# $^{51}$V NMR of the Layered δ-LiV$_2$O$_5$

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Magnetic susceptibility indicates an apparent similarity in the electronic structure of δ- and γ-LiV$_2$O$_5$. However, $^{51}$V ($I = \frac{7}{2}$) NMR clearly demonstrates a significant difference between the two: While at room temperature, γ has a broad asymmetric line, which narrows and splits up as the temperature is lowered; δ at room temperature exhibits three lines, a central split line from $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition (17.318 MHz) flanked on both sides by broad lines from spin paired singlets (17.489 MHz) and hyperfine shifted isolated V$^{4+}$ spins (17.237 MHz). At 100 K, the $^{51}$V NMR line of δ is unshifted, though considerably broadened and intensified. NMR indicates that γ undergoes a structural distortion around 150 K, whereas the already highly distorted δ undergoes no further distortion. Finally NMR and susceptibility studies point to the possibility of bipolaron formation (even at room temperature) in δ-LiV$_2$O$_5$, as in Pb$_x$V$_2$O$_5$ ($x = 0.44$). © 1989 Academic Press, Inc.

## Introduction

Much interest in the study of the structural and electronic properties of lithium-inserted metal oxides of V$_2$O$_5$ (Li$_x$V$_2$O$_5$) has been generated. Several alkali metal (Li, Na, K, Cu, Ag, etc.) vanadium bronzes can be prepared at high temperatures (*1–3*), whereas at ambient temperature only Li can be intercalated (*4–6*). The room-temperature (rt) phases ε and δ are metastable and are readily converted to the high-temperature phases β and γ at higher temperatures (Fig. 1). Both δ and γ are stoichiometric compounds (LiV$_2$O$_5$) with different layered structures (*6, 7*). Recently, it has been shown by Cava *et al.* (*8*) from neutron and X-ray diffraction studies that the distortion in the δ phase is quite unusual and

involves a buckling in the corner-shared pyramids and a puckering of the layers to accommodate the Li ions (Fig. 2). However, in contrast to γ-Na bronze, which contains two molecules per unit cell (as does V$_2$O$_5$ itself) there is a cell doubling (*8, 9*) in γ- and δ-LiV$_2$O$_5$ with a lattice expansion along the *c* direction (Table I).

In δ-LiV$_2$O$_5$ there is only one kind of vanadium site (*8*), so V$^{4+}$ (produced by the introduction of Li into the V$_2$O$_5$ matrix) has no preferential sites as in γ. Thus V$^{4+}$ can occupy two neighboring sites, if the coulomb repulsion between them can be overcome or V$^{4+}$ can have V$^{5+}$ as its neighbor. As a result, there is a possibility of random pairing of V$^{4+}$, as well as of direct electron exchange between V$^{4+}$ and V$^{5+}$ causing valence fluctuation. Even cluster forma-
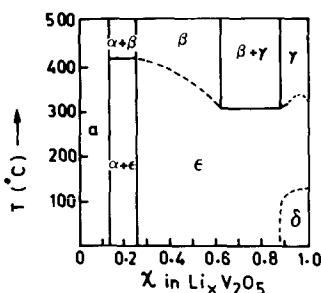
FIG. 1. Phase diagram of $Li_xV_2O_5$ (5).

tion in the $\alpha$ phase of rt $Li_xV_2O_5$ has been indicated by EPR studies (10). The indirect hyperfine coupling between $V^{5+}$ and $V^{4+}$ sites through oxygen also must be taken into account. In the present work, $^{51}V$ NMR has been employed to study the electronic and magnetic structure of $\delta$-$LiV_2O_5$. Similar studies of some other intercalated compounds containing vanadium have been done by $^{51}V$ NMR (11, 12). $^{51}V$ NMR studies are expected to shed light on the nature of distortion in $\delta$-$LiV_2O_5$ and its variation with temperature. The results have been compared with the closely related $\gamma$-$LiV_2O_5$ in order to obtain a better understanding of the intercalated $V_2O_5$ system.

## Results and Discussion

Except for $\delta$-$LiV_2O_5$ (M) (courtesy of Dr. D. W. Murphy of AT&T Bell Laboratories), all compounds prepared at ambient temperature, including that previously reported by us (13) as $\delta$-$LiV_2O_5$ (possibly transformed to $\varepsilon$-$LiV_2O_5$ through drying above ambient temperature), show well-defined $^{51}V$ NMR at 15 MHz in a CW Variac WL spectrometer at room temperature (Fig. 3a). For $\delta$-$LiV_2O_5$ (M), no signal could be detected at room temperature, even with a signal averager. However, a weak signal (split line) was observable below 218 K, which increased in intensity on further cooling. Eventually, with a modified CXP 90 Bruker FT NMR spectrometer and the pulse-echo (PE) method, a three-line spectrum was observed at room temperature (Fig. 3b) at 17 MHz. The $\frac{1}{2} \rightarrow -\frac{1}{2}$ transition of $^{51}V$ ($I = \frac{7}{2}$) corresponds to the narrow central split line flanked on two sides by two broad lines. These broad lines were not observed in the room temperature spectra of $^{51}V$ by the CW method (Figs. 3a and 3b). The possibility of the two broad lines being satellites of the central line ($\frac{1}{2} \rightarrow -\frac{1}{2}$) is ruled out by the following considerations: (1) other satellites corresponding to $I = \frac{7}{2}$ should have been observed because the broad lines are quite intense at low temperatures, and (2) the intensity distribution of the lines changed considerably at 100 K, which is not expected in the case of satellites.

At this stage, a comparison of the PE spectra of $\delta$ with the CW spectra of rt $Li_xV_2O_5$ is relevant. The $^{51}V$ NMR in the $\alpha$
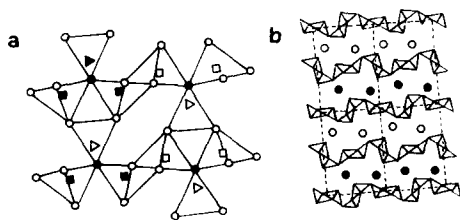


FIG. 2. Crystal structure of (a) δ-LiV₂O₅ lithium, △; vanadium, □; oxygen, ○ (8); (b) γ-LiV₂O₅ (7).

TABLE I

X-RAY DATA OF $Li_xV_2O_5$

| Sample | $a$ (Å) | $b$ (Å) | $c$ (Å) | (°) |
|---|---|---|---|---|
| $V_2O_5$ | 11.50 | 3.565 | 4.374 | 90 |
| $\alpha$-$LiV_2O_5$ (6) | 11.498 | 3.566 | 4.382 | 90 |
| $\beta$-$LiV_2O_5$ (6) | 10.03 | 3.60 | 15.38 | 110.40 |
| $\gamma$-$LiV_2O_5$ (7) | 9.702 | 3.607 | 10.664 | 90 |
| $Li_{0.1}V_2O_5$ ($\alpha$) (6) | 11.495 | 3.565 | 4.386 | 90 |
| $Li_{0.45}V_2O_5$ ($\varepsilon$) (6) | 11.413 | 3.565 | 4.518 | 90 |
| $LiV_2O_5$ ($\delta$) (8) | 11.2423 | 3.6018 | 9.9054 | 90 |
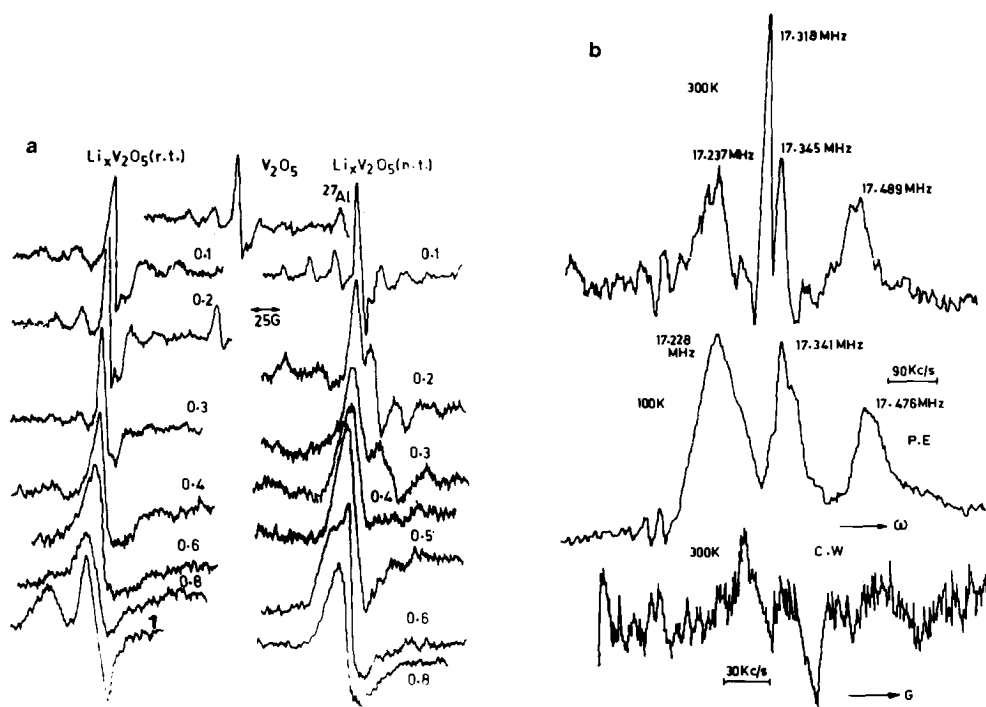
Fig. 3. (a) $^{51}$V NMR of Li$_x$V$_2$O$_5$ at 15 MHz at 300 K. (b) $^{51}$V NMR of δ-LiV$_2$O$_5$ (M) by PE and CW methods.

phase of rt Li$_x$V$_2$O$_5$ (Fig. 3a) is quite similar to that of V$_2$O$_5$ (13), and the central line ($\frac{1}{2}$ → $-\frac{1}{2}$) with chemical shift anisotropy exhibits satellites (~57 Kc/s). As $x$ increases, the central line broadens and the satellites gradually disappear. Ultimately at $x = 0.8$ a shoulder on the low-field side appears and becomes prominent at $x = 1$. This splitting (~30 Kc/s) is also present in room temperature and low temperature spectra of δ-LiV$_2$O$_5$ (M) by the CW and PE methods (Fig. 3b). As noted by Gossard et al. (14), the line at highest frequency (lowest field) is assigned to paired (V$^{4+}$–V$^{4+}$) singlets, the central line to V$^{5+}$, and the lowest frequency line (highest field) to mixed-valent V$^{4+}$. At 100 K, the intensity of the lines increases considerably. However, the intensity distribution is different from that at room temperature, though no appreciable

shift of the lines occur. This indicates that there is no further structural distortion on going from room temperature to 100 K.

The temperature dependence of $^{51}$V NMR in δ-LiV$_2$O$_5$ (M) results from contributions from relaxation processes, increased spin pairing, and the hyperfine field from isolated V$^{4+}$ spins. At room temperature, the relaxation time $T_1$ is mainly dominated by flip-flop processes within the spin pairs, causing a fluctuating magnetic field. As temperature is lowered, the flip-flop process decreases, stabilizing the spin pairs and decreasing the fluctuating magnetic moment, thereby increasing $T_1$. This is manifested in line narrowing, i.e., an increase in intensity with a lowering of temperature. Simultaneously, the hyperfine field increases as the temperature is lowered, resulting in line broadening.
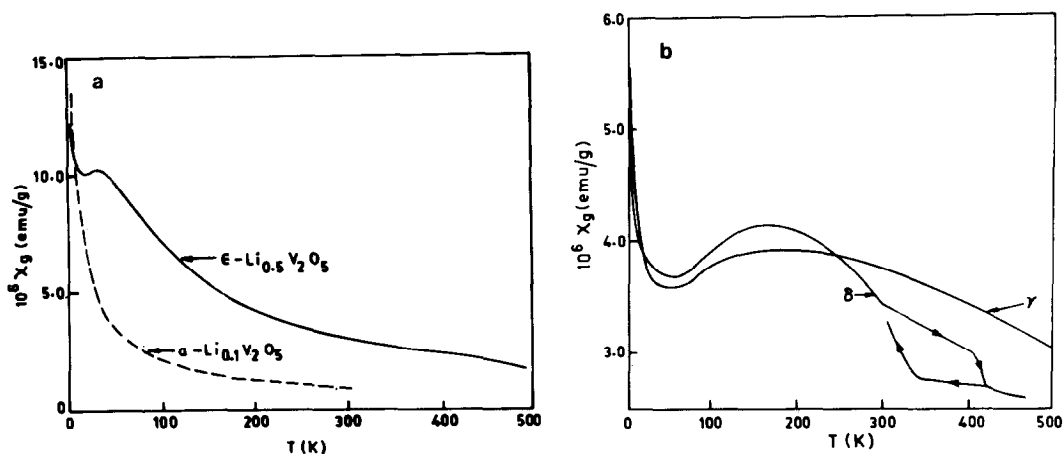
FIG. 4. (a) $\chi$–$T$ plot of $\alpha$- and $\varepsilon$-LiV$_2$O$_5$. (b) $\chi$–$T$ plot of $\gamma$- and $\delta$-LiV$_2$O$_5$.

Murphy et al. (5) found that both $\gamma$ and $\delta$ exhibited maxima in the $\chi$–$T$ plot in the range 100–300 K (Fig. 4b). However, the peak is broad and flat in $\gamma$, whereas it is comparatively much sharper in $\delta$. Further, the low $\chi$ value of $\delta$ despite the large num-



FIG. 5. $^{51}$V NMR of $\gamma$-LiV$_2$O$_5$.

ber of V$^{4+}$ spins compared to that of $\varepsilon$ (Fig. 4a) indicates considerable spin pairing in the former at room temperature.

At this stage, a comparison with $^{51}$V NMR spectra of the high temperature $\gamma$-LiV$_2$O$_5$ (15) is illuminating (Fig. 5). Contrary to the narrow central line in $\delta$-LiV$_2$O$_5$ (M) at 300 K, one observes an asymmetric broad line, arising from V$^{5+}$ with a shoulder on the high-field side. From the structural data (7), it is known that there are two types of sites for vanadium in $\gamma$-LiV$_2$O$_5$: smaller bipyramidal sites for V$^{5+}$ and larger ones for V$^{4+}$. Moreover, V$^{4+}$–V$^{4+}$ distances (2.98 Å) are close to $R_c$ (2.95 Å) leading to d–d overlap with spin pairing, as suggested by Goodenough (16). As the temperature is lowered, the overall linewidth of the spectra decreases and the line intensity increases. Ultimately, up to 157 K the line splits with a shift in the line position, after which the shift is unaltered (15). Apparently, around 157 K some structural change occurs. This is in direct contrast to $\delta$, wherein no structural distortion occurs with a lowering of temperature. Structural distortion similar to that in $\gamma$ has been observed with other rt intercalates like LiVS$_2$
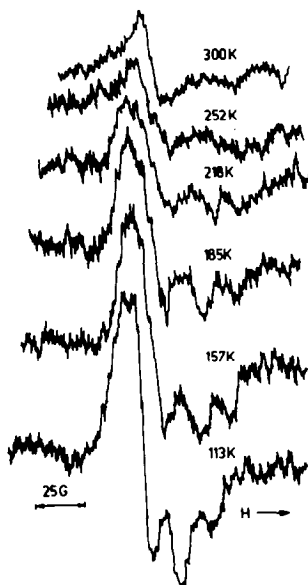
(*11*) and LiVSe₂ (*12*). Quadrupolar satellites are very indistinct in $LiVSe_2$, but slightly below 300 K the $^{51}V$ NMR signal changes form and splits into several components. The effect has been attributed to a possible structural transition.

## Conclusion

Spin pairing has been observed in $\beta$-$Na_{0.4}V_2O_5$ by NMR, EPR, and X-ray diffraction studies (*17–20*). Chakravarty et al. (*21*) postulated that pairing of spins on neighboring sites could occur if electron-phonon interaction is strong enough to allow sufficient local deformation to overcome the nearest-neighbor coulomb repulsion. This intersite bipolaron has a spin-singlet ground state and shows characteristic phenomena such as $\chi$ maximum, a Knight-shift minimum, and X-ray satellites (*17–20*). Recently, in $Pb_xV_2O_5$, the formation of bipolarons (*22*) with binding energies of 150 K and 350 K for $x = 0.18$ and 0.44, respectively, has been suggested by NMR, EPR, and susceptibility studies. Thus in $Pb_xV_2O_5$ (*22*), in contrast to $\beta$-Na and Li bronzes, bipolaron formation occurs for higher $x$ values also. For $x = 0.44$, 0.88 electron per formula unit is present in $Pb_xV_2O_5$, which is comparable to that in $\delta$-$LiV_2O_5$. Although $Pb_xV_2O_5$ showed a non-Curie behavior for $x = 0.44$, unlike $\beta$-Na bronze it exhibited neither a Knight-shift minimum nor X-ray satellite reflections from the polycrystalline specimen. Thus $Pb_xV_2O_5$ was postulated to be a "bipolaron glass" as opposed to the "bipolaron crystal" of $\beta$-Na bronze.

In the absence of low temperature X-ray data for $\delta$-$LiV_2O_5$, the question of satellite reflection as evidence for bipolaron formation is not relevant. However, the peak in the $\chi$–$T$ plot and also the intensification of the lines in the NMR spectra point to the possibility of bipolaron formation even at room temperature as in $Pb_xV_2O_5$.

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