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Crystal Structures of the Rare-Earth Orthovanadates

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The structure of $NdVO_4$ is refined from single-crystal X-ray diffraction data. A discrepancy index of 2.8% and oxygen positional parameters $u = 0.1801(6)$, $v = 0.3284(9)$ are obtained. Theoretical calculations of the positional parameters for a series of vanadates are carried out by minimizing the lattice energy with respect to u and v, and assuming the experimental space group and lattice parameters. The results are in good agreement with a simple model, in which the VO_4 geometry remains unchanged.

Introduction

Rare-earth orthovanadates crystallize with the zircon-type structure conforming to space group $I4_1/amd$. The rare-earth ions are in $4(a){:}(0,0,0)$, etc; the vanadium ions in $4(b){:}(0,0,\frac{1}{2})$, etc; and the oxygens in $16(h){:}(0,u,v)$, etc. (For convenience in lattice energy calculations in the origin is chosen at $\bar{4}m2$ and not at the center of symmetry $(0,\frac{1}{4},\frac{1}{8})$). The oxygen parameters have been determined for yttrium vanadate by Broch (*1*) and refined by Baglio and Gashurov (*2*). Patscheke, Fuess, and Will (*3*) have refined the $ErVO_4$ structure.

Since some of these compounds are important luminescent materials, it is of interest to have more precise positional coordinates for all 14 members of the series. Experimental determination of oxygen positional parameters for all rare-earth vanadates by X-ray diffraction methods would be extremely time consuming, and the expected accuracy probably does not warrant such an effort. It would, therefore, be of considerable importance to be able to predict these parameters from a theoretical model. Encouraging results were obtained in crystal energy calculations for *C*-type cubic rare-earth oxides R_2O_3, employing a point-charge model and an additional inverse-power repulsive potential between M^{3+} and O^{2-} (*4*). The purpose of the present paper is to determine whether a similar model yields atomic positions correct to ±0.01 Å for the rare-earth vanadates. In comparison to the oxides, these compounds exhibit several new features, such as a tetragonal crystal class, the presence of three rather than two atomic species, and a probable high degree of covalency in the VO_4^{3-} groups. The important question to be answered is whether the positions of atoms within the unit cell are predicted sufficiently well by a model as simple as that employed for the oxides. To this end, a refinement of the structure of $NdVO_4$ was carried out, and the results were used as experimental data in lattice energy calculations.

X-Ray Studies of $NdVO_4$

The single crystal of neodymium vanadate chosen for X-ray data collection had dimensions of 0.10, 0.10, and 0.21 mm in the **a**, **b**, and **c** directions, respectively. Intensities from hkl ($l = 0,8$) were measured using a Philips "Pailred" automatic diffractometer with graphite-monochromatized Mo$K\alpha$ radiation and scintillation detector. Reflections were scanned at 0.5°/min through an angle of 5.0°. Background was measured for 0.2 min at the extremes of each scan. Only those reflections for which $\Delta I/I \leqslant 0.2$, as estimated from counting statistics, were processed for refinement. A total of 331 independent reflections were collected, each one representing the average of two or more symmetry related reflections.

The intensities were corrected for Lorentz factors, polarization, and absorption. The method used for the latter was that of Busing and Levy (*5*). The direction cosines needed to make these corrections for upper layer lines were calculated from equations

TABLE I

VANADATE LATTICE PARAMETERS

Compound	a_o	c_o
$CeVO_4$	7.3990	6.4960
$PrVO_4$	7.3633	6.4652
$NdVO_4$	7.3290	6.4356
$SmVO_4$	7.2652	6.3894
$EuVO_4$	7.2365	6.3675
$GdVO_4$	7.2126	6.3483
$TbVO_4$	7.1772	6.3289
$DyVO_4$	7.1434	6.3130
$HoVO_4$	7.1214	6.2926
$ErVO_4$	7.0975	6.2723
$TmVO_4$	7.0712	6.2606
$YbVO_4$	7.0435	6.2470
$LuVO_4$	7.0243	6.2316
YVO_4	7.123	6.292

derived by Wells (*6*). No extinction corrections were applied. The lattice parameters for this as well as all other vanadates were those of Swanson, Morris, and Evans (*7* and *8*) and are shown in Table I.

Refinements of the structure were carried out by the full-matrix least squares method. Cromer and Waber's (*9*) values of the scattering factors, together with Cromer's (*10*) values of $\Delta f'$ were used for Nd^{3+} and V^{5+}. No imaginary dispersion corrections were used. The atomic scattering factors for O^{2-} were those evaluated by Tokonami (*11*). The function minimized was $\Sigma w(F_o - F_c)^2$. Two different weighting schemes were used. The first was $w = 1/\Delta I$, where ΔI was estimated from counting statistics and in the other scheme $\sqrt{w} = 100/|F_o|$ for $|F_o| \geqslant 100$ and $\sqrt{w} = 1$ for $|F_o| < 100$. These weighting schemes gave identical oxygen positional coordinates, while the thermal parameters differed by less than one estimated standard deviation. Initial positional and anisotropic thermal parameters were taken from YVO_4. The data were placed on a common scale during the course of the refinement by calculating separate layer line constants after each cycle. The final discrepancy index, $R = \Sigma |F_o - |F_c|| / \Sigma F_o$, was 2.8%. Table II gives the values of the positional and thermal parameters. Observed and calculated structure factors are listed in Table III. Table IV lists interionic distances and angles, and Fig. 1 shows that part of the unit cell which is relevant to the values listed in Table IV.

TABLE II

FINAL COORDINATES AND STANDARD DEVIATIONS[a]

Positional Parameters

$u = 0.1801$	$v = 0.3284$
(0.0006)	(0.0009)

Thermal Parameters × 1000
$[\exp(-B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + B_{23}kl + B_{13}hl + B_{12}hk)]$

	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Nd	1.76	1.76	1.88	0.0	0.0	0.0
	(0.03)	(0.03)	(0.11)			
V	1.73	1.73	3.36	0.0	0.0	0.0
	(0.08)	(0.08)	(0.32)			
O	5.27	4.45	6.92	−3.84	0.0	0.0
	(1.37)	(0.66)	(1.79)	(2.27)		

[a] Origin at Nd; estimates of standard deviations are given in parentheses.

Lattice Energy Calculations

In order to obtain bond lengths and angles for the remaining lanthanide vanadates from existing experimental results, two courses of action may be followed. Powder-diffraction determinations of the lattice parameters (a_o, c_o) would be used in either case. The first possibility is to make the observation that the VO_4 group geometry is nearly identical in the three vanadates whose structures have been refined. Experimental V–O bond distances and O–V–O angles in $NdVO_4$, YVO_4, and $ErVO_4$ are equal, to nearly within the experimental errors. Under this assumption, the expressions for V–O bond length and O–V–O angle in terms of a_o, c_o, u, v may be set equal to weighted averages of the three sets of experimental values. Using (a_o, c_o) from powder diffraction measurements gives two equations for the two unknown oxygen parameters (u, v) in any vanadate. This approach has the disadvantage that there is no way of determining whether the hypothesis is correct, other than by noting that it seems to apply to the three structures that have been determined. Furthermore, these structures were done at different levels of refinement, and consequently the less accurate $ErVO_4$ results may introduce errors in bond lengths equivalent in magnitude to their variation over the entire lanthanide series.

An alternate approach involves energy considerations. Positional parameters which minimize the lattice energy are obtained, with the unit cell parameters constrained to experimental values. Our reasons for following this avenue are twofold: to determine whether reasonable positional para-

TABLE III

Calculated and Observed Structure Factors for $NdVO_4$

H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC	H	K	L	10FO	10FC
0	2	0	2768	-2977	1	3	4	299	293	2	7	3	494	-465	3	10	7	261	-266	5	6	7	350	-364	7	9	2	1028	996
0	2	2	666	-637	1	3	6	1425	1439	2	7	5	544	549	3	11	2	955	-965	5	7	2	1310	-1254	7	9	6	782	-763
0	2	8	1223	-1219	1	4	1	669	627	2	7	7	468	460	3	11	6	830	811	5	7	6	1109	1097	7	10	1	334	-340
0	3	1	1439	-1410	1	4	3	759	-730	2	8	0	1231	1210	3	12	1	369	391	5	8	1	370	354	7	10	3	331	329
0	3	3	803	-807	1	4	5	663	-640	2	8	4	1310	-1292	3	12	3	291	-298	5	8	3	420	-414	7	10	5	278	276
0	3	5	435	440	1	4	7	549	546	2	8	8	980	982	3	13	2	821	834	5	8	5	496	-476	7	11	2	805	-785
0	3	7	369	377	1	5	2	1853	1731	2	9	1	529	517	3	13	6	608	-603	5	8	7	425	428	7	11	6	749	743
0	4	0	2580	2546	1	5	6	1530	-1502	2	9	3	355	348	3	14	5	299	277	5	9	2	1135	1081	7	12	3	269	-280
0	4	2	334	294	1	6	1	630	-608	2	9	5	436	-450	3	14	7	240	-236	5	9	6	906	-900	7	13	2	694	695
0	4	4	1743	-1722	1	6	3	775	751	2	9	7	344	-368	3	15	2	638	-673	5	10	1	322	-323	7	13	6	564	-569
0	4	8	1117	1108	1	6	5	428	423	2	10	0	1122	-1098	3	15	6	512	515	5	10	3	405	412	7	14	5	248	241
0	5	1	600	585	1	6	7	375	-394	2	10	4	1005	1025	3	16	3	207	-200	5	10	5	314	312	7	15	2	583	-572
0	5	3	929	913	1	7	2	1570	-1500	2	10	8	787	-793	3	17	2	481	525	5	10	7	259	-298	7	17	2	393	455
0	5	5	458	-439	1	7	6	1210	1210	2	11	3	385	-367	4	4	0	1829	1792	5	11	2	835	-834	8	8	0	873	872
0	5	7	421	-429	1	8	1	446	441	2	11	5	360	380	4	4	4	1555	-1580	5	11	6	871	864	8	8	4	982	-956
0	6	0	2246	-2167	1	8	3	438	-445	2	11	7	329	356	4	4	8	1112	1089	5	12	3	342	-343	8	8	8	803	776
0	6	4	1416	1404	1	8	5	562	-546	2	12	0	920	904	4	5	1	481	474	5	13	2	747	735	8	9	1	362	363
0	6	8	954	-936	1	8	7	469	473	2	12	4	825	-838	4	5	3	654	635	5	13	6	638	-654	8	9	3	254	250
0	7	1	646	-638	1	9	2	1284	1255	2	12	8	638	668	4	5	5	555	-543	5	14	5	269	268	8	9	5	342	-348
0	7	3	656	-650	1	9	6	950	-972	2	13	1	324	314	4	5	7	484	-489	5	14	7	258	-254	8	9	7	306	-294
0	7	5	377	377	1	10	1	390	-396	2	13	3	213	237	4	6	0	1732	-1666	5	15	2	606	-601	8	10	0	854	-818
0	7	7	334	339	1	10	3	438	450	2	13	5	269	-298	4	6	4	1327	1321	5	17	2	431	475	8	10	4	831	797
0	8	0	1479	1443	1	10	5	337	347	2	13	7	259	-258	4	6	8	939	-934	6	6	0	1616	-1552	8	10	8	654	-647
0	8	4	1263	-1253	1	10	7	294	-319	2	14	0	641	-665	4	7	1	532	-526	6	6	4	1144	1133	8	11	3	250	-267
0	8	8	914	914	1	11	2	952	-941	2	14	4	694	718	4	7	3	491	-476	6	6	8	826	-807	8	11	5	288	302
0	9	1	580	580	1	11	6	924	931	2	14	8	592	-606	4	7	5	479	465	6	7	1	504	-496	8	11	7	281	286
0	9	3	453	484	1	12	1	311	320	2	15	3	198	-200	4	7	7	411	399	6	7	3	504	-501	8	12	0	692	702
0	9	5	301	-312	1	12	3	365	-369	2	15	5	241	242	4	8	0	1221	1176	6	7	5	324	328	8	12	4	681	-675
0	9	7	254	-263	1	13	2	813	817	2	16	0	593	604	4	8	4	1228	-1188	6	7	7	288	295	8	12	8	545	556
0	10	0	1261	-1266	1	13	6	664	-691	2	16	4	506	-561	4	8	8	932	909	6	8	0	1165	1146	8	14	0	524	-542
0	10	4	995	991	1	14	3	216	233	2	18	0	443	-474	4	9	1	519	493	6	8	4	1064	-1036	8	14	4	602	588
0	10	8	742	-732	1	14	5	281	293	3	3	2	2324	-2357	4	9	3	359	360	6	8	8	815	793	8	16	0	502	494
0	11	1	304	-330	1	14	7	297	-271	3	3	6	1167	1190	4	9	5	382	-385	6	9	1	464	462	9	9	2	922	885
0	11	3	458	-473	1	15	2	653	-659	3	4	1	942	928	4	9	7	316	-320	6	9	3	392	388	9	9	6	674	649
0	11	5	288	269	1	15	6	562	582	3	4	3	507	-500	4	10	0	1089	-1068	6	9	5	297	-274	9	10	1	324	-341
0	11	7	278	270	1	16	3	233	-238	3	4	5	577	-582	4	10	4	960	955	6	10	0	1071	-1040	9	10	3	266	264
0	12	0	1025	1026	1	17	2	489	515	3	4	7	448	454	4	10	8	744	-739	6	10	4	864	847	9	11	2	709	-714
0	12	4	801	-809	2	2	0	1935	-1941	3	5	2	1826	1762	4	11	3	382	-370	6	10	8	668	-651	9	11	6	649	635
0	12	8	620	617	2	2	4	1920	2054	3	5	4	253	242	4	11	5	339	329	6	11	3	388	-384	9	12	1	289	271
0	13	1	340	347	2	2	8	1269	-1298	3	5	6	1274	-1271	4	11	7	293	314	6	11	5	259	241	9	12	3	236	-230
0	13	3	276	315	2	3	1	1087	-1096	3	6	1	806	-793	4	12	0	892	885	6	11	7	248	241	9	13	2	620	635
0	14	0	702	-751	2	3	3	435	-432	3	6	3	583	572	4	12	4	783	-788	6	12	0	876	868	9	14	1	271	211
0	14	4	689	697	2	3	5	711	709	3	6	5	388	390	4	12	8	616	626	6	12	4	725	-709	9	15	2	502	-527
0	14	8	565	-567	2	3	7	530	532	3	6	7	309	-321	4	13	3	235	245	6	12	8	559	556	10	10	4	709	677
0	15	3	243	-257	2	4	0	1965	1899	3	7	2	1623	-1517	4	14	0	630	-659	6	13	3	248	265	10	10	8	555	-545
0	16	0	628	667	2	4	4	1752	-1781	3	7	6	1073	1028	4	14	4	666	680	6	14	0	630	-656	10	11	3	269	-270
0	16	4	521	-545	2	4	8	1182	1188	3	8	1	593	574	4	14	8	566	-570	6	14	4	641	618	10	12	0	689	662
0	18	0	471	-517	2	5	1	474	463	3	8	3	347	-330	4	15	3	203	-206	6	15	3	218	-220	10	12	4	590	-581
1	1	2	2142	2360	2	5	3	669	637	3	8	5	519	-506	4	16	0	583	595	6	16	0	567	585	10	14	0	522	-520
1	1	6	1653	-1738	2	5	5	671	-654	3	8	7	410	402	4	18	0	430	-467	7	7	2	1170	-1137	11	11	2	628	-590
1	2	1	606	-620	2	5	7	575	-566	3	9	2	1332	1272	5	5	2	1459	1402	7	7	6	944	917	11	11	6	603	610
1	2	3	737	725	2	6	0	1924	-1775	3	9	6	835	-829	5	5	6	1357	-1325	7	8	1	383	382	11	12	3	216	-234
1	2	5	818	790	2	6	4	1489	1455	3	10	1	473	-491	5	6	1	494	-472	7	8	3	329	-322	11	13	2	534	531
1	2	7	618	-634	2	6	8	1043	-1013	3	10	3	352	356	5	6	3	666	648	7	8	5	410	-411	12	12	0	565	576
1	3	2	2393	2400	2	7	1	583	-550	3	10	5	326	323	5	6	5	395	381	7	8	7	362	355	12	14	0	421	-461
																									13	13	2	438	-477

meters may be calculated by this method, as well as to have more confidence in the invariance of the VO_4 group if this turns out to be true.

TABLE IV

Interionic Distances and Angles

Atoms	Distances (Å)	Atoms	Angles (°)
V–O	1.721 ± 0.005	O(1)–Nd–O(2)	155.7 ± 0.2
Nd–O(1)	2.398 ± 0.004	O(1)–Nd–O(3)	92.5 ± 0.2
Nd–O(5)	2.492 ± 0.005	O(5)–Nd–O(6)	64.0 ± 0.2
O(5)–O(6)	2.640 ± 0.006	O(5)–Nd–O(7)	136.0 ± 0.2
O(3)–O(5)	2.811 ± 0.008	O(5)–V–O(6)	100.2 ± 0.2
O(5)–O(9)	2.892 ± 0.007	O(5)–V–O(9)	114.3 ± 0.2
O(1)–O(5)	3.135 ± 0.006		
O(1)–O(3)	3.466 ± 0.005		

Lattice energy calculations were performed for $ZrSiO_4$ by Sahl and Zemann (*12*). The assumptions in their paper were thought to be inadequate for our purposes for several reasons. Sahl and Zemann show that a minimum in the lattice energy is obtained for a model quite near the experimentally determined structure, using effective charges of +4, +2, and −1.5 for Zr, Si, and O, respectively. This calculation has no predictive value, however, due to constraints placed on the Zr–O and Si–O bond lengths, as well as due to omission of short-range repulsive forces between atom pairs other than oxygen–oxygen.

The use of effective charges makes the model unreasonable in at least two ways. First, the value of the lattice energy calculated by Sahl and Zemann is only approximately one half of the experimental value. Second, the observation may be made that the bare charge (+4, +4, and −2 for Zr,Si,O)

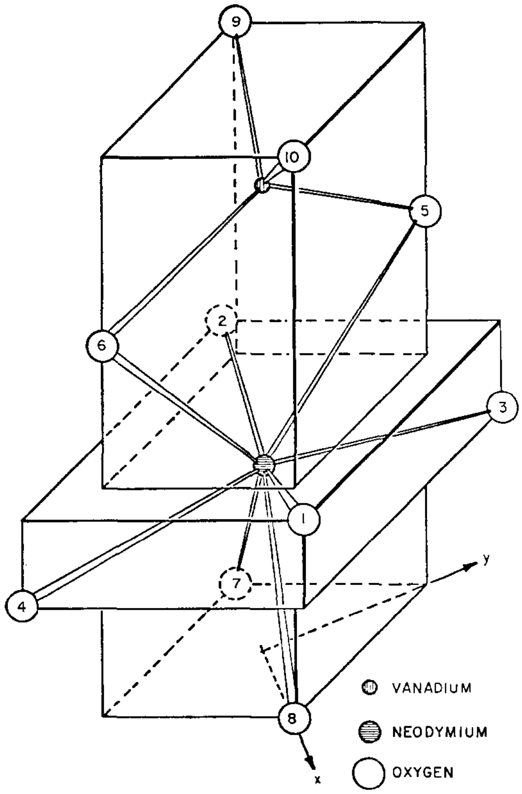

FIG. 1. Near neighbors of a neodymium ion in the $NdVO_4$ lattice.

potential is indeed a bona fide part of the lattice energy expression. Delocalization of the valence electrons around Si and O should properly be accounted for by calculating the magnitude of the electrostatic interaction between such electron distributions, as well as their attraction to the nuclei. If such detailed calculations are not carried out, then it is convenient to assume that these interactions are accounted for by introducing additional non-Coulomb terms in the energy expression.

Another possible model to follow would be that used by Busing (*13*) for alkaline-earth chlorides. The contribution to the energy from each pair of ions in the lattice in Busing's work consists of three terms: bare-charge Madelung part, van der Waals attraction, and exponential repulsion. Not nearly enough data are available to fix reasonable values for the constants involved in the two latter interactions for lanthanide vanadates, and a more simplified model must be adopted.

Our model includes all the features essential to permit unconstrained variation of the oxygen positional parameters. The experimentally determined space group ($I4_1/amd$) and tetragonal lattice parameters (a_o, c_o) are assumed for the vanadate MVO_4. The crystal energy is expressed as

$$E(u,v) = 1/2e^2 \sum_{i \neq j} \frac{q_i q_j}{r_{ij}} + C_M \sum_{M,O} \frac{1}{r_{MO}^m} + C_V \sum_{V,O} \frac{1}{r_{VO}^n}. \tag{1}$$

The point charges in the Madelung term are assumed to be +3 for M, +5 for V and −2 for O. Of all remaining interactions, only short-range repulsive forces between metal and oxygen atoms are included. They are represented by the second and third terms of Eq. (1), where the exponents m and n are chosen according to the rules given by Pauling (*14*). For M=R (a lanthanide), $m = 9.5$; if M = yttrium, $m = 8.5$; for the V–O repulsion, $n = 8$. This model has the virtue of containing only two adjustable parameters (C_M and C_V), while accounting for the salient features of all six types of interatomic interactions. In the model of Sahl and Zemann, the M–O and V–O repulsions are omitted in favor of an extra term for the O–O repulsion, which already appears in the Madelung energy.

There remains the problem of choosing the constants C_M and C_V. Two alternative approaches to the choice of parameters were explored. Both employed experimental data from structure refinements of $NdVO_4$, YVO_4, and $ErVO_4$.

The first approach (Model I) employs values of C_Y and C_R from previous work on Y_2O_3 and the lanthanide oxides R_2O_3 (*4*). To a good approximation, C_R for the lanthanide oxides is a linear function of atomic number: $C_R/10^3 = 511 - 5.845\,Z$ (the units of energy are kcal/mole if distances are in angstroms). In order to determine the vanadium–oxygen repulsion parameter C_V, experimental data on YVO_4, $NdVO_4$, and $ErVO_4$ are employed in the following way. It is required that

$$\sum \frac{1}{(\Delta p_i)^2} \cdot \left(\frac{\partial E(MVO_4)}{\partial p_i} \right)^2 = \text{minimum}, \tag{2}$$

where M = Y, Nd, Er, $p_1 = u$, $p_2 = v$, and Δp_i is the experimental error in the parameter p_i. The minimum requirement is applied for the experimentally measured values of (u,v) of the three vanadates. The weighting factors $1/(\Delta p_i)^2$ are included in Eq. (2) in order to allow the more reliable experimental data to play a larger role in determining repulsion parameters. Since the dependence of lattice energies on the repulsion constants is linear, and C_Y, C_{Nd}, and C_{Er} are fixed, a single differentiation of Eq. (2) with respect to C_V gives a linear equation for its optimum value. The purpose of Model I, then, is

TABLE V

Repulsive Constants and Positional Parameters of Vanadates

	C_M	C_V	u	v
YVO_4				
Experimental	—	—	0.1846(12)	0.3273(13)
Theo., Model I	54 500	13 200	0.1866	0.3300
Theo., Model II	46 800	12 300	0.1868	0.3302
$NdVO_4$				
Experimental	—	—	0.1801(6)	0.3284(9)
Theo., Model I	160 300	13 200	0.1829	0.3339
Theo., Model II	91 600	12 300	0.1800	0.3284
$ErVO_4$				
Experimental	—	—	0.187(2)	0.325(3)
Theo., Model I	113 500	13 200	0.1859	0.3270
Theo., Model II	53 300	12 300	0.1858	0.3234

solely to determine whether metal-oxygen repulsion constants can be transferred from oxides to vanadates.

In the second approach (Model II), all four parameters (C_Y, C_{Nd}, C_{Er}, and C_V) are determined from Eq.(2) at the experimental values of u and v for YVO_4, $NdVO_4$, and $ErVO_4$. As a consequence of the linear dependence of lattice energy on the repulsion constants, the minimum requirement leads to a set of four linear equations for C_Y, C_{Nd}, C_{Er}, and C_V. Repulsion constants for the remaining members of the lanthanide series are obtained by drawing a straight line on a plot of C_R vs. Z through the Nd and Er points. This yields $C_R/10^3 = 379 - 4.788\ Z$, a line nearly parallel to the oxide results. Model II is expected to yield much better results for the vanadates than Model I, since in the former case all repulsion constants reflect the experimental structures of three vanadates.

Comparison of numerical values of the repulsion constants obtained by the two methods should give some indication of the validity of the present models. The values are shown in the second and third columns of Table V. There is fair agreement between C_Y and C_V obtained from the two models, but the values of C_{Nd} and C_{Er} differ by almost a factor of two. Thus the essential difference between Models I and II is the larger magnitude of the metal-oxygen repulsion terms in the former.

Employing the repulsion constants of Table V and the inverse powers of Eq. (1), the problem of calculating positional parameters of a vanadate becomes one of locating the minimum energy (Eq. (1)) as a function of u and v. The point-charge part of $E(u,v)$ was calculated by the method of Bertaut (*15*) with a convergence correction given by Templeton (*16*). The repulsion energy converges much more rapidly and was evaluated by direct summation.

Since neither model contains enough adjustable parameters to constrain $E(u,v)$ to be a minimum at exactly the experimental $NdVO_4$, YVO_4, and $ErVO_4$ structures, another test of the validity of the present approach is obtained by calculating the (u,v) parameters which do minimize $E(u,v)$ of these three vanadates. If these positional parameters show good agreement with the experimental values, then the variation of the lattice energy given by the models must be reasonably correct. Minima are indeed obtained for positional parameters close to the experimental values. The results are shown in the last two columns of Table V. Theoretical parameters calculated with the second set of repulsion constants are within experimental error of the observed parameters for $NdVO_4$ and $ErVO_4$ and within two standard deviations for YVO_4. Larger discrepancies are found with the repulsion constants of Model I. This is not surprising in view of the fact that there is only one adjustable parameter in Model I, in contrast to four for Model II. Good agreement between calculated and experimental parameters indicates that Eq. (1) provides an adequate representation of the variation of lattice energy with respect to positional parameters. The lattice energy of YVO_4 obtained from thermodynamic data in a Born–Haber cycle is approximately 5700 kcal/mole plus the (unknown) standard heat of formation of YVO_4, which must be several hundred kcal/mole. Our calculated lattice energy is 5550 and 5650 kcal for Models I and II, respectively. Despite the discrepancy between these values and the thermodynamic data, the potential surface of Eq. (1) is apparently nearly parallel to the true surface. The discrepancy in lattice energy is probably largely due to covalent bonding in the VO_4 group.

Under the further assumption of linearity of the repulsion constants C_R with atomic number, the variation of (u,v) may be calculated for the series of all lanthanide vanadates. The experimental lattice parameters (a_o, c_o) are used, and a minimum is sought in $E(u,v)$ of Eq. (1). The energy surface is quite flat in the neighborhood of the minimum, especially along the approximate direction $u + v =$ constant, where changes of ± 0.001 in u and v produce a change of only approximately ± 0.05 kcal/mole in $E(u,v)$.

Figures 2 and 3 show the resulting optimum positional parameters as functions of atomic

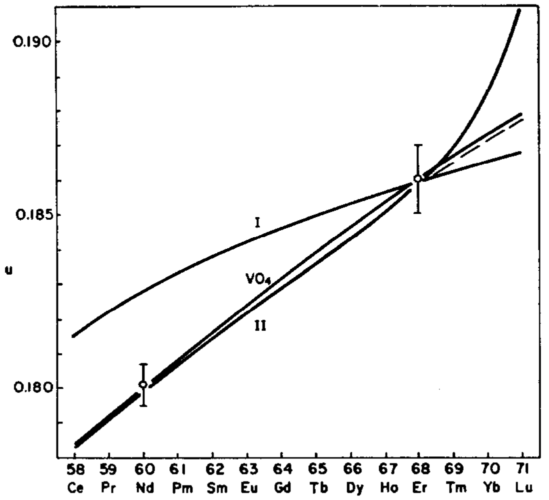

FIG. 2. Oxygen positional parameter u in RVO_4 vs. atomic number of cation R. The curve labeled VO_4 is obtained by assuming that VO_4^{3-} preserves its geometry as a weighted average of those observed in $NdVO_4$, YVO_4, and $ErVO_4$. Curves labeled I and II are obtained from lattice energy calculations using Models I and II described in the text.

number. Also included are curves calculated with the assumption that the VO_4^{3-} geometry (bond distance and angles) remains unchanged from those experimentally observed for $NdVO_4$, YVO_4, and $ErVO_4$; again, experimental values of a_o and c_o are used. Smooth curves, rather than discrete points, are shown; this leads to no errors perceptible on the scale of these figures. Since the ionic radius of a trivalent lanthanide ion varies approximately linearly with its atomic number, there is no advantage in plotting against the former quantity. Least-squares analytical expressions for the variation of u and v with atomic number are

$$u = 0.09841 + 1.905 \times 10^{-3} Z - 9.066 \times 10^{-6} Z^2,$$
$$v = 0.42278 - 2.421 \times 10^{-3} Z + 14.491 \times 10^{-6} Z^2,$$

on the assumption that the VO_4^{3-} geometry is a weighted average of those found for $NdVO_4$, YVO_4, and $ErVO_4$. (The weighting factors are assumed to be inversely proportional to the experimental errors in (u, v)). Experimental values of (u, v) for $NdVO_4$, and $ErVO_4$, together with their probable errors, are indicated in the graphs. The anomalous behavior of positional parameters of $TmVO_4$, $YbVO_4$, and $LuVO_4$ in Model II is probably due to inadequacy of the linear approximation for C_R as a function of Z. It extrapolates to $C_R = 0$ at $Z \approx 79$, whereas the true functional behavior probably shows some curvature. Indeed, if the Tm, Yb, and Lu C_R are taken to be equal to C_{Er}, the anomaly is not as large, as indicated by the dashed lines in Figs. 2, 3, and 4. Figure 4 shows similar plots of the lanthanide–oxygen and vanadium–oxygen bond lengths, r_{RO}, r'_{RO}, r_{VO}. Taking into account the spread of experimental values in $NdVO_4$, YVO_4, and $ErVO_4$ on the one hand, and the spread of calculated values for Models I and II on the other hand, it appears that lattice energy minimization predicts vanadate structures that are in essential agreement with those obtained by assuming an invariant VO_4^{3-} group. Of course, minor departures from the calculated values may occur, due to minor variations in lattice energies which are not accounted for in the present model.

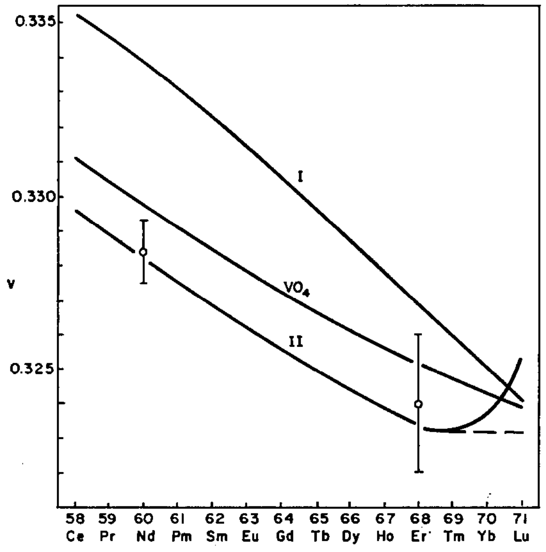

FIG. 3. Oxygen positional parameter v in RVO_4 vs. atomic number of cation R. The curve labeled VO_4 is obtained for constant VO_4^{3-} geometry; curves I and II are obtained from Models I and II.

The main features of Fig. 4 are (a) constancy of the V–O bond length and (b) shortening of the two metal-oxygen distances with increasing atomic number of the lanthanide. The latter correlates with the lanthanide contraction and, in the present model, must be primarily due to the use of experimental lattice parameters which also mirror this effect. Quantitatively, the decrease of the four shorter R–O distances r_{RO}, from $CeVO_4$ to $LuVO_4$ (0.19 Å), agrees well with the difference in ionic radii (*17*) of Ce^{3+} and Lu^{3+} (0.17 Å). The corresponding decrease in the set of four longer R–O distances, r'_{RO} (0.07 Å), is less than one-half of this value.

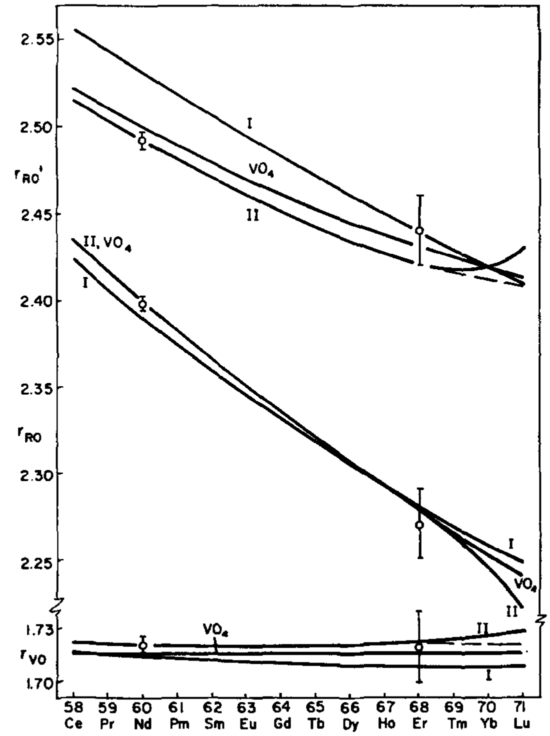

FIG. 4. Lanthanide–oxygen and vanadium–oxygen distances in RVO_4 vs. atomic number of cation. The top and middle sets of three curves show far and near R–O distances r_{RO}', and r_{RO}, respectively; the bottom set shows the V–O distance r_{VO}. Curves labeled VO_4 is for constant VO_4^{3-} geometry, and curves labeled I and II are obtained from Models I and II, respectively.

Further confirmation of the predictions of Figs. 2–4 would be provided by a structure refinement for the vanadate of some lanthanide of high atomic number, such as $LuVO_4$. Although Y^{3+} and Ho^{3+} have essentially equal ionic radii, YVO_4 does not properly belong in this series of compounds because of the different closed shell structure of Y^{3+} and consequent smaller value of the Y–O repulsive exponent.

Attempts to calculate the lattice parameters by allowing a_0 and c_0 to be independent variables in the lattice energy (Eq. (1)) did not yield reasonable results. This indicates that the interionic potentials employed in our models are sufficiently accurate to fix oxygen positions within the unit cell, but additional terms are needed to describe the potential well enough to yield correct unit cell dimensions.

Discussion

It appears that a fairly simple model of the lattice energies of tetragonal rare-earth vanadates gives reasonable oxygen positional parameters, and bond distances of better than 0.01 Å accuracy. The question of VO_4^{3-} covalency has been bypassed by employing experimental data. It would be of interest to repeat these calculations with values of C_V derived from independent sources, such as lattice energy calculations for V_2O_5.

The next major step in calculations such as those described in this paper should be improvement of the quantitative description of interionic potentials, perhaps along the lines considered by Busing (*13*), to make possible accurate calculations of lattice parameters and phase changes, as well as atomic positions of 0.001 Å accuracy. For example, it is well known (*18*) that the stable phase of $LaVO_4$ at room temperature and atmospheric pressure is not the zircon structure. Similarly, the lanthanide phosphates and arsenates show transitions between monoclinic and tetragonal structures between $GdPO_4$ and $TbPO_4$, and between $NdAsO_4$ and $SmAsO_4$, respectively (*19*). The present model constrains the lattice to the $I4_1/amd$ space group and says nothing about the relative stability of the monoclinic form of $LaVO_4$. Extension to calculations of relative stabilities of monoclinic and tetragonal modifications is much more complicated, because lattice parameters as well as positional coordinates must be considered as independent variables for both forms. For calculations relating luminescence properties to crystal structures, bond lengths of 0.001 Å accuracy are probably necessary. As more knowledge is accumulated about interionic potentials, such calculations should become feasible.

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