal and the $LaNbO_4$ crystal, are larger.

Conclusion

There exists a certain relationship between the total crystal field splitting ΔE of the Nd^{3+} ion manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$) and the ratio of the charge to radius of ion A and ion B in various ABO_n-type compounds. The total crystal field splitting ΔE of the Nd^{3+} ion manifolds ($^4I_{9/2}$, $^4I_{11/2}$, $^4I_{13/2}$, and $^4I_{15/2}$) can be evaluated by means of an empirical formula, and the calculated results are very close to the experimental data. In some cases, on the basis of the calculated total crystal field splitting ΔE, we can check whether the highest Stark level or the lowest Stark level in the Stark levels observed in experiments is the true highest Stark level or the true lowest Stark level for some manifolds of the Nd^{3+} ion. We have discussed why there exists a certain relationship between the total crystal field splitting ΔE of the Nd^{3+} ion manifolds and the ratio of the charge to radius of ions A and B in various different ABO_n (n = 2–4) compounds.

References

1. R. D. Shannon, *Acta. Crystallogr. Sect. A* **32,** 751 (1976).
2. V. A. Antonov, P. A. Arsenev, Sh. A. Vakhidov, E. M. Ibragimova, and D. S. Petrova, *Phys. Status Solidi A* **41,** 45 (1977).
3. V. T. Gabrielyan, A. A. Kaminskii, and L. Li, *Phys. Status Solidi A* **3,** K37, K42 (1970).
4. A. M. Morozov, M. N. Tolstoi, and P. P. Feofilov, *Opt. Spektrosk.* **22,** 258 (1967). [In Russian]
5. F. Auzel, *Mater. Res. Bull.* **14,** 223 (1979).
6. M. J. Weber and T. E. Wartimos *J. Appl. Phys.* **42,** 4996 (1971).
7. Kh. S. Bagdasarov, A. A. Kaminskii, A. M. Kevorkov, L. Li, A. M. Prokhorov, T. A. Tevosyan, and S. E. Sarkisov, *Dokl. Akad. Nauk. SSSR* **224,** 798 (1975). [In Russian]
8. N. Karayians, C. A. Morriso, and D. E. Wortman *J. Chem. Phys.* **62,** 4125 (1975).
9. N. A. Godina, M. N. Tolstoi, and P. P. Feofilov, *Opt. Spektrosk.* **23,** 756 (1967). [In Russian]
10. Kh. S. Bagdasarov, G. A. Bogomolova, M. M. Gritsenko, A. A. Kaminskii, and A. M. Kevorkov, *Kristallografiya* **17,** 415 (1972). [In Russian]
11. P. A. Arsenev and K. E. Binert, *Zh. Prinkl. Spektrosk.* **17,** 1084 (1972). [In Russian]
12. A. A. Kaminskii, A. O. Ivanov, S. E. Sarkisov, I. V. Mochalov, V. A. Ferdorov, and L. Li, *Zh. Eksp. Teor. Fiz.* **71,** 984 (1976). [In Russian]
13. V. A. Antonov, P. A. Arsenev, Kh. S. Bagdarov, A. M. Kevorkov, D. I. Korolev, and A. V. Potenmkin *Opt. Spektrosk.* **54,** 1033 (1983). [In Russian]