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Lithiated Rare-Earth Thiospinels and Selenospinels[*,†]

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The spinels $A[Ln_2]X_4$ with A = Cd or Mg and X = S or Se were prepared for Ln = Ho, Er, Tm, Yb, and $Y_{2-x}Yb_x$ (x = 0.0, 1.0, or 2.0). Lithiation with *n*-butyllithium was attempted in the hope of obtaining both mixed-valent and intermediate-valent compounds as well as a continuous variation of the Fermi energy from below to within a localized $4f^n$ configuration. Formation of the mixed-valent compounds $Li_xMg[Yb^{3+}_{2-x}Yb^{2+}_x]X_4$, X = S or Se, with the spinel $[Yb_2]X_4$ framework was accomplished, but lithium displaced cadmium from the cadmium spinels and magnesium from $Mg[Tm_2]Se_4$, which frustrated attempts to obtain an intermediate-valent compound of variable electron/atom ratio.

Introduction

A rare-earth compound containing like rare-earth atoms with both $4f^n$ and $4f^{n+1}$ configurations on crystallographically equivalent lattice sites is said to be *mixed valent* if the Fermi energy lies in an energy gap between broadband electronic states and to be *intermediate valent* if the Fermi energy lies within a broadband of electronic states that overlaps the $4f^{n/n+1}$ redox potential. In general, mixed-valent rare-earth compounds are *small-polaron* conductors (*1*) whereas intermediate-valent compounds exhibit *heavy-fermion* (heavy-electron) (*2*) behavior.

Among the heavy-rare-earth monochalcogenides, semiconducting YbS and YbSe contain single-valent $Yb^{2+} : 4f^{14}$ configurations whereas TmSe is in an intermediate-valence state (*3*). These compounds have the rock salt structure with a 5*d*-like conduction band of t_{2g}-orbital parentage that is broadened by *Ln–Ln* interactions across shared octahedral-site edges; Fig. 1 illustrates schematically the densities of states for the relevant energy bands.

The spinel structure can be derived from the rock salt structure by removal of half the octahedral-site cations—those occupying the empty sites 16*c* of Fig. 2—and introducing tetrahedral-site cations *A* in position 8*a* of the resulting interstitial space to give eight $A[B_2]X_4$ formula units per cubic unit cell. Like the 16*d* sites occupied by the octahedral-site cations *B*, the empty 16*c* sites form a three-dimensionally interconnected network of edge-shared octahedra; each tetrahedral 8*a* site shares its four faces

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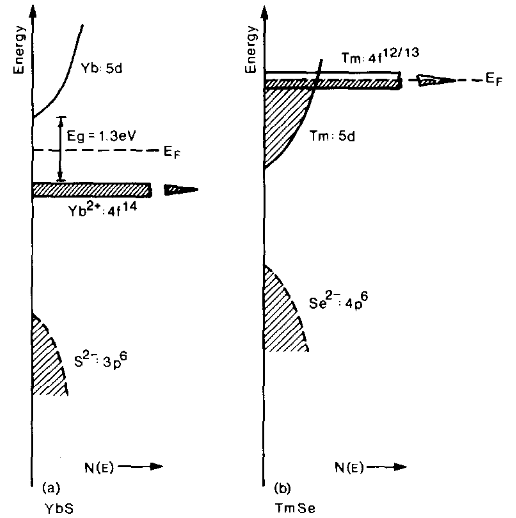

FIG. 1. Schematic densities of states for the relevant energy bands of (a) semiconducting YbS and (b) intermediate-valent TmSe.

with empty $16c$ sites. Thus the $8a$ and $16c$ sites together form a three-dimensional space interstitial to the $[B_2]X_4$ framework of the spinel structure.

The discovery (*4*) that room-temperature lithiation of transition-metal oxospinels leaves the $[B_2]O_4$ framework structurally intact has opened up the possibility of exploring this reaction for both technical applications (*5, 6*) and scientific studies (*7*). In this paper we report an extension of the reaction to thiospinels and selenospinels in an attempt to vary the electron/atom ratio of $[Ln_2]X_4$, X = S or Se, host frameworks for both mixed-valent and intermediate-valent systems.

Preparation of the spinels $A[Ln_2]X_4$ with A = Cd, Mg, or Mn and X = S or Se has already been reported in the literature for the heavier rare-earth atoms Ln (*8, 9*). In the $[Ln_2]X_4$ host, each lanthanide ion has six nearest-neighbor lanthanide ions sharing common octahedral-site edges; in the analogous rock salt structure LnX each has 12 such neighbors. Therefore, we can expect narrower $5d$ conduction bands of t_2-orbital parentage in the $[Ln_2]X_4$ host than in the corresponding LnX compound with the rock salt structure. Hence it follows from Fig. 1 that the Yb : $4f^{13/14}$ redox couple should lie unambiguously below the bottom of the $5d$ conduction band in the $A[\mathrm{Yb}_2]X_4$, X = S or Se, spinels; the Tm : $4f^{12/13}$ redox couple lies closer to the bottom of the conduction band, but whether it lies above or below the bottom of the $5d$ band becomes ambiguous from these qualitative arguments.

On the other hand, the question of particular significance for our proposed experiment is the position of the bottom of the $5d$ band relative to the vacuum reference energy. The middle of the $5d$ band of t_2-orbital parentage is raised from its position on an isolated Ln^{3+} ion by a combination of the electrostatic Madelung energy and Ln–X π-bond covalent mixing; both of these destabilizing factors are greater at a Ln^{3+} ion than at a Ln^{2+} ion, so the $5d$ conduction band must lie at an unambiguously higher absolute energy in the spinel than in the rock salt structure. How much higher is best determined experimentally, but it does not automatically follow that the rare-earth ions of a spinel can be reduced by insertion of electrons into the $5d$ conduction band just because these bands are readily ac-

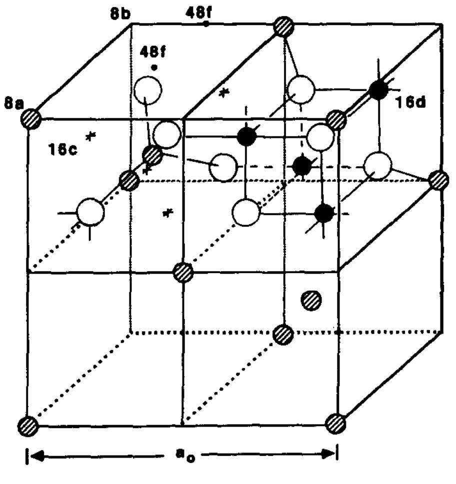

FIG. 2. The spinel structure, space group $Fd3m$.

cessible in the rock salt structure. It was hoped that the reducing power of *n*-butyllithium would be sufficient to reduce the heaviest rare-earth ions in a spinel host in view of the stability of an intermediate-valence state in TmSe, but displacement of magnesium from the spinel lattice proved to be energetically favored over injection of electrons into the Tm–5*d* bands. However, injection of electrons into the $Yb^{3+}:4f^{13}$ levels to reduce Yb^{3+} to $Yb^{2+}:4f^{14}$ was accomplished.

Experimental

Spinel preparation. The starting spinels $M[Ln_2]X_4$ were synthesized in two stages: first, the metal chalcogenides MX and Ln_2X_3 were prepared; second, the chalcogenides were reacted in stoichiometric proportions to form the spinel. Due to the sensitivity of the starting materials and the products to oxygen and moisture, care was taken to work in an atmosphere free of both. All manipulations were done in an argon-atmosphere glove box, and all reactions were done in evacuated silica ampoules.

In the first step, the metal was placed at one end of a horizontal, evacuated silica ampoule and the chalcogenide—in a small excess of the stoichiometric proportion—was placed at the opposite end. The ampoule was placed horizontally in a furnace, and the temperature was raised slowly (ca. 1 deg/min) up to 900°C (1100–1150°C for thulium) and left at that temperature for a short time (<5 hr). The commercial cadmium chalcogenides (Koch-light and Alfa Chemicals) were found to be of good quality.

In the second step, correct molar ratios of the chalcogenides were first carefully ground together. Larger batches were prepared by grinding smaller portions (ca. 0.3 g) at a time. The mixtures were placed in an evacuated silica ampoule and reacted at 1200°C for 16 hr for M = Mg and at 900°C for 2 hr for M = Cd. The heating rate is not critical in this step.

Lithiation. Lithiation of the spinels was carried out by reaction with concentrated *n*-butyllithium (Koch-light, 15% w/w solution in hexane). The reaction was carried out in a Schlenk flask under dry argon or nitrogen by continuously stirring with a magnetic stirrer for several days to several weeks. Since full lithiation of the sample was desired, an excess amount of *n*-butyllithium was used. Once the reaction was completed, the excess *n*-butyllithium was extracted and the compound washed several times with dry petrol. The petrol that could not be extracted was evaporated by slowly applying a vacuum.

X-ray. Powder X-ray diffraction (Philips diffractometer) was used at each stage of the preparation to check on the crystal structures and to record any changes in lattice parameter with lithiation. Lithiation reduces the particle size, so the diffraction lines of the lithiated samples were broadened.

Results

Cadmium Spinels

The cadmium spinels were easier to prepare than the magnesium spinels; CdS and CdSe are quite mobile at 900°C. On the other hand, lithiation of the spinels $Cd[Ln_2]X_4$ took a long time, 1–3 weeks, to complete. Two experiments were performed.

Experiment 1. On the assumption that lithiation would reduce the lanthanide ions, we prepared the series of compounds $Li_xCd[Ln_2]X_4$ with X = S or Se and Ln = Ho, Er, Tm, or Yb. We expected that $Yb^{3+}:4f^{13}$ would be reduced to $Yb^{2+}:4f^{14}$ and that Ho and Er would be reduced by accepting $x/2$ electrons per Ln atom into 5*d*

TABLE I

LATTICE PARAMETERS AND PERCENTAGE CHANGE AFTER LITHIATION OF $Cd[Ln_2]X_4$, X = S OR Se, BEFORE (O) AND AFTER FIRST (I) AND SECOND (II) LITHIATION

	Sulfides		Selenides	
Ln	a_0	Δa_0 (%)	a_0	Δa_0 (%)
Ho	O: 11.157 ± 0.007		11.616 ± 0.004	
	I: 10.914 ± 0.006	−2.18 ± 0.08	11.356 ± 0.006	−2.24 ± 0.06
	II: 10.912 ± 0.005	−2.20 ± 0.08	11.344 ± 0.013	−2.34 ± 0.12
Er	O: 11.125 ± 0.003		11.579 ± 0.005	
	I: 10.887 ± 0.007	−2.14 ± 0.08	11.352 ± 0.024	−1.96 ± 0.21
	II: 10.871 ± 0.011	−2.28 ± 00.03	11.311 ± 0.018	−2.31 ± 0.16
Tm	O: 11.085 ± 0.004		11.536 ± 0.004	
	I: 10.853 ± 0.004	−2.10 ± 0.05	11.315 ± 0.005	−1.91 ± 0.05
	II: 10.844 ± 0.008	−2.18 ± 0.08	11.335 ± 0.012	−1.74 ± 0.11
Yb	O: 11.051 ± 0.002		11.521 ± 0.007	
	I: 10.867 ± 0.012	−1.66 ± 0.08	11.284 ± 0.007	−2.05 ± 0.09
	II: 10.809 ± 0.008	−2.19 ± 0.08	11.278 ± 0.004	−2.11 ± 0.07

bands of t_2-orbital parentage. In the case *Ln* = Tm, we hoped to find an intermediate-valent state, which would have prompted the determination of a critical Li concentration x_c at which the Fermi energy intersected the Tm : $4f^{12/13}$ redox couple. In view of the smaller reduction in lattice parameter for $Cd[Yb_2]S_4$ on the first lithiation reaction, all samples were subjected to a second reaction in order to determine whether lithiation had been complete.

The variations in lattice parameter after the first and second lithiation are given in Table I and compared in Fig. 3 with values for a hard-sphere theoretical model (dashed line) based on $4f^n$ configurations for Ln^{3+} ions and displacement of Cd^{2+} ions from the smaller 8*a* tetrahedral sites to the larger 16*c*

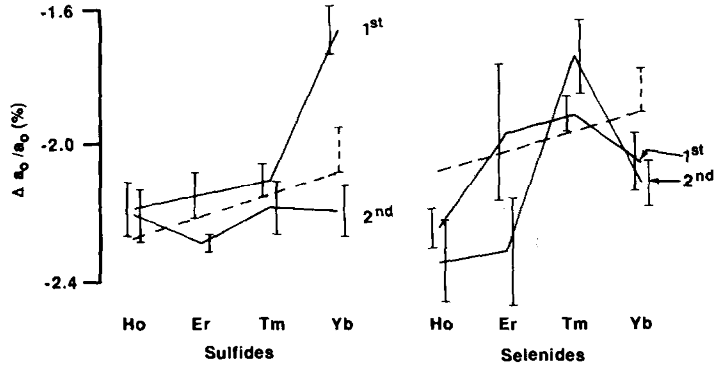

FIG. 3. Percentage lattice-parameter change of $Cd[Ln_2]S_4$ spinels after first and second lithiation reactions compared to theory (dashed line) based on a hard-sphere model, Ln^{3+} : $4f^n$ configurations, and 16*c* octahedral-site Li^+ and Cd^{2+} ions. Vertical dashed line represents effect of changing Yb valence from 3+ to 2.9+.

octahedral sites. The Li^+ ions were also located on the 16*c* sites, and the x electrons from $x \leq 1$ lithium were assumed to occupy 5*d* bands where they contribute little to the lattice-parameter variation. From Fig. 4, we can conclude that the rare-earth ions have the $Ln^{3+}:4f^n$ configuration and the 8*a* sites have become vacant, but these data alone cannot distinguish whether the 16*c* sites are occupied by Li^+ ions only or by a mixture of Li^+ and Cd^{2+} with electrons in the 5*d* bands. However, failure to reduce $Yb^{3+}:4f^{13}$ to $Yb^{2+}:4f^{14}$ as predicted suggested that two Li had displaced Cd^{2+} from the structure in the reaction

$$2Li + Cd^{2+}_{8a} \rightarrow 2Li^{+}_{16c} + Cd^0. \quad (1)$$

TABLE II

STRUCTURAL DATA AND [Li] AND [Cd] CONCENTRATIONS PER FORMULA UNIT AFTER LITHIATION FOR $Cd[Y_{2-x}Yb_x]S_4$, x = 0.0, 1.0, OR 2.0

x	a_0	Δa_0 (%)	[Li]	[Cd]
0.0	11.198 ± 0.003			
Lithiated	10.914 ± 0.006	−2.54 ± 0.06	1.77	1.02
1.0	11.095 ± 0.004			
Lithiated	10.833 ± 0.018	−2.46 ± 0.0.17	2.06	0.54
2.0	11.074 ± 0.003			
Lithiated	10.805 ± 0.004	−2.43 ± 0.05	2.05	0.70

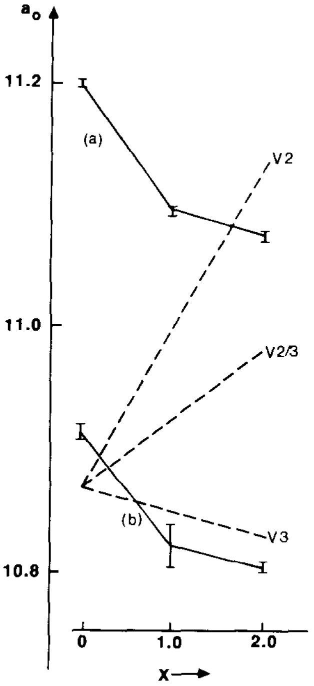

FIG. 4. Lattice parameters for $Cd[Y_{2-x}Yb_x]S_4$ (x = 0.0, 1.0, or 2.0) (a) before and (b) after lithiation compared to theory (dashed lines) for a hard-sphere model ($V2 = Yb^{2+}:4f^{14}$, $V\frac{2}{3} = Yb^{2+}:4f^{14} + Yb^{3+}:4f^{13}$, $V3 = Yb^{3+}:4f^{13}$) with Li^+ and Cd^{2+} in 16*c* octahedral sites.

Experiment II. To test whether the $Yb:4f^{13/14}$ redox level lies above the bottom of the 5*d* band, contrary to our qualitative reasoning, the compounds $Cd[Yb_xY_{2-x}]S_4$ (x = 0.0, 1.0, or 2.0) were prepared and lithiated. The Y–4*d* conduction band should be at a higher energy than the Yb–5*d* conduction band, so doping $Cd[Y_2]S_4$ with Yb substituting for Y should reduce the density of any conduction-band states below the $Yb:4f^{13/14}$ redox couple. It follows that lithiation, if it reduces the Yb^{3+} ions, should introduce sufficient electrons to create $Yb:4f^{14}$ configurations, which would be reflected in an expansion of the lattice parameter.

As can be seen from Table II and Fig. 4, the lattice parameter in this case also behaves as though the ytterbium remains $Yb^{3+}:4f^{13}$. Therefore, we concluded that the $Yb:4f^{13/14}$ redox couple probably does lie below the bottom of the conduction band as originally asserted, but lithiation results in a displacement of the Cd^{2+} ions from the lattice as elemental Cd according to reaction (1); the structural data are not compatible with a lithiation reaction that displaces Cd^{2+} from sites 8*a* to sites 16*c* and reduces the $[Ln_2]X_4$ host matrix.

As a further check on this conclusion, chemical analyses were made for Cd and Li with atomic-absorption spectroscopy. As can be seen from Table II, the Li concentration approaches two atoms per formula unit in accordance with reaction (1); all the octahedral sites would be occupied with one Li per formula unit if the Cd^{2+} ions were displaced from 8*a* to 16*c* sites. Moreover, the concentration of Cd is clearly reduced, proving that at least some Cd is displaced from the lattice and dissolved into the butyllithium–hexane solution. We presume that the Cd analysis indicates the concentration of metallic cadmium remaining at the surface of the particles.

With this evidence that the lithiation reaction had led to displacement of the Cd^{2+} ions from the lattice as described by reaction (1), we decided to substitute Mg for Cd. Rare-earth spinels $M[Ln_2]X_4$ exist for M = Cd, Mg, and Mn. Magnesium has a smaller second-ionization energy than cadmium, and the monochalcogenides MgX, X = S or Se, have larger energy gaps than the corresponding CdX compounds (*10*), so displacement of Mg^{2+} ions from the lattice on lithiation would be less likely. Moreover, the Mg^{2+} ion, like Cd^{2+}, carries no atomic moment whereas the Mn^{2+} ion would carry a high-spin, localized d^5 configuration.

Magnesium Spinels

The number of rare-earth ions that form $Mg[Ln_2]X_4$, X = S or Se, spinels is more restricted than in the case of $Cd[Ln_2]X_4$ (Table III) (*8, 11*).

Experiment I. The compounds $Mg[Tm_2]Se_4$, $Mg[Yb_2]Se_4$, and $Mg[Yb_2]S_4$ were made and lithiated. The results are shown in Tables IV and V. From Table IV it is clear that the thulium compound behaves similarly to the cadmium spinels whereas the two ytterbium compounds are lithiated much more easily and do not indicate any loss of magnesium from the lattice. Lithiation of the ytterbium compounds appears, therefore, to be as originally expected and can be represented as

$$x\mathrm{Li} + \mathrm{Mg}[\mathrm{Yb}_2]X_4 \rightarrow \{\mathrm{Li}_x\mathrm{Mg}\}_{16c}\,[\mathrm{Yb}_2]X_4, \quad (2)$$

where the Mg^{2+} ions are displaced from 8*a* to 16*c* sites and $x \leq 1$ is required since the Li^+ ions also occupy the 16*c* sites. In this reaction, each Li donates an electron to the $[Yb_2]X_4$ spinel framework.

TABLE IV

PERCENTAGE CONVERSION (X-RAY DETERMINATION) AND [Li] AND [Mg] CONCENTRATIONS PER FORMULA UNIT AFTER LITHIATION FOR *t* DAYS OF THREE $Mg[Ln_2]X_4$ SPINELS

Compound	*t* (days)	% Conversion	[Li]	[Mg]
$Mg[Tm_2]Se_4$	18	40–60	1.41	0.57
$Mg[Yb_2]Se_4$ (1)	0.75	100	0.81	1.00
$Mg[Yb_2]S_4$ (I)	2.75	100	0.79	1.03

Note. (I) refers to compound I.

The changes in lattice parameter on lithiation are given in Table V and compared in Fig. 5 to theoretical predictions based on a hard-sphere model. These data are compatible with a Yb : $4f^{13/14}$ redox couple below the bottom of the conduction band; in this case $Li_xMg[Yb_2]X_4$ corresponds to $(2 - x)Yb^{3+} : 4f^{13} + xYb^{2+} : 4f^{14}$ ions per formula unit. The fact that the observed de-

TABLE III

STRUCTURES OF $MgLn_2X_4$ COMPOUNDS (*8, 11*)

	Ln							
X	Dy	(Y)	Ho	Er	Tm	Yb	Lu	(Sc)
S	O	O	O	O	O/S	S	S	S
Se	A	S	S	S	S	S	S	S

Note. S = spinel, O = orthorhombic MnY_2S_4 type, A = other.

TABLE V

STRUCTURAL DATA FOR THREE $Mg[Ln_2]X_4$ SPINELS

Compound		a_0	a_0 (lithiated)	Δa_0 (%)
$Mg[Tm_2]Se_4$		11.452 ± 0.007	11.281 ± 0.008	−1.49 ± 0.09
$Mg[Yb_2]Se_4$	I	11.452 ± 0.002	11.373 ± 0.008	−0.70 ± 0.07
	II	11.468 ± 0.004	11.399 ± 0.003	−0.61 ± 0.04
$Mg[Yb_2]S_4$	I	10.971 ± 0.002	10.868 ± 0.002	−0.93 ± 0.02
	II	10.981 ± 0.004	10.863 ± 0.003	−1.07 ± 0.04

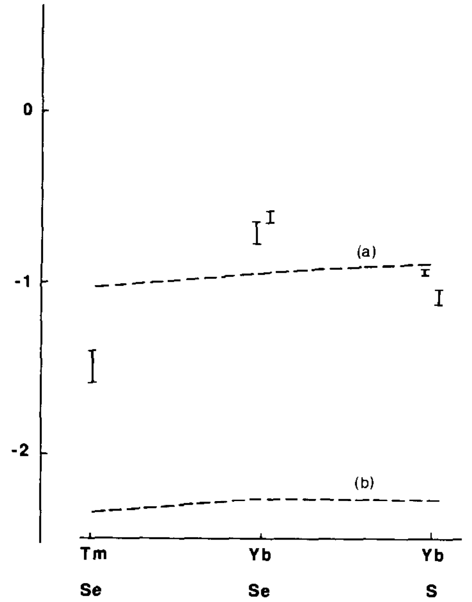

FIG. 5. Percentage lattice-parameter change of $Mg[Tm_2]Se_4$, $Mg[Yb_2]Se_4$, and $Mg[Yb_2]S_4$ after lithiation (bars) compared to theory (dashed lines) for a hard-sphere model with Li^+ and Cd^{2+} in 16*c* octahedral sites. (a) $Ln^{3+}Ln^{2+}$ and (b) Ln_2^{3+}.

crease in lattice parameter for lithiated Mg $[Tm_2]Se_4$ is somewhat less than predicted could mean an incomplete displacement of the magnesium from the lattice, but it more probably reflects the inadequacy of a hard-sphere model in selenides. We thus conclude that the Yb : $4f^{13/14}$ redox couple is stable relative to the energy required to reduce Mg^{2+} to elemental Mg^0, but that the bottom of the 5*d* conduction band is not.

Experiment II. The concentration *x* of Li in $Li_xMg[Yb_2]Se_4$ was next varied by lithiating for different lengths of time. The results are given in Table VI. Chemical analysis shows that within experimental error, no magnesium is lost and that there is a progressive increase in total lithium concentration with the time of the lithiation reaction.

X-ray diffraction of the samples lithiated for 2 and for 4 hr clearly showed the presence of two phases, one having the lattice parameter of the unlithiated sample and the other that of the fully lithiated sample. As the second phase begins to appear on the diffractogram, the superposition of some peaks tends to shift the position of the combined peaks to give the impression of a shift of lattice parameter with initial lithiation. For the sample lithiated for 4 hr, it was possible to correct for this effect, and the corrected lattice parameter corresponds to that of the nonlithiated compound.

Experiment III. A small amount of the fully lithiated sample was sealed in an evacuated silica ampoule, heated to 700°C for 20–30 min, and air quenched.

After this heat treatment, the compound had the same color—black with a hint of green—but X-ray powder diffraction showed a change of structure to an apparent primitive cubic cell of size $\tilde{a}_0 = 2.845 \pm 0.002$ Å, nearly four times smaller than the original unit cell. Such a small unit cell corresponds to the mean volume of a single atom!

This apparent paradox is quickly resolved by a comparison of the mean dispersive power of the metals and that of selenium:

$$68Yb^{2+} + 67Yb^{3+} + 2Li^{+} + 10Mg^{2+} = 146$$

$$4 \times 36(4Se^{2-}) = 144$$

This close match suggests that the metal

TABLE VI

STRUCTURAL DATA AND [Li] AND [Cd] CONCENTRATION PER FORMULA UNIT FOR $Mg[Yb_2]Se_4$ LITHIATED FOR *t* HOURS

t (h)	a_0 (phase I)	a_0 (phase II)	[Li]	[Mg]
0	11.447 ± 0.003		0	1.03
1	11.455 ± 0.007		0.20	0.96
2	11.465 ± 0.007	11.377 ± 0.017	0.34	0.99
4	11.445 ± 0.012	11.361 ± 0.004	0.62	1.02
8		11.360 ± 0.003	0.84	0.96

atoms of $Li_xMg[Yb_2]Se_4$, $x \leq 1$, have become randomly distributed on the octahedral sites of the cubic-close-packed selenium array to give a rock salt structure of lattice parameter

$$a_0 = 2\bar{a}_0 = 5.689 \pm 0.003 \text{ Å}.$$

A search for the reflections suppressed by the almost equal diffractive power of the anions and cations revealed two very small peaks at the first two angles corresponding to the indices 111 and 311. A computation of the annihilations to be expected for a disordered rock salt structure conform to the experimental results.

This observation shows that it would be difficult to sinter the sample and retain the unusual cation ordering obtained by low-temperature lithiation.

Conclusions

Low-temperature (<60°C) lithiation of the spinels $Mg[Yb_2]X_4$, X = S or Se, leads to a rock salt structure having the peculiar cation ordering $\{Li_xMg\}_{16c}[Yb_2]_{16d}X_4$, where sites 16$c$ and 16d are the octahedral sites of a cubic-close-packed anion array in space group $Fd3m$. Each lithium donates an electron to the $[Yb_2]X_4$ framework by reducing an $Yb^{3+}:4f^{13}$ configuration to $Yb^{2+}:4f^{14}$. A two-phase region separates the unlithiated spinel and the lithiated compound. The $Yb:4f^{13/14}$ redox couple lies below the bottom of the 5d conduction band, so the ordered rock salt $\{Li_xMg\}_{16c}[Yb_2]_{16d}X_4$ is a mixed-valent compound.

Attempts to prepare an intermediate-valent compound $Li_xMg[Tm_2]Se_4$ were frustrated; lithium slowly displaces magnesium from the spinel in the reaction

$$2Li + Mg[Tm_2]Se_4 \rightarrow \{Li_2\}_{16c}[Tm_2]_{16d}Se_4 + Mg^0,$$

which leaves all the thulium as Tm^{3+}.

The displacement of cadmium from the $Cd[Ln_2]X_4$ spinels is easier than displacement of magnesium, so displacement reactions are preferred over reduction of the $[Ln_2]X_4$ framework in every lithiation, including the lithiation of $Cd[Yb_2]X_4$, X = S or Se.

The fact that displacement of magnesium is energetically preferred over donation of electrons to the rare-earth 5d conduction band is a surprise in view of the 5d-band occupation in the monochalcogenides LnX. This result shows the importance of covalence and Madelung energies for the positioning of the energy bands.

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