Lattice instabilities near the critical V-V separation for localized versus itinerant electrons in $LiV_{1-y}M_yO_2$ (M = Cr or Ti) and $Li_{1-x}VO_2$

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From the compositional dependences of the lattice parameters in the system $LiV_{1-y}Cr_yO_2$, a critical V-V separation $R_c = 2.90 \pm 0.01$ Å has been determined for an array of octahedral-site V^{3+} ions sharing common octahedral-site edges with six like nearest neighbors. A first-order transition on passing from the itinerant-electron regime $R < R_c$ to the localized-electron regime $R > R_c$ was also established. In $LiVO_2$, the electron instability associated with an $R \approx R_c$ is manifest by V_3 trimer formation at temperatures $T < 490$ K with $R < R_c$ within a trimer and $R > R_c$ between trimers. Introduction of a mixed valence in $Li_{1-x}VO_2$ results in a two-phase mixture in the interval $0 < x \lesssim 0.12$; the metastable $Li_{1-x}VO_2$ phase in the interval $0.12 \lesssim x \lesssim 0.33$ disproportionates above a $T_t' \approx 550$ K into $LiVO_2$ and $Li[V_2]O_4$. Comparisons are made between the instabilities associated with a $W \approx U$ in the copper oxide superconductors and those in the layered and spinel vanadium oxides. In particular, attention is called to evidences for dynamic charge-density fluctuations that appear to be associated with superconductivity in the copper oxides, but not in the vanadium oxides.

I. INTRODUCTION

$LiVO_2$ crystallizes in an ordered rocksalt structure with Li^+ and V^{3+} ions occupying alternate (111) planes. Like the antiferromagnetic semiconductor La_2CuO_4, the compound $LiVO_2$ has a half-filled, essentially two-dimensional (2D) $3d$ band. In addition, the on-site correlation energies U are large enough to inhibit the formation of a negative-U charge-density wave (CDW) in any known vanadium or copper oxide. In a negative-U CDW, electrons are transferred from one subset of like cations to another as in $BaBiO_3$ where $2Bi(IV) \rightarrow Bi_I(IV-\delta) + Bi_{II}(IV+\delta)$. On the other hand, La_2CuO_4 has a bandwidth W arising from nearly 180° Cu-O-Cu interactions whereas $LiVO_2$ has a bandwidth arising from V-V interactions across shared octahedral-site edges.

In the superconductor compositions $La_2CuO_{4+\delta}$ and $La_{2-x}Sr_xCuO_4$, oxidation of the CuO_2 sheets beyond $(CuO_2)^{2-}$ creates a condition $W \approx U$, and it has been conjectured[1] that the origin of the high-T_c superconductivity resides in strong electron-phonon interactions associated with lattice instabilities that inevitably arise where the condition $W \approx U$ is present. Others[2] have also conjectured that there are inherent lattice instabilities in the superconductive copper oxides, but they attribute them to a Van Hove singularity at, or near, the Fermi energy. Of course, there have been many other speculations concerning the mechanism of high-T_c superconductivity that ignore any role associated with lattice instabilities.[3] It is precisely for this reason that we focus attention here on the question of lattice instabilities in compounds with a bandwidth $W \approx U$.

$LiVO_2$ exhibits a first-order structural transition with an order of magnitude increase in the magnetic susceptibility on increasing the temperature through $T_t \approx 490$ K (Ref. 3); this transition has been interpreted[4] to be due to formation of a CDW created by a clustering of the V atoms within a V plane into V_3 trimers, and Bongers[5] has provided experimental evidence to support this interpretation. In this paper we argue that the V-V separation within a basal plane of $LiVO_2$ is $R \approx R_c$, where R_c is a critical separation corresponding to a $W \approx U$. In $LiVO_2$ and $Li_{1-x}VO_2$, the lattice displacements that express the instability inherent in a $W \approx U$, i.e., $R \approx R_c$, are static whereas in the copper oxide superconductors they are postulated to be dynamic. Whether this difference is due to metal-metal interactions in the one case and metal-oxygen-metal interactions in the other remains an open question. However, recent magnetic-susceptibility[6] and NMR data[7] on the spinel system $Li_xZn_{1-x}[V_2]O_4$ indicate that the V^{3+} ions in $Zn[V_2]O_4$ and Zn-rich regions of $Li_xZn_{1-x}[V_2]O_4$ may exhibit below 500 K a dynamic V-V clustering with $R \rightarrow R_c$. What we are interested in establishing is the appearance of inherent lattice instabilities associated with a $W \approx U$; we believe these are significant whether they find expression in a static CDW or in dynamic fluctuations with/without superconductivity. If lattice instabilities are an intrinsic aspect of a system with $W \approx U$, then it is not necessary to invoke a Van Hove singularity to account for the high-T_c superconductivity found in the copper oxides with $W \approx U$.

We report here an investigation of the systems $LiV_{1-y}Cr_yO_2$ and $LiV_{1-y}Ti_yO_2$ to determine a critical V-V separation R_c for the transition from strongly ($R > R_c, W < U$) to weakly ($R < R_c, W > U$) correlated electrons in a V $3d$ band associated with octahedral-site V^{3+} ions sharing common octahedral-site edges with six like nearest neighbors in an oxide. Moreover, we demonstrate that the transition is not smooth, but first-order, in support of the contention that lattice instabilities are implicit in any system where $R \approx R_c$, i.e., $W \approx U$. We also

distinguish the value of R_c obtained for a single-valent system from the value of R at which the transport properties change, in a mixed-valent system, from small-polaron behavior with a motional enthalpy $\Delta H_m > 0$ to transport where $\Delta H_m = 0$. However, identification of the latter may be complicated by the formation of distinguishable electronic pathways in a system made mixed-valent by doping.

In addition, we demonstrate the existence of a distinguishable low-temperature phase with a different transition temperature T_t' in the system $Li_{1-x}VO_2$ obtained by room-temperature extraction of Li from $LiVO_2$. The transition in $LiVO_2$ is reversible on thermal cycling through T_t; heating $Li_{1-x}VO_2$ ($0.12 \leq x \leq 0.33$) through its transition temperature $T_t' \approx 550$ K results in the disproportionation reaction[8]

$$Li_{1-x}VO_2 \rightarrow (1-2x)LiVO_2 + x\,Li[V_2]O_4 \ , \qquad (1)$$

which is irreversible. We present the compositional dependences of T_t and T_t' and the enthalpy changes ΔH on crossing T_t and T_t'; we also argue that they support a model in which T_t and T_t' are determined by the change in lattice energy due to the structural change rather than by the enthalpy ΔH of the transition.

II. EXPERIMENTAL

The $LiV_{1-y}M_yO_2$ (M = Ti or Cr) samples were obtained by firing an intimate mixture of required quantities of Li_2CO_3, V_2O_5, and Cr_2O_3 or TiO and TiO_2 under flowing H_2 atm first at 770 K for 5 h to release CO_2 and then at 970 K for 15 h. Although this firing schedule leads to single-phase material for $y = 0$, it also produces traces of impurity phases for $y > 0$. Therefore all products with $y > 0$ were further fired in flowing N_2 at 1020 K for 24 h for M = Cr and at 970 K for 15 h for M = Ti; they were then quenched in N_2 atm to ambient temperature. The additional heat treatment yielded single-phase samples for $0 < y \leq 0.2$ with M = Ti. The end member $LiCrO_2$ was prepared by firing required quantities of Li_2CO_3 and Cr_2O_3 under flowing N_2 at 770 K for 5 h, 970 K for 15 h, and finally 1070 K for 24 h. Since commercial Cr_2O_3 is too refractory, a "soft" Cr_2O_3 was used. The soft Cr_2O_3 was obtained by the precipitation of $Cr_2O_3 \cdot x H_2O$ gel from $Cr(NO_3)_3 \cdot \xi H_2O$ with NH_4OH and driving off the water from the gel at 600 °C for 1 h.

The $Li_{1-x}VO_2$ samples with $0 \leq x \leq 0.33$ were obtained by extracting Li from $LiVO_2$ at room temperature with a calculated amount of Br_2 (0.05 N in chloroform solution).[8,9] Since oxidants absorbed on the surface of $LiVO_2$ are known to extract Li from the bulk at ambient temperature,[8] exposure to air was avoided; the samples were stored in an argon-filled dry box immediately after preparation.

All samples were characterized by x-ray powder diffraction recorded with a Philips diffractometer and Cu $K\alpha$ radiation. The Li content was determined by atomic absorption with a Perkin-Elmer 1100 atomic absorption spectrometer after calibrating the instrument with a lithium carbonate solution of known concentration. Differential scanning calorimetry (DSC) plots were recorded in N_2 atm at 10 °C min^{-1} with a Perkin-Elmer Series 7 thermal analysis system.

III. A CRITICAL V-V SEPARATION R_c

A. Review of the problem

The V^{3+} ions of $LiVO_2$ occupy octahedral sites sharing common octahedral-site edges with $z = 6$ like near neighbors in a close-packed V^{3+}-ion plane. Each V^{3+} ion has two $3d$ electrons; the trigonal crystalline field removes the t_2-orbital degeneracy to create an empty a_1 orbital normal to the plane and twofold-degenerate e_π orbitals directed toward nearest-neighbor V^{3+} ions within a basal plane. Thus the crystal symmetry removes an orbital degeneracy to create a narrow, half-filled, two-dimensional (2D) $3d$ band of e_π parentage. The band is twofold-degenerate, and the bandwidth—in tight-binding theory $W \approx 2zb$—varies exponentially with the V-V separation R via the matrix element

$$b \equiv (\psi_i, H'\psi_j) \approx \varepsilon(\psi_i, \psi_j) \ , \qquad (2)$$

where H' is the perturbation of the e_π-electron potential at $\mathbf{R}_j$ due to the presence of a neighboring like atom at $\mathbf{R}_i$, ε is a one-electron energy, and (ψ_i, ψ_j) is an overlap integral. A $(\psi_i, \psi_j) \sim \exp(-R/\rho)$, where ρ is a parameter of units of R, arises from the overlap integral for a V-V interaction across an interatomic distance R. At low temperature $T < T_t$, the formation of V_3 trimers, Fig. 1, would change the translational symmetry so as to split the 2D half-filled V $3d$ band in two; an $R < R_c$ within a cluster and an $R > R_c$ between clusters would result in the capture of conduction electrons within molecular orbitals. A change in translational rather than point-group symmetry is taken[4] to signal an $R \lesssim R_c$ at temperatures $T > T_t$, and a more recent report[10] that strong infrared bands appearing below T_t disappear on crossing T_t supports this view. Bongers[3] reported that on increasing the temperature through T_t, the axial c/a ratio (hexagonal basis) decreases from $a = 2.83, c = 14.87$ Å to $a = 2.89$, $c = 14.48$ Å. This observation renders $R = 2.89$ Å $\lesssim R_c$.

Based on the idea that V_3 trimers are formed below T_t in $LiVO_2$ because of an $R \leq R_c$ and the observation of localized V^{3+}-ion moments ($R > R_c$) in the normal spinel $Mn[V_2]O_4$, it was thought possible to determine experimentally the room-temperature value of R_c in the vanadium oxides for an array of octahedral-site V^{3+} ions sharing octahedral-site edges with $z = 6$ nearest like neighbors.[11] In such a determination, it is necessary to distinguish oxides containing vanadium atoms with a single-valence state from those with vanadium in a mixed-valence state as occurs, for example, in $Li[V_2]O_4$.

Conceptually, as R decreases to R_c in a single-valent system, the bandwidth W increases and the on-site correlation energy U decreases toward crossover where the compound changes from a magnetic semiconductor with $R > R_c$ and $W < U$ to a metal with $R < R_c$ and $W > U$.[12] Increased screening of the on-site $3d$-electron interactions with decreasing R creates a rapid change in U with R

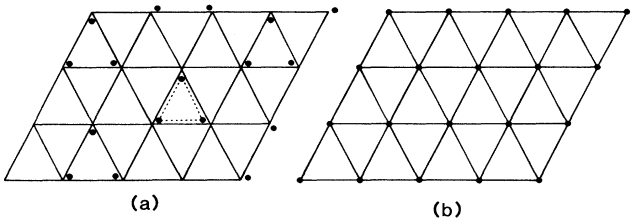

FIG. 1. Proposed arrangement of atoms in vanadium planes of $LiVO_2$ (a) below T_t and (b) above T_t showing V_3 clustering below T_t.

near $R \approx R_c$, which may cause the change from $R > R_c$ to $R < R_c$ to be discontinuous via a first-order phase change. A demonstration of the character of the changeover would be instructive.

An initial attempt to determine an R_c experimentally involved a study of the normal spinels $A^{2+}[V_2]O_4$, where A = Mg, Mn, Fe, Co, and Zn.[11] In these normal spinels, an array of octahedral-site V^{3+} ions shares common edges with $z = 6$ nearest neighbors as in $LiVO_2$. However, the layered oxide $LiVO_2$ has a degree of freedom—namely, the variation of the c/a ratio—that is not available to the cubic spinels where the $[V_2]O_4$ framework is three dimensional. All the spinels contained localized V $3d$ electrons, so the study only gave an upper limit of 2.97 Å for R_c, the V-V separation in $Co[V_2]O_4$.

Following the observation[13] that Li can be inserted at room temperature into the spinel structure $A[B_2]O_4$ without perturbing the $[B_2]O_4$ framework, the ordered rocksalt $Li_2[V_2]O_4$ was prepared[8,14,15] by room-temperature Li insertion into the mixed-valent spinel $Li[V_2]O_4$. This "soft-chemistry" procedure allowed preparation of a single-valent spinel framework $[V_2^{3+}]O_4$ with a V-V separation $R = 2.93$ Å. However, $Li_2[V_2]O_4$ is an antiferromagnetic semiconductor, which renders $R_c < 2.93$ Å. In view of the evidence for V_3 trimer formation in $LiVO_2$, which has a V-V separation at T_t of 2.89 Å, it was concluded[8,15] that the critical V-V separation is restricted to the narrow range

$$2.89 \lesssim R_c < 2.93 \text{ Å} \tag{3}$$

for oxides containing octahedral-site V^{3+} ions sharing common octahedral-site edges with $z = 6$ nearest neighbors.

On the other hand, Reuter *et al.*[16,17] used infrared spectroscopy to identify a smooth transition from semiconductor to metallic behavior at $x \approx 0.55$ for $A_{1-x}Li_x[V_2]O_4$ mixed-valent spinels with A = Mg or Zn. The V-V separation at this transition led to an apparent $R_c \approx 2.94$ Å for a $V^{4+/3+}$ mixed-valent system. However, the paramagnetic susceptibility of the metallic end member $Li[V_2]O_4$ obeys a Curie-Weiss law typical of localized magnetic moments on the vanadium atoms but without undergoing magnetic ordering to lowest temperatures.[15,18,19] This observation indicates that the electrons remain strongly correlated in metallic $Li[V_2]O_4$ and that the transition identified by Reuter *et al.*[16,17] needs further consideration. Indeed, recent experiments on the system $Li_xZn_{1-x}[V_2]O_4$ reveal a somewhat more complex behavior. First, although the Seebeck data[20] were consistent with a smooth semiconductor-metal transition with increasing x in the range $0.3 < x_c < 0.4$, they could be interpreted in terms of the coexistence of two types of conductive pathways within a single atomic phase: band conduction in one and variable-range hopping in the other. Second, magnetic-susceptibility[21] and neutron-diffraction[22] data indicate antiferromagnetic order at lowest temperatures in $Zn[V_2]O_4$ with a V^{3+}-ion atomic moment $\mu_v \approx (0.8 \pm 0.4)\mu_B$ and the appearance of a weak ferromagnetic component (phase) on the initial substitution of Li for Zn. Third, the magnetic-susceptibility data[21] also revealed two distinguishable paramagnetic temperature domains, $T > 500$ K and $T_N < T < 500$ K, each with distinguishable Curie-Weiss parameters. For $T > 500$ K the parameters were typical for localized, mixed-valent V^{3+}, V^{4+} configurations; for $T < 500$ K, the Curie constant C and Weiss constant Θ had larger magnitudes in $Zn[V_2]O_4$. Moreover, NMR data in the temperature range $10 < T < 300$ K (Ref. 7) revealed the presence of two distinguishable electronic pathways (phases) within an atomically single-phase system $Li_xZn_{1-x}[V_2]O_4$; a metallic pathway associated with mixed-valent V^{4+}, V^{3+} ions neighboring A-site Li^+ ions and a semiconductor pathway associated with single valent regions of V^{3+} ions neighboring all A-site Zn^{2+} ions. The semiconductor-metal transition observed in $Li_xZn_{1-x}[V_2]O_4$ at a critical Li concentration x_c was therefore interpreted to represent a percolation threshold for the metallic pathway (electronic phase). Surprisingly, the NMR data also revealed little electronic crossover between the two phases and a nonmagnetic V^{3+}-ion ground state in the semiconductor pathway (electronic phase). A nonmagnetic ground state below 400 K in the semiconductor pathway implies strong antiferromagnetic ordering within cluster fluctuations within the $[V_2]O_4$ spinel framework. The strong spin pairing within cluster fluctuations is apparently broken up by the introduction of V^{4+} ions, and this breakup of the cluster fluctuations produces a distinguishable electronic pathway that coexists with the spin-paired pathway.

The picture that emerges from these experiments is the existence of an intrinsic electronic instability associated with an $R \rightarrow R_c$ that, in a single-valent system, may be manifest as a static charge-density wave (CDW). In a mixed-valent-system, segregation into two distinguishable electronic phases within an atomically single-phase system may also occur. The two electronic phases may be statically separated where there is a mixed array of counter cations; however, it is also possible to envisage a dynamic segregation via charge-density fluctuations (CDF's) as has been postulated[1] to occur in the high-T_c copper oxide superconductors.

B. Pinpointing R_c

To narrow further the range (3) for R_c, we have returned to $LiVO_2$ and inquired at what concentration y of

Cr in $LiV_{1-y}Cr_yO_2$ a transition occurs from $R < R_c$ to $R > R_c$. Figure 2 shows the variation with y of the lattice parameters, c/a ratio, and the cell volume at room temperature and at $250\,^\circ > T_t$. In the compositional range $0 \le y \le 0.25$, the substitution of a smaller ($r_{Cr} = 0.615$ Å) Cr^{3+} ion for a V^{3+} ion ($r_V = 0.64$ Å) causes an anomalous increase with y in the room-temperature a parameter and volume; at $T \approx 250\,^\circ C > T_t$ these parameters decrease as expected, but more rapidly than in the interval $0.3 < y < 1.0$. Note that the strong temperature dependence of the parameters in the region $0 < y \lesssim 0.25$ is due to the traversal of T_t between room temperature and 250 °C.

The discontinuity in the variations with y of lattice parameters and cell volume at $y \approx 0.25$ suggests that the compositions with $0 \le y \lesssim 0.25$ belong to a phase electronically distinguishable from the one for compositions with $0.3 \lesssim y \le 1.0$. This conclusion is supported by the fact that, although samples with $0 \le y \le 0.25$ and $0.35 \le y \le 1.0$ could be made easily, the $y = 0.3$ sample was difficult to obtain as a single-phase material.

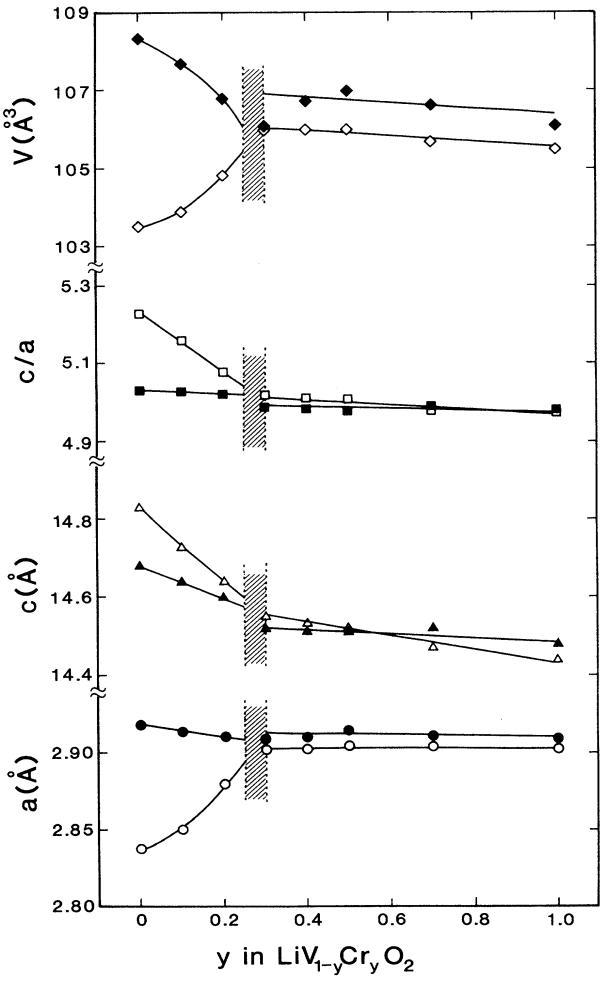

FIG. 2. Variations of lattice parameters and cell volume with y for $LiV_{1-y}Cr_yO_2$; shaded area indicates a two-phase region. The open and solid symbols refer to the data recorded, respectively, at room temperature and 250 °C.

An octahedral-site Cr^{3+} ion carries a localized $^4A_{2g}$ $3d$-electron configuration $a_1^1 e_\pi^2 e_\sigma^0$, where the two e_σ orbitals are σ bonding whereas the a_1 and e_π orbitals have t_2-orbital parentage in the absence of a trigonal component to the crystalline field. The e_π-e_σ hybridization increases with the strength of the trigonal component of the crystalline field. In $LiCrO_2$ these localized configurations can be expected to impart a Cr^{3+}-ion magnetic moment of approximately $3\mu_B$ with antiferromagnetic Cr-Cr superexchange interactions within a plane; there is no clustering into Cr_3 trimers and the condition $R > R_c$ is applicable in $LiCrO_2$. In the system $LiV_{1-y}Cr_yO_2$, the Cr^{3+} ions retain their localized configurations, and the condition $R > R_c$ holds for the Cr-V interactions. Reduction of the mean number $\bar{z}$ of near-neighbor V-V interactions at a V^{3+} ion reduces the tight-binding bandwidth $W \approx 2\bar{z}b$, where b is given by Eq. (2). As a result, R_c decreases with increasing y more rapidly than does the V-V separation R at $T > T_t$; this decrease can be expected to be enhanced by any induced localization of the V $3d$ electrons at V^{3+} ions neighboring a Cr^{3+} ion. Consequently, the critical V-V separation R_c must be traversed with increasing y at some critical composition $y = y_c$. Therefore we conclude that the phase transition that occurs on crossing the compositional range

$$0.25 \le y_c \le 0.3 \tag{4}$$

represents a transition from $R < R_c$ to $R > R_c$ at the V^{3+} ion array. The fact that the transition is not smooth, but appears to be separated by a narrow two-phase region, has two important implications:

(i) The localized-electron (strongly correlated) and itinerant electron (weakly correlated) regimes for a single-valent array represent two thermodynamically distinguishable states.

(ii) At $R \approx R_c$, which corresponds to a $W \approx U$, a single-valent system is intrinsically unstable relative to a disproportion into phases with $R < R_c$ and $R > R_c$.

The lattice-parameter variations with y for $y > y_c$ appear to obey a normal Végard's law. Extrapolation of the room-temperature a parameter to $y = 0$ from the localized-electron domain $0.3 < y \le 1.0$ gives an upper limit for R_c of 2.905 Å. Given a lower limit of 2.89 Å in $LiVO_2$ itself, we believe the data demonstrate a critical separation distance

$$R_c = 2.90 \pm 0.01 \text{ Å} . \tag{5}$$

The volume dilatation predicted to occur on passing from an $R < R_c$ to an $R > R_c$ (Ref. 12) is present, but somewhat obscured by the crystallographic transformation occurring in the $y < y_c$ ($R \gtrsim R_c$) phase; a similar discontinuous volume increase has been found to occur in several copper oxide systems on passing from the superconductor to the antiferromagnetic phase.[23,24] The large volume expansion on passing from $T < T_t$ to $T > T_t$ reflects the first-order character of that transition; the data suggest that in $LiVO_2$ the lattice vibrations just

above T_t are probably anomalously large at 250 °C in anticipation of the structural transformation.

In the itinerant-electron phase ($0 \leq y < y_c$), the remarkable decrease in the a parameter at room temperature from its value at 250 °C reflects not only the anomalous expansion at $T > T_t$, but also an added basal-plane V-V bonding at $T < T_t$. The localized-electron configurations of the Cr^{3+} ions would not share in this basal-plane V-V bonding, so we can anticipate not only an increase in the a parameter with y despite the smaller size of a Cr^{3+} ion, but also a decrease with increasing y of both T_t and of the enthalpy change ΔH at T_t. From the DSC data of Figs. 3 and 4, it is apparent that T_t falls nearly linearly with increasing y to about room temperature at $y \approx 0.2$ whereas ΔH drops much more rapidly, falling to about a tenth of its magnitude in $LiVO_2$ at $y \approx 0.2$. In fact, although the lattice-parameter variation with y indicates a $T_t > 280$ K for $y = 0.2$, we were unable to detect with DSC a phase transition in any sample with $y \geq 0.2$ down to 77 K. The enthalpy ΔH measures the difference between the change in electronic energy that drives the first-order transition and the elastic-energy change that inhibits it; the transition temperature T_t appears to be controlled by the change in the lattice energy on passing through the transition. Consequently T_t remains finite throughout the compositional range $0 \leq y < y_c$, disappearing discontinuously on entering the localized-electron phase $y_c < y \leq 1.0$. On the other hand, ΔH drops to a small value within the compositional range $0 \leq y < y_c$.

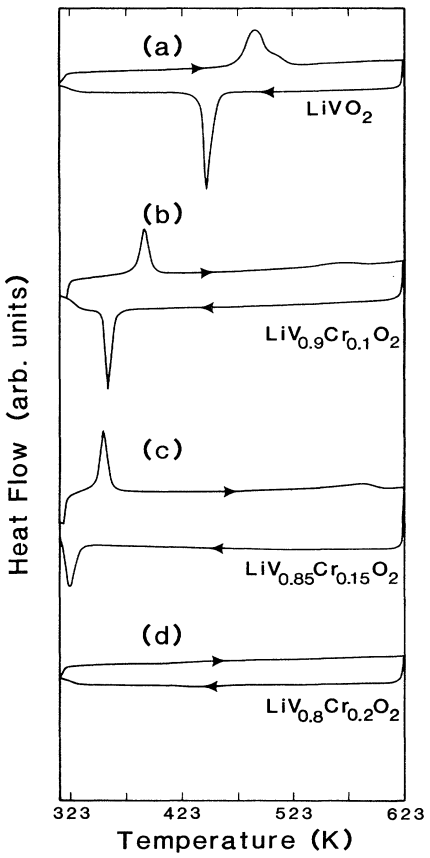

FIG. 3. DSC plots recorded on heating and cooling in N_2 atm at 10 °C min^{-1} for (a) $y = 0.0$, (b) $y = 0.1$, (c) $y = 0.15$, and (d) $y = 0.2$ in $LiV_{1-y}Cr_yO_2$.

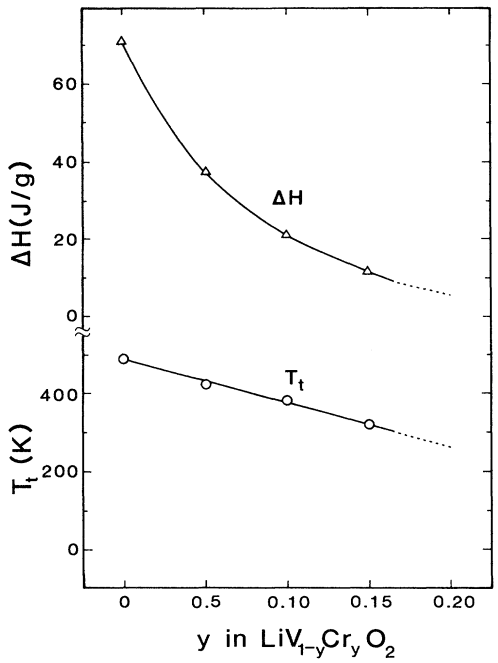

FIG. 4. Variations of enthalpy change ΔH and transition temperature T_t with y for $LiV_{1-y}Cr_yO_2$ in the phase $0 \leq y < 0.25$.

Finally, the formation of cation clusters with $R < R_c$ within a cluster (molecular orbitals) and $R > R_c$ between clusters may be considered an internal disproportionation into $R < R_c$ and $R > R_c$ distances via atomic displacements rather than by atomic diffusion. In this sense, formation of V_3 trimers is an expression of the intrinsic instability associated with a phase having $R \approx R_c$, i.e., $W \approx U$.

C. The system $LiV_{1-y}Ti_yO_2$

Unlike Cr_2O_3, which is an antiferromagnetic insulator, Ti_2O_3 contains itinerant $3d$ electrons and exhibits a smooth semiconductor-metal transition associated with a band-edge crossing on raising the temperature.[25] Therefore, a Ti^{3+} ion might participate with V^{3+} ions in the formation of cation clusters. However, with only one $3d$ electron per Ti^{3+} ion, any triangular clusters containing Ti^{3+} ions would be electron deficient. Moreover, the difference in electronic potentials at the Ti^{3+} and V^{3+} ions makes less stable the participation of a Ti^{3+} ion in molecular-orbital formation with V^{3+} ions; stronger Ti-Ti interactions could become competitive. Therefore ΔH and T_t can be expected to decrease with y in $LiV_{1-y}Ti_yO_2$ also, but somewhat less steeply than occurs in $LiV_{1-y}Cr_yO_2$, and strong Ti-Ti interactions could lim-

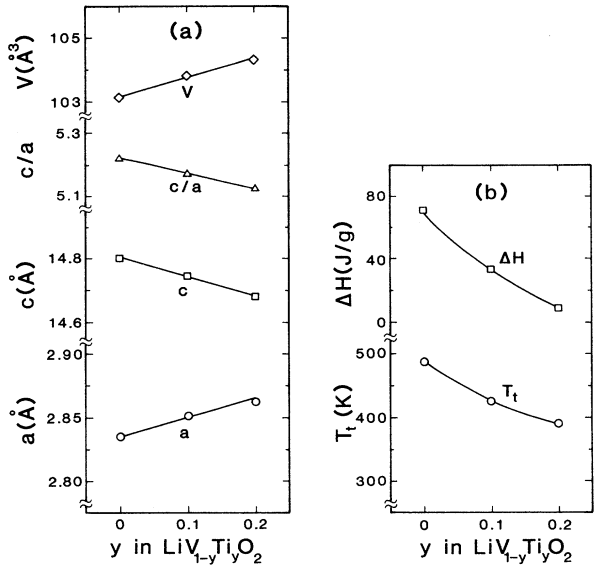

FIG. 5. Variations of (a) lattice parameters and cell volume and (b) enthalpy change ΔH and transition temperature T_t with y for $LiV_{1-y}Ti_yO_2$.

it the range of solid solubility.

Indeed, x-ray powder diffraction revealed that the solid solution of Ti in $LiV_{1-y}Ti_yO_2$ is limited to the range $0 \leq y \leq 0.2 < y_c$. The variation with y of the room-temperature ($T < T_t$) lattice parameters and cell volume is shown in Fig. 5(a); the variation of T_t and ΔH with y is shown in Fig. 5(b). In this system also, the drop in ΔH with increasing y is much more precipitous than the drop in T_t, but neither of these variables drops as steeply with y as they do in $LiV_{1-y}Cr_yO_2$.

Although no direct information on the value of R_c is forthcoming from this system, the data are consistent with an instability for $R \approx R_c$ that extends in this system to $y = 1$; even the end member $LiTiO_2$ is reported to be contaminated with other phases such as Li_2TiO_3.[26]

IV. THE SYSTEM $LiVO_2$-VO_2

DSC plots for the system $Li_{1-x}VO_2$ are shown in Fig. 6; the different compositions were obtained by extracting Li from $LiVO_2$ at room temperature with a Br_2 solution. As observed previously,[8] the T_t obtained in the first heating cycle increases from 490 K at $x = 0$ to 550 K at $x = 0.125$, but it remains constant for all x in the interval $0.125 \leq x \leq 0.33$ although ΔH, Fig. 7, decreases monotonically with x throughout the range $0 \leq x \leq 0.33$. The disproportionation reaction (1) above T_t into $LiVO_2$ and $Li[V_2]O_4$ returns the observed T_t to 490 K on cooling and on the second heating cycle for all x; the phase $Li[V_2]O_4$ contributes no signal. Of particular interest for this study is the behavior below T_t in the range $0 < x < 0.125$, which has not previously been explored.

On heating, the DSC curves exhibit two peaks in the range $0 < x < 0.125$, which indicates the presence of two

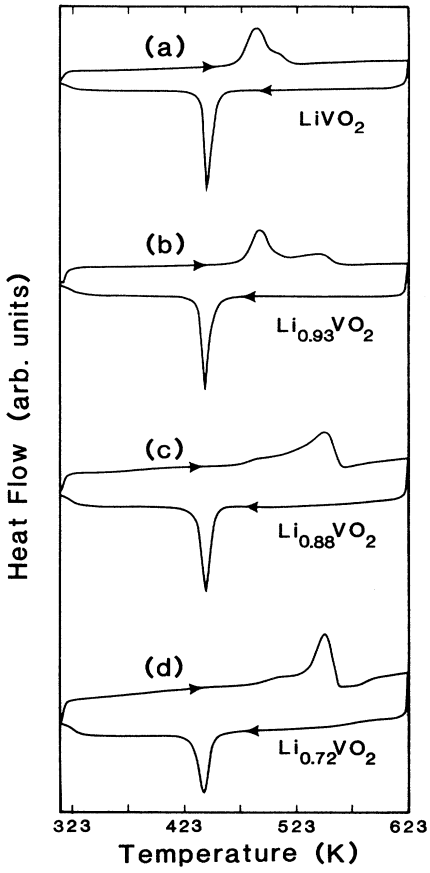

FIG. 6. DSC plots recorded on heating and cooling in N_2 atm at 10 °C min^{-1} for (a) $x = 0.0$, (b) $x = 0.07$, (c) $x = 0.12$, and (d) $x = 0.28$ in $Li_{1-x}VO_2$.

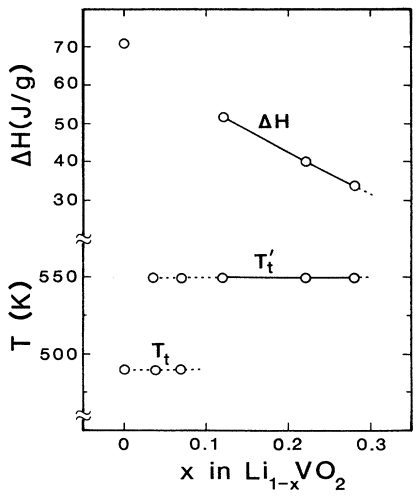

FIG. 7. Variations of enthalpy change ΔH and transition temperatures T_t or T_t' with x for $Li_{1-x}VO_2$. In the two-phase region $0 < x < 0.12$, the ΔH values are not shown.

distinguishable low-temperature phases each with its own value of T_t. We designate them $T_t \approx 490$ K for $LiVO_2$ and $T_t' \approx 550$ K for $0.12 < x \leq 0.33$.

An increase in T_t with decreasing electron concentration in the clusters would seem to be inconsistent with the stabilization of V_3 trimers below T_t in $LiVO_2$. Therefore, it was postulated[8] that this anomaly probably reflects the introduction of a ferroelectric-type displacement of V^{4+} ions away from each other across a broken bond in a trimer deficient in two electrons. Such a model requires the capture of two holes per electron-deficient trimer at two vanadyl units $(VO)^{2+}$ in $V(VO_2)$ clusters coexisting with V_3 trimers. In order to test this speculation, room-temperature infrared data for $Li_{0.7}VO_2$ and VO_2 were taken and compared. It is known that the transition below 67 °C in VO_2 involves not only the formation of dimers, but also the rocking of the dimers to form vanadyl $(VO)^{2+}$ species.[12,27] In VO_2, an infrared peak appears near 980 cm^{-1}, the position for the vanadyl ion[28]; in $Li_{0.7}VO_2$ this peak is absent. Therefore, we seem forced to conclude that there is no vanadyl formation in the oxidized VO_2 planes of $Li_{1-x}VO_2, 0.12 < x \leq 0.33$. This conclusion is also consistent with a monotonic decrease in ΔH with x. Thus, these results reinforce the deduction that the transition temperature T_t is controlled more by the lattice-energy change through the distortion than by the ΔH of the transition; indeed, the low-temperature phases for $LiVO_2$ and $Li_{1-x}VO_2$ with $0.12 < x \leq 0.33$ must be structurally distinguishable since they represent distinguishable phases.

These studies, together with the detailed investigation of the $Li_{1-x}VO_2$ and $Li_{1+x}V_2O_4$ systems reported previously,[8] yield the phase diagrams of Figs. 8 and 9 for the system $LiVO_2$-VO_2. $LiVO_2$ is a line phase—limited solubility range not determined—that is stable to at least 750 °C. It undergoes a structural transformation at $T_t \approx 490$ K. The spinel phase $Li[V_2]O_4$ may also be obtained by high-temperature synthesis,[29] but more easily by room-temperature extraction of half of the Li from $LiVO_2$ followed by heating to above 550 K.[8] The spinel phase undergoes no structural transformation to lowest temperatures. The end member VO_2 is also accessible by high-temperature synthesis; it undergoes a structural transformation at 67 °C.[30] This relatively simple phase diagram is given in Fig. 8.

Two distinct metastable phase diagrams may be obtained below 550 K; Fig. 9 is relevant under conditions where Li is extracted from $LiVO_2$; another (not shown) can be obtained by Li insertion/extraction into/from the spinel $Li[V_2]O_4$. Figure 9 shows a metastable phase in the compositional range $0.12 < x \leq 0.33$ that disproportionates above $T_t' = 550$ K into $LiVO_2$ and $Li[V_2]O_4$. Two-phase regions exist for $0 < x \lesssim 0.12$ and $0.33 < x < 0.67$. The phase $LI_{0.33-x}VO_2$ is stabilized by an ordered arrangement of one-third of the V atoms in the planes that were originally all Li atoms.[31] Room-temperature electrochemical extraction of Li from $LiVO_2$ (Ref. 32) indicates the presence of phases over the range $0.33 < x < 0.67$ whereas the domain $0.125 \leq x \leq 0.33$ shows an open-circuit voltage V_{oc} varying smoothly with x as for a solid-solution range. Like ΔH, the open-circuit voltage tracks the total number of electrons active in V-V bonding whereas T_t reflects some other parameter—presumably the change in lattice energy through the structural transformation.

The metastable phase diagram obtained from Li insertion into $Li[V_2]O_4$ is much simpler; it yields the solid-solution range $Li_{1+x}[V_2]O_4$, $0 \leq x \leq 1$, in which the $[V_2]O_4$ spinel framework stays intact and the Li^+ ions occupy an increasing proportion of octahedral sites with increasing x until, at $x = 1$, the ordered rocksalt phase $Li_2[V_2]O_4$ is obtained. What happens on extraction of Li from $Li[V_2]O_4$ has not been studied carefully. It appears that there is no large solid-solution range between $Li[V_2]O_4$ and cubic $[V_2]O_4$—as occurs, for example, in the system $Li_{1-x}[Mn_2]O_4$, but rather a conversion to the

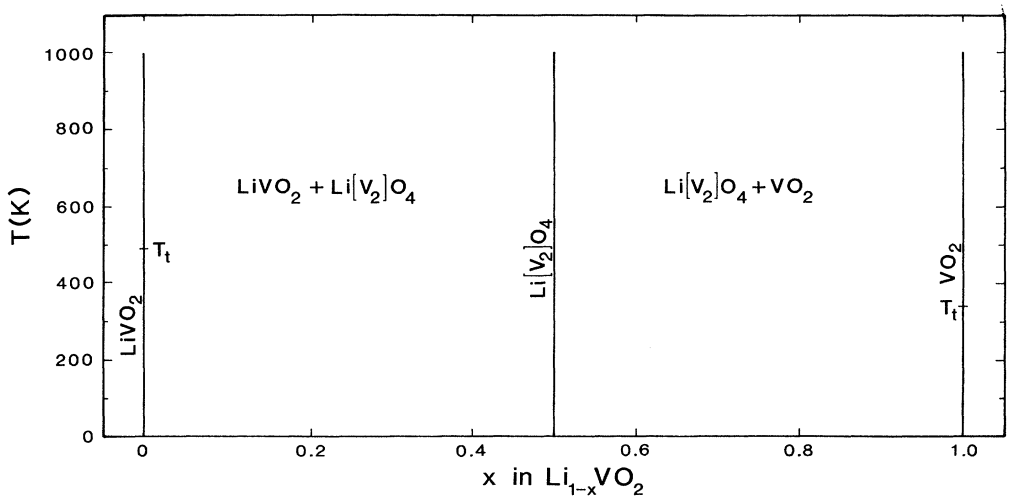

FIG. 8. Equilibrium phase diagram for the system $LiVO_2$-VO_2 prepared above 550 K.

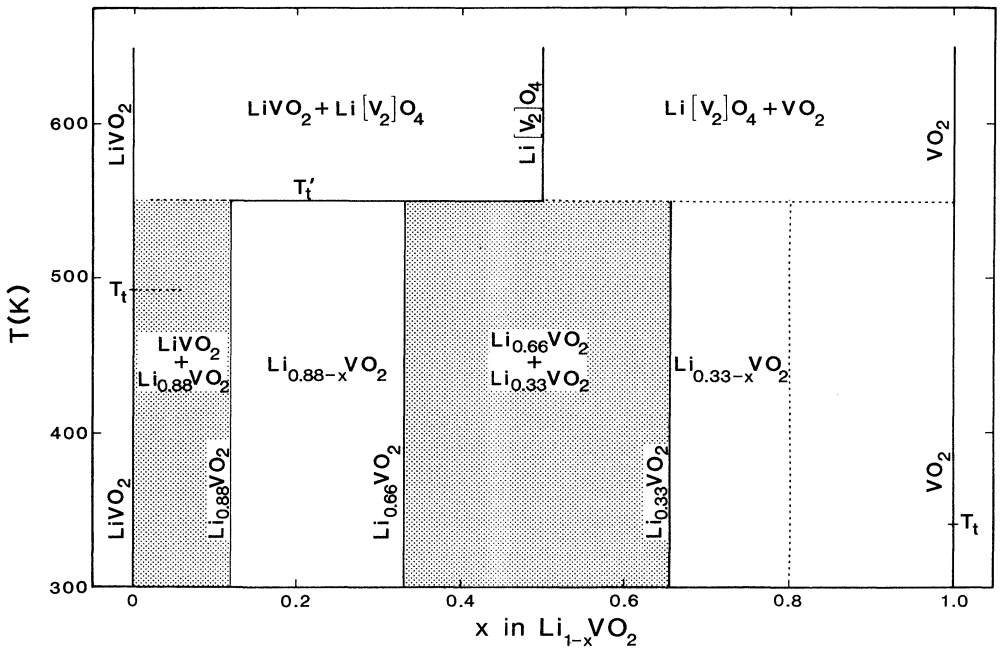

FIG. 9. Phase diagram for the system $LiVO_2$-VO_2 obtained on heating samples prepared by room-temperature extraction of Li from $LiVO_2$.

layered phase $Li_{0.33}V_2O_4$. It may prove significant that $2.93 > R > 2.91 \gtrsim R_c$ in the range $Li_2[V_2]O_4$ to $Li[V_2]O_4$. Extraction of Li in $Li_{1-x}[V_2]O_4$ forces the condition $R \approx R_c$, which we predict to be unstable.

V. CONCLUSIONS

We have demonstrated that $R_c \approx 2.90 \pm 0.01$ Å for the room-temperature V-V separation in an oxide with an array of V^{3+} ions sharing common octahedral-site edges with $z = 6$ like near neighbors. We have shown that the condition $R \approx R_c$, which corresponds to a $W \approx U$, is intrinsically unstable. In the single-valent system $LiV_{1-y}Cr_yO_2$, for example, this instability is manifest in a two-phase compositional range separating $R < R_c$ for $y < y_c$ from $R > R_c$ for $y > y_c$. In the system $Li_{1-x}VO_2$, the single-valent end member ($x = 0$) forms V_3 trimers below $T_t \approx 490$ K, and a two-phase region in the interval $0 < x \leq 0.12$ separates the single-valent phase from the mixed-valent compositional range. Moreover, the mixed-valent compositions disproportionate above $T_t' = 550$ K into $LiVO_2$ and the spinel $Li[V_2]O_4$. We have also shown that the transition temperature T_t below which a CDW is formed is controlled more by the lattice-energy change associated with the structural transformation than by the total enthalpy change ΔH associated with the transition.

Metastable phase diagrams below 550 K have been obtained for the $LiVO_2$-VO_2 system by room-temperature Li extraction from $LiVO_2$ and by Li insertion or extraction into or from $Li[V_2]O_4$.

Comparisons have been made between the high-T_c copper oxides and the vanadium oxides. In the superconductor copper oxides, the condition $W \approx U$ is also encountered; a large on-site U inhibits the formation of a negative-U CDW, as is also the case in the vanadium oxides discussed. The bandwidth W in the copper oxides is associated with nearly 180° Cu-O-Cu interactions; it is sensitive to the hole concentration in an oxidized CuO_2 layer because the covalent-mixing parameter λ_σ reflects a system near crossover from a more ionic to a more covalent Cu:3d-O:2p_σ bonding.[33] The bandwidth W in the vanadium oxides discussed is associated with V-V interactions that vary exponentially with the V-V separation R across shared octahedral-site edges. In both the copper oxides and the vanadium oxides, intrinsic lattice instabilities appear to be associated with the condition $W \approx U$. These instabilities are manifest as static phase segregations, static charge-density waves, and—it would appear—also as dynamic charge-density fluctuations. Where the dynamic charge-density fluctuations give rise to superconductivity and where they give rise to some other phenomenon represents an open and fascinating field of investigation.

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[1]J. B. Goodenough and J.-S. Zhou, Phys. B. **42**, 4276 (1986).
[2]R. S. Markiewicz, *Superconductivity and its Application (Buffalo, 1990),* Proceedings of the Fourth Annual Conference on Superconductivity and its Application, AIP Conf. Proc. No. 219, edited by Yi-Han Kao, Philip Coppens, and Hoi-Sing Kwok (AIP, New York, 1991).
[3]P. F. Bongers, Ph.D. dissertation, University of Leiden, Leiden, The Netherlands, 1957.
[4]J. B. Goodeneough, *Magnetism and the Chemical Bond* (Interscience and Wiley, New York, 1963), p. 269.
[5]P. F. Bongers, in *Crystal Structure and Chemical Bonding in Inorganic Chemistry,* edited by C. J. M. Rooymans and A. Rabenau (Elsevier, New York, 1975), Chap. 4.
[6]F. Takagi, K. Kawakami, I. Maekawa, Y. Sakai, and N. Tsuda, J. Phys. Soc. Jpn. **56**, 444 (1987).
[7]Y. Amako, T. Naka M. Onoda, H. Nagasawa, and T. Erata, J. Phys. Soc. Jpn. **59**, 2241 (1990).
[8]A. Manthiram and J. B. Goodenough, Can. J. Phys. **65**, 1309 (1987).
[9]K. Vidyasagar and J. Gopalakrishnan, J. Solid State Chem. **42**, 217 (1982).
[10]T. A. Hewston and B. L. Chamberland, J. Solid State Chem. **65**, 100 (1986).
[11]D. B. Rogers, R. J. Arnott, A. Wold, and J. B. Goodenough, J. Phys. Chem. Solids **24**, 347 (1963).
[12]J. B. Goodenough, Prog. Solid State Chem. **5**, 145 (1971).
[13]M. M. Thackeray, W. I. F. David, and J. B. Goodenough, Mater. Res. Bull. **17**, 785 (1982); M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, *ibid.* **18**, 461 (1983).
[14]L. A. de Picciotto and M. M. Thackeray, Mater. Res. Bull. **20**, 1409 (1985).
[15]J. B. Goodenough, A. Manthiram, A. C. W. P. James, and P. Strobel, in *Solid State Ionics,* edited by F. Nagri, R. A. Muggins, and D. F. Shriner, MRS Symposia Proceedings No. 135 (Materials Research Society, Pittsburgh, PA, 1989), p. 391.
[16]B. Reuter and J. Jaskowsky, Ber. Bunsten-Ges. Phys. Chem. **70**, 189 (1966).
[17]B. Reuter and K. Müller, Naturwissenschaften **54**, 164 (1967).
[18]H. Kessler and M. Sienko, J. Chem. Phys. **55**, 5414 (1971).
[19]B. L. Chamberland and T. A. Hewston, Solid State Commun. **58**, 693 (1986).
[20]K. Kawakami, Y. Sakai, and N. Tsuda, J. Phys. Soc. Jpn. **5**, 3174 (1986).
[21]Muhtar, F. Takagi, K. Kawakami, and N. Tsuda, J. Phys. Soc. Jpn. **57**, 3119 (1988).
[22]S. Niziol, Phys. Status Solidi A **18**, K11 (1973).
[23]J. B. Goodenough and A. Manthiram, Physica C **157**, 439 (1989).
[24]A. Manthiram, X. X. Tang, and J. B. Goodenough, Phys. Rev. B **42**, 138 (1990).
[25]L. L. Van Zandt, J. M. Honig, and J. B. Goodenough, J. Appl. Phys. **39**, 594 (1968).
[26]T. A. Hewston and B. L. Chamberland, J. Solid State Chem. **59**, 168 (1985).
[27]R. Heckingbottom and J. W. Linnet, Nature **194**, 678 (1962).
[28]G. Ladwig, Z. Anorg. Allgem. Chem. **364**, 234 (1969).
[29]D. B. Rogers, J. B. Goodenough, and A. Wold, J. Appl. Phys. **35**, 1069 (1964); D. B. Rogers, J. L. Gillson, and I. E. Gier, Solid State Commun. **5**, 263 (1967).
[30]G. Andersson, Acta Chem. Scand. **10**, 623 (1956).
[31]M. M. Thackeray, L. A. de Picciotto, W. I. F. David, P. G. Bruce, and J. B. Goodenough, J. Solid State Chem. **67**, 285 (1987).
[32]L. A. de Picciotto, M. M. Thackeray, W. I. F. David, P. G. Bruce, and J. B. Goodenough, Mater. Res. Bull. **19**, 1497 (1984).
[33]J.-S. Zhou, J. B. Goodenough, K. Allan, and A. Champion (unpublished).