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Concentration and Temperature Dependence of Magnetic Susceptibilities in Lithium Vanadium Oxide Bronzes in the Cryogenic Region[†]

HENRI KESSLER[‡] AND M. J. SIENKO

Baker Laboratory of Chemistry, Cornell University, Ithaca, New York 14850

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A series of β-phase lithium vanadium oxide bronzes, $Li_xV_2O_5$, ranging in lithium content from $x = 0.25$ to $x = 0.49$, have been measured by the Gouy method from 1.2°K to 300°K. Although the data above 60°K can be represented by laws of the Curie–Weiss type with negative Weiss temperatures, below 60°K the effective magnetic moment defined by $(\chi T)^{1/2}$ rapidly goes to zero as T approaches zero. Over the entire range of temperature studied the μ_{eff} vs. T curve can be calculated from a ligand-field model in which V^{4+} levels are split by the combined effect of axial distortion and spin-orbit coupling to yield a lowest-lying nonmagnetic $\Gamma_6(E)$ state. As lithium content increases, the spin-orbit coupling constant is observed to increase from 0.012 eV to 0.021 eV, the electron localization to decrease from 0.9 to 0.6, and the axial distortion to remain essentially unchanged at about 0.007 eV. A discontinuous transition from localized to collective electron behavior is predicted at $x = 0.37$, but no such discontinuity appears in the magnetic behavior. However, there are observed small inflections in the χ^{-1} vs. T curve in the range 7–10°K when x exceeds 0.35, which suggest incipient antiferromagnetic ordering, but these inflections are not evident in the μ_{eff} vs. T curve. When x exceeds 0.35, a small break also appears in the χ^{-1} vs. T curve at 170°K. As supported by DTA measurements, imperceptible structure changes may be occurring which the system adopts to avoid a metallic transition.

Introduction

The vanadium bronzes, $M_xV_2O_5$, represent a series of nonstoichiometric compounds in which univalent metals M are inserted in a distorted V_2O_5 structure (*1*). Although conceptually much like the tungsten bronzes, M_xWO_3, there are marked differences in properties—e.g., the vanadium bronzes are Curie-Weiss paramagnetic and semiconducting (*2*) whereas the tungsten bronzes are degenerate with Pauli-Peierls susceptibility and metallic conduction (*3*). The tungsten bronzes are adequately described by a model in which valence electrons from metal atoms M have been transferred to band states of the WO_3 host matrix, but a suitable model for the vanadium bronzes needs to be more complex in that the transferred electrons apparently are not in band states of the host but are localized in crystal-field states of the vanadium atoms. In the case of $Na_{0.33}V_2O_5$ quite good agreement with observed conductivity, magnetic susceptibility, Seebeck effect, and Hall voltage data has been obtained under the assumption that the valence electron of M is trapped by a vanadium atom of the V_2O_5 matrix to give a V^{4+} ion, the levels of which are those characteristic of a d^1 ion under tetragonal distortion with moderate spin-orbit coupling (*4*). The trapped electron is equivalent to the small polaron of Holstein (*5*), and the observed carrier mobility is exponentially dependent on temperature as required by the diffusion motion of the small polaron.

From an alternate point of view the vanadium bronzes can be considered to have localized electrons arising from Coulomb repulsions on the semiconductor side of the Mott transition (*6*). In its most elementary form, Mott's theory predicts that the activation energy for electron transfer should abruptly vanish when the mean distance between electrons is sufficiently decreased. For the vanadium bronzes, this critical distance is attained when the density of M in V_2O_5 approaches an x value

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[‡] On leave from the Ecole Supérieure de Chimie, Mulhouse, France.

in $M_xV_2O_5$ of 0.37. It would be reasonable to suppose that at this critical concentration, not only would the conductivity change from semiconducting to metallic but the associated magnetism might also go from Curie-Weiss paramagnetic to Pauli-Peierls metallic. Although extensive other studies are accessible for the sodium vanadium bronzes, the homogeneity limit for the β-phase, $0.22 < x < 0.40$, appears to lie too close to the predicted Mott limit to permit extensive study. Because the lithium vanadium bronzes have been reported as a β-phase over a wider range of concentration (*7*), it was decided to investigate the magnetic susceptibility of $Li_xV_2O_5$ over a wide range of temperature and composition in an attempt to find magnetic evidence for the existence of the elusive Mott transition.

Experimental

Preparation of Materials. The β-phase lithium vanadium bronzes were made by solid state reaction between VO_2, V_2O_5, and $LiVO_3$ according to the equation

$$x\mathrm{VO_2} + x\mathrm{LiVO_3} + (1-x)\,\mathrm{V_2O_5} \rightarrow \mathrm{Li}_x\mathrm{V_2O_5}$$

following the method of Hagenmuller, Galy, Pouchard, and Casalot (*7*). The starting materials were ground under nitrogen to 325 mesh, heated for 24 hr at 550°C in a platinum boat under a slow current of dry argon, reground under nitrogen, heated again for 24 hr at 550°C under argon flow, reground under nitrogen, and finally heated for 24 hr at 650°C under argon flow. If after the third heat, X-ray examination with a General Electric XRD-5 diffractometer (CuKα radiation, Ni filter, 0.4°/min scan) failed to show only the β-phase present, regrinding and reheating cycles were repeated until a homogeneous phase was obtained. For the first heating it was important to stay below the melting point of $LiVO_3$ (620°C) to avoid segregation and, hence, incomplete reaction. For x values below 0.4, the second heating at 550°C could be dispensed with. For x values lying between 0.4 and 0.5 the second heat at 550°C was needed to avoid segregation by melting of the δ-phase $Li_{1+x}V_3O_8$ (m.p. 601°C). Although Hagenmuller *et al.* (*7*) report that the homogeneity range of the β-bronze $Li_xV_2O_5$ extends from 0.22 to 0.62 at 650°C, it was not possible to reproduce their results above $x = 0.49$. Attempts with $x = 0.50, 0.55$, and 0.60 invariably led to products showing to X-ray analysis trace contamination with either δ phase, γ phase, or both.

Starting materials for the above reactions were Mallinckrodt reagent-grade Li_2CO_3 and Vanadium Corporation of American purified V_2O_5. $LiVO_3$ was made by heating V_2O_5 and Li_2CO_3 in a platinum boat under oxygen at 550°C followed by grinding and heating under oxygen at 550°C until no trace of $Li_{1+x}V_3O_8$ was present. VO_2 was made by heating equimolar amounts of V_2O_3 and V_2O_5 in platinum or Vitreosil, first for 24 hr at 600°C under argon, grinding, then heating again for 24 hr at 700°C under argon. The V_2O_3 was prepared by reduction of V_2O_5 with hydrogen at 800°C for 10 hr. Weight monitoring confirmed the stoichiometry changes as indicated above. Chemical analyses, by cerium oxidation for V^{4+} and flame photometry for Li, were performed as previously described (*8*).

Magnetic Measurements. Magnetic susceptibilities were measured by the Gouy method over the range 1.2–300°K, using the magnet and cryogenic system previously described (*2*). Samples were sieved to 325 mesh and packed in 0.4-cm-diameter silica tubes up to a height of about 20 cm. Extreme care was taken to ensure uniform density by adding the powder in 2-mm increments, dropping the tube three times from uniform height, discharging with a Staticmaster, and repeating the process with constant monitoring of the height-to-weight ratio. In no case did the height-to-weight ratio increase by more than 2%; in general, it stayed within 1%. Several independent packings were made for each sample and several measurements were made down to 1.2°K on each packing. In general, susceptibility results were reproducible to 1 or 2%.

The temperature cycle for the magnetic measurements was done in two stages, one using liquid nitrogen alone, the other using liquid helium. The first stage went from 300°K to 77°K, to 270°K, to 77°K, and finally to 46°K for full pumping on the liquid nitrogen. The second stage went from 4.2°K to 1.2°K (for full pumping on the liquid helium), then to 45°K (with heater current plus liquid helium), and finally to 300°K. Data were reproducible to 1 or 2%.

The magnetic field was varied from 1500 to 6000 oersted at each temperature. Down to 10°K, plots of susceptibility vs. reciprocal field were flat within 1 or 2% except for the two low-field points. In the range 1.2–10°K, the χ vs. H^{-1} plots were also flat, but the highest field point was always up by about 1%, though still within the error limits.

Treatment of Data. Fields were calibrated with standard solutions of nickel chloride. Observed forces were corrected for the diamagnetism of the silica tube. Net forces were then calculated as volume susceptibilities and extrapolated to zero

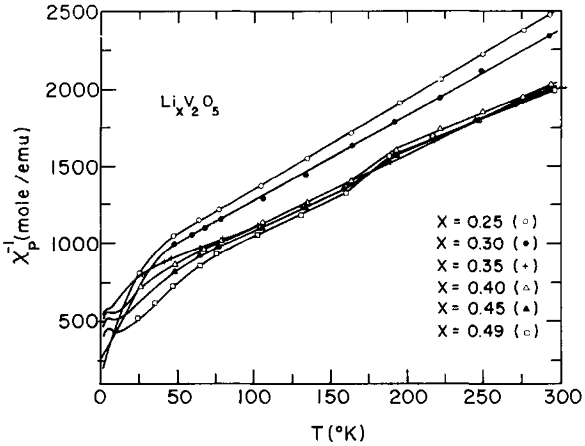

FIG. 1. Observed reciprocal molar paramagnetic susceptibility of $Li_xV_2O_5$ as a function of temperature. Lithium concentrations and graph symbols for data points are shown on extreme right.

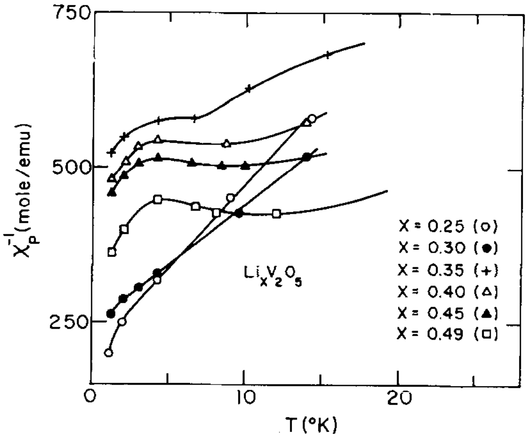

FIG. 2. Observed reciprocal molar paramagnetic susceptibility of $Li_xV_2O_5$ as a function of temperature in the liquid helium region. Lithium concentrations and graph symbols for data points are shown on extreme right.

reciprocal field. Observed packing densities were used to convert volume to gram susceptibilities and eventually to a molar susceptibility per gram-formula-unit of $Li_xV_2O_5$. Corrections for the diamganetism of the ion cores were taken from Selwood (*9*) except for the oxide ion, for which the value used was -9.8×10^{-6}, as appears appropriate for a solid-state network (*10*).

Figure 1 shows the magnetic results presented as plots of the reciprocal of the paramagnetic susceptibility (after subtraction of diamagnetic corrections) per mole of $Li_xV_2O_5$ as functions of temperature. Figure 2 shows the detailed data in the liquid helium region. If it is assumed that the high-temperature data can be represented by laws of the Curie-Weiss type, $\chi = C/(T - \theta)$, where the Curie constant C gives a measure of a constant magnetic moment $\mu = 2.828\ C^{1/2}$ and the Weiss temperature θ gives a measure of the interaction between such moments, then the moments and interaction constants would be as shown in Table I. In Table I, the Curie constants are given per mole of $Li_xV_2O_5$, but the magnetic moments μ are calculated per mole of Li—i.e., $\mu = 2.828\ (C/x)^{1/2}$. If, on the other hand, the magnetic moment is not constant but changes with temperature, the data can be presented in terms of an effective magnetic moment, μ_{eff}, defined by the relation $\mu_{eff} = 2.828\ (\chi T)^{1/2}$. Figure 3 shows the μ_{eff} vs. T plots for $x = 0.25$, 0.30, and 0.35, and Fig. 4, for $x = 0.40$, 0.45, and 0.49.

Discussion

As shown in Figure 1, the magnetic susceptibility of $Li_xV_2O_5$ closely follows a Curie-Weiss law above about 60°K with a moment of about 2.2 BM and a Weiss temperature of about −130°. The negative Weiss temperature suggests an interaction between the moments of the antiferromagnetic type, and

TABLE I

MAGNETIC PARAMETERS FOR LITHIUM VANADIUM BRONZES, $Li_xV_2O_5$

Composition x		Curie constant C per mole $Li_xV_2O_5$	Weiss constant θ	Magnetic moment μ per g-atom Li
0.25		0.167 emu deg	−130°	2.32 BM
0.30		0.184	−133	2.21
0.35		0.213	−130	2.21
0.40	Above 170°K	0.232	−180	2.16
	Below	0.214	−140	2.06
0.45	Above 170°K	0.233	−175	2.03
	Below	0.218	−136	1.97
0.49	Above 170°K	0.256	−211	2.04
	Below	0.209	−120	1.85

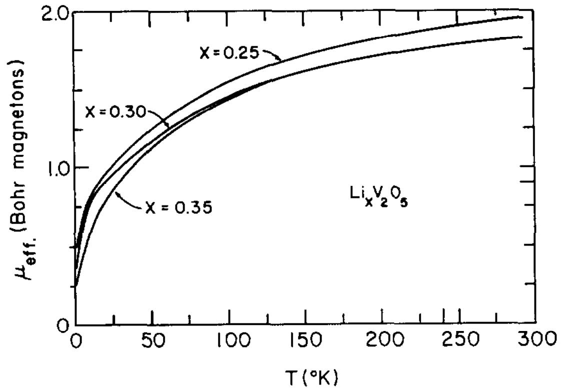

FIG. 3. Observed effective magnetic moment defined by $\mu_{eff} = 2.828\,(\chi T)^{1/2}$ vs. temperature for three compositions of lithium vanadium bronzes.

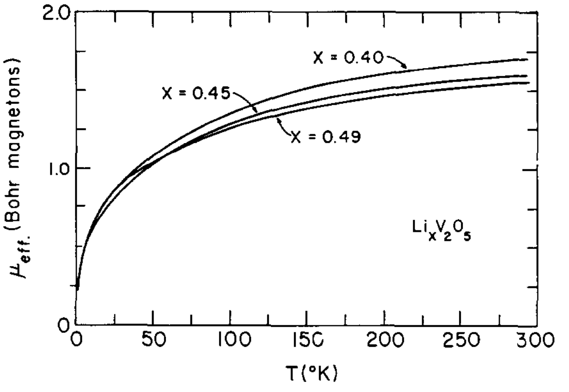

FIG. 4. Observed effective magnetic moment defined by $\mu_{eff} = 2.828\,(\chi T)^{1/2}$ vs. temperature for three compositions of lithium vanadium bronze.

there is some confirmation of this in the appearance of small dips in the χ^{-1} vs. T curves in the temperature range 7–10°K when the lithium content exceeds $x = 0.35$. A minimum in the χ^{-1} vs. T curve is generally taken to be a Néel temperature, characteristic of antiferromagnetic ordering, but such an interpretation is not obviously the case here since the hint of antiferromagnetic ordering is not carried through by decreasing χ at still lower temperature. Instead, χ is observed to *increase* and that, more rapidly than expected.

If, as seems probable for reasons discussed below, the magnetic moment is not a constant but decreases with decreasing temperature, then the incipient antiferromagnetic ordering (already very weak, as suggested by the very low "Néel temperature") may actually disappear at lower temperatures as the magnetic moment drops below the critical value needed for ordering interaction.

In the case of a temperature-dependent magnetic moment, the use of a Curie Weiss description $\chi = C/(T - \theta)$ is not significant and no simple interpretation can be assigned to θ as an interaction constant. Instead, it is more meaningful to describe the magnetic behavior in terms of the "effective magnetic moment," μ_{eff}, defined by the observed paramagnetic susceptibility, χ, as $(3k/N\mu_B{}^2)^{1/2}\,(\chi T)^{1/2}$, or $2.828\,(\chi T)^{1/2}$. In this expression, k is Boltzmann's constant, N is the Avogadro number, and μ_B is the Bohr magneton. The assumptions then are that there are no interactions between magnetic moments and the observed temperature dependence of susceptibility reflects both an internal thermal change of the moment at an ion site as well as the usual thermal disorientation effect on that moment. Perlstein and Sienko have shown (*4*) that such a temperature-dependent magnetic moment is indicated for the vanadium oxide bronzes not only on the basis of magnetic susceptibility but also on the basis of a host of other evidence, including electrical conductivity, Hall effect, thermoelectric power, and electron-spin-resonance absorption.

In the β-bronze structure of the vanadium oxide bronzes, the vanadium atoms are surrounded by six oxygen atoms in an extremely distorted octahedron. The symmetry of the oxygens is approximately C_{4v} corresponding to a shift of the oxygens along one of the four-fold axes of an octahedron so as to give unequal V–O distances. Assuming that the Li in $Li_xV_2O_5$ transfers its electron to the vanadium to give a V^{4+} ion, then, as shown by Perlstein and Sienko (*4*) for $Na_{0.33}V_2O_5$, the problem becomes one of calculating the magnetic moment of a d^1 ion in an asymmetric ligand field. Following the procedure of Figgis (*12*), we can use three parameters to describe the interaction: λ, the spin-orbit coupling constant; Δ, the energy-level separation due to the axial field in the absence of spin-orbit coupling; and k, the delocalization constant indicating the fraction of the time the d electron is on the vanadium atom (as opposed to the ligand oxygen network). As given by Figgis, the energy levels into which the sixfold degenerate ${}^2T_{2g}$ term of the octahedral field is split by the combined action of spin-orbit coupling and axial distortion are as follows:

$$1/2(-\Delta/3 + \lambda/2 + \xi) \text{ designated } \Gamma_7\ (E)$$

$$1/2(-\Delta/3 + \lambda/2 - \xi) \text{ designated } \Gamma_6\ (E)$$

$$\Delta/3 - \lambda/2 \qquad \text{designated } \Gamma_7\ (B)$$

where $\xi = (\Delta^2 + \Delta\lambda + 2.25\lambda^2)^{1/2}$. The gamma notation is that of Bethe for irreducible representations of the double groups including spin. The effect of the axial distortion Δ is to split the $^2T_{2g}$ term into a fourfold degenerate E level and a twofold degenerate B level; the effect of spin-orbit coupling λ is to split the E level into two twofold levels, Γ_6 (E) and Γ_7 (E). The Γ_6 (E) level, for which the wave functions are $|2\ {-1}\ 1/2>$ and $|2\ 1\ {-1/2}>$ in the Dirac notation, is non-magnetic; orbital and spin moments are in cancelling opposition to each other, so that, to first order, there is no splitting in the magnetic field. The Γ_7 (E) level, for which the wave functions are $|2\ 1\ 1/2>$ and $|2\ {-1}\ {-1/2}>$, and the Γ_7 (B) level, for which the wave functions are $2^{-1/2}(|2\ 2\ 1/2> - |2\ {-2}\ 1/2>)$ and $2^{-1/2}(|2\ 2\ {-1/2}> - |2\ {-2}\ {-1/2}>)$, are both magnetic in that the magnetic moment operator $|L_z + 2S_z|$ does not vanish. At a specific temperature the average moment per V^{4+} will depend on the relative thermal population of the Γ_7 (B), Γ_7 (E), and Γ_6 (E) levels, which in turn depends on the relative magnitudes of Δ and λ. Only if the Γ_6 (E) level is lowest, will the moment tend to zero as T approaches 0°K.

Figgis (*12*) has computed the effective magnetic moment expected as a function of temperature for various combinations of λ, Δ, and k of a d^1 ion. His results, presented in tabular form, show that μ_{eff} is mainly decided at high temperatures by λ and at low temperatures by the ratio of Δ to λ. Furthermore, any increase in electron delocalization (corresponding to a decrease in k) serves to reduce the magnetic moment. Although the fitting of the observed data to the theoretical parameters is not very precise, particularly in the case of λ, we have attempted to select parameter combinations that best describe the observed magnetic behavior of the lithium vanadium bronzes. The parameters chosen are shown in Table II. Values were taken on the basis of mean-square deviations between calculated and observed effective moments for kT/λ values of 0.1, 0.2, 0.3, 0.5, 0.75, 1.0, 1.5, and 2.0, respectively. Figure 5 shows a comparison between observed moments (circles) and calculated values (continuous curve) for the specific case of $Li_{0.25}V_2O_5$. Figure 6 shows the corresponding splitting diagram. In constructing Figure 6, Δ was chosen to be positive. In the Figgis notation, this corresponds to having the orbital singlet B lower than the orbital doublet E.

TABLE II

LIGAND-FIELD PARAMETERS FOR LITHIUM VANADIUM BRONZES

Composition	Spin-orbit λ, eV	Axial distortion Δ, eV	Delocalization constant, k
$Li_{0.25}V_2O_5$	0.012	0.008	0.9
$Li_{0.30}V_2O_5$	0.014	0.007	0.8
$Li_{0.35}V_2O_5$	0.016	0.006	0.9
$Li_{0.40}V_2O_5$	0.018	0.007	0.7
$Li_{0.45}V_2O_5$	0.019	0.006	0.7
$Li_{0.49}V_2O_5$	0.021	0.010	0.6

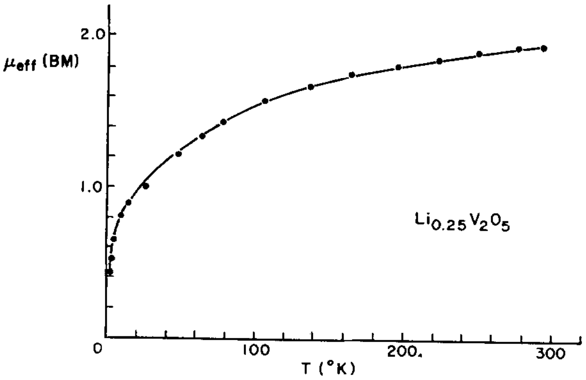

FIG. 5. Comparison of effective magnetic moment vs. temperature for $Li_{0.25}V_2O_5$ as observed and as calculated by Figgis theory. Circles represent observed data points; solid curve is calculated with $\lambda = 0.012$ eV, $k = 0.9$, and $\Delta = 0.0084$ eV.

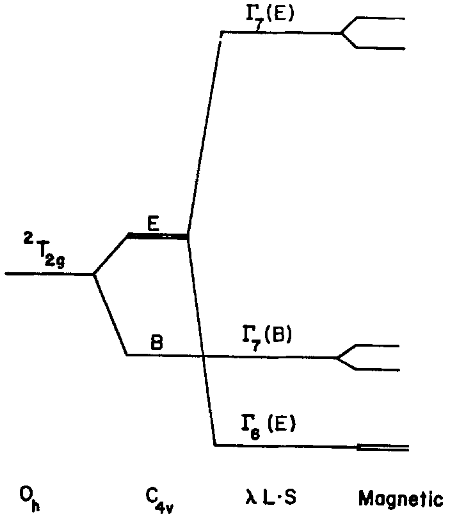

FIG. 6. Energy-level diagram showing the combined effect of axial distortion Δ and spin-orbit coupling λ. Levels at extreme right are those in a magnetic field.

Perlstein (*13*), on the other hand, took Δ to be negative thus making the orbital doublet the lower. Our data, which are more extensive than those Perlstein worked from particularly in the low-temperature range, are clearly better fitted with a positive Δ than with a negative Δ. In any case, to agree with the observed precipitous drop in μ_{eff} at very low temperature, the λ-split Γ_6 (E) level has to end up being lowest.

The actual numerical values shown in Table II have considerable uncertainty—i.e., about 0.003 eV for λ, about 0.002 eV for Δ, and about 0.1 for k. In spite of the imprecision, there does seem to be a regularity in the values worthy of comment. The general change with increasing lithium content is to increase λ, decrease k, and keep Δ about constant. The increase in spin-orbit coupling brings the values closer to the free-ion value for V^{4+} (viz., 0.0312 eV). Increasing departure from free-ion values is generally attributed to an increasing percentage of covalent bonding due to electron donation from ligands to metal atom. Consequently, the effect of added lithium in increasing λ can be interpreted as a reduction of the σ bonding or an increase in the π bonding between the oxide ligands and the vanadium atoms. This would be consistent with the predicted role of added Li^+ ions as Coulomb centers for attracting oxide-ion electron density. It might also be argued that addition of the lithium valence electrons to localized sites on some of the vanadium atoms would enhance the vanadium–vanadium repulsion and hence would expand the lattice. This, however, overlooks the attractive role of the added lithium ions. In any event, precise X-ray monitoring of the lattice parameters in this investigation disclosed no detectable change in unit-cell constants.

The rather appreciable decrease in k that is observed to accompany increasing lithium addition indicates that the $3d^1$ electron of V^{4+} is increasingly delocalized over the surrounding network. There are two ways in which this can come about—by the d-orbital overlap mechanism suggested by Gendell, Cotts, and Sienko (*14*) or by the $d\text{-O}p_\pi\text{-}d$ interaction proposed by Goodenough (*15*). In the former, advantage is taken of the fact that the $3d_{xy}$ orbitals of the vanadium atoms are favorably situated both as to angular orientation and spatial separation so as to overlap in the tunnel direction of the vanadium bronze structure. In the latter, anion p_π orbitals overlap with cation-near-neighbor d-wave functions to produce antibonding crystalline π^* states. In either case, the substantive effect is to add an element of vanadium–vanadium bonding which serves to reduce the magnetic moment.

The rough constancy of the axial distortion parameter Δ suggests that the deviation from O_h symmetry does not undergo any marked change as lithium content is increased. This agrees with the above-mentioned observation that X-ray studies failed to show any crystallographic deviations. However, in the regime of energies here concerned it is unlikely that atom movements would be big enough to show up in our X-ray studies.

Although the above picture is generally satisfactory in accounting for the gross features of the magnetic behavior in the range of 1–300°K, it does not explain two second-order effects observed for the more concentrated lithium vanadium bronzes. One of these effects is the discontinuous jump in susceptibility that occurs when the temperature is decreased below about 170°K. In $Li_{0.49}V_2O_5$, for example, the jump in susceptibility (hence, presumably also in magnetic moment) is found to be equal to 4%. For lower lithium contents, the break is less pronounced becoming imperceptible for $Li_{0.35}V_2O_5$. Only a slight shift in the oxygen environment of V^{4+}, with a consequent change in ligand-field parameters, would account for the rise in susceptibility. However, X-ray powder photographs taken at lower temperatures fail to show any difference from those taken at room temperature. Nevertheless, DTA measurements, which are currently being elaborated, disclose a small but definite heat effect occurring at the temperature of the discontinuity (*16*). For $Li_{0.49}V_2O_5$, for example, the heat on cooling corresponds to evolution of about 65 cal per mole. Both the heat effect and the magnetic anomaly could have their origin in small structure-parameter changes that may be associated with motion of lithium ions in the structure. As reported by Gendell, Cotts, and Sienko (*14*), the NMR spin-lattice relaxation time of Li^7 in $Li_{0.35}V_2O_5$ shows a pronounced minimum at 163°K, attributed to the onset of side-to-side motion of Li^+ ions in the tunnels of the β-bronze structure. A further motion along the tunnels of the structure was believed to set in at somewhat higher temperature.

The second effect that the Figgis theory does not account for is the small dip in the χ^{-1} vs. T curve in the temperature range 7–10°K when the lithium content exceeds $x = 0.35$. The suggestion that these dips reflect antiferromagnetic ordering of the magnetic moments appears untenable in the light of neutron diffraction evidence. Studies kindly performed for us by Drs. J. M. Hastings and L. M. Corliss at Brookhaven National Laboratory showed no evidence either at room temperature or at liquid helium temperature for magnetic ordering within the limit of ordered moment sensitivity of about 0.5 BM. Because, in the light of the findings mentioned above, it appears that DTA studies may be more sensitive than X-rays or neutrons in picking up minute structural changes that can appreciably affect magnetic moments, DTA experiments are being extended into the liquid helium range.

On the basis of the experimental findings described above, it must be admitted that there is no clear evidence for the existence of a Mott transition as the lithium content in V_2O_5 is increased. Still, there is the intriguing possibility that, rather than undergo a Mott transition, the lithium vanadium bronzes choose to undergo small structural distortions and thereby spread the transition over a range of temperature. It is unfortunate that the thermodynamic properties of these materials are such that single-crystal preparation is extraordinarily difficult. Otherwise, single-crystal electrical studies over a range of composition and temperature would probably resolve many of the above questions.

Acknowledgment

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