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A Comparative Study of $V_6O_{13.27}$ and V_6O_{13}

MONISHA BOSE

Bose Institute, Calcutta 700 009, India

AND ANJALI BASU

Saha Institute of Nuclear Physics, Calcutta 700 009, India

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A comparative study of the oxygen-enriched $V_6O_{13.27}$ and stoichiometric V_6O_{13} is made from susceptibility and ^{51}V NMR. Instead of a susceptibility peak at 150 K as in V_6O_{13}, a plateau was observed in this region. A single broad ^{51}V NMR line was observed in $V_6O_{13.27}$ at room temperature, which narrowed on lowering of temperature. Close to 150 K, three different lines, corresponding to the three inequivalent sites as in V_6O_{13}, were observed. Though occurrence of spin-pairing at 150 K has been recognized for some time, a bipolaronic mechanism for this pairing in V_6O_{13} itself is proposed for the first time. Interestingly, though susceptibilitywise $V_6O_{13.27}$ and V_6O_{13} show very different behavior, bipolaronic spin-pairing possibly occurs in $V_6O_{13.27}$ also. However, at 50 K, antiferromagnetic ordering as in V_6O_{13} does not occur in $V_6O_{13.27}$ as the latter has fewer V^{4+} spins than required, due to the presence of excess oxygen.

Introduction

In recent years, V_6O_{13} has been found to be one of the best cathode materials in conjunction with polymeric electrolytes, suitable for use in lithium-based solid-state batteries (*1*). Stoichiometric V_6O_{13} has the formal oxidation assignment of $V_4^{4+}V_2^{5+}$ but behaves as a mixed-valent compound (*2*, *3*). V_6O_{13} at room temperature has a monoclinic structure (Fig. 1) with space group *C*/2*m*. Thus, one has nominal $V^{5+}O_6$ octahedra (V_2) sandwiched between nominal $V^{4+}O_6$ octahedra (*4*) involving V(1) and V(3).

V_6O_{13} exhibits metallic luster with conductivity 10^{-1} (ohm cm)$^{-1}$ and has been described in the literature as a metal (*2*, *5*). The sharp drop in χ at 150 K has been ascribed to a metal insulator (*M–I*) transition, with a crystallographic distortion (*4*) from a symmetry of *C*/2*m* to *C*/2. The lattice parameters also show the corresponding discontinuous changes (*4*). The shortest V–V distance in V_6O_{13} is for V(2)–V(3) along the double zigzag ribbon (3.009 Å); next, one encounters the V(1)–V(1) separation across shared octahedral edge (3.049 Å). The largest separation is for V(2)–V(3) in the *a–c* plane (3.38 Å). The temperature dependence of conductivity (σ) of pure V_6O_{13} (Fig. 2) is that of a semiconductor (*6*) and not that of a metal. Thus from room temperature down to 150 K, there is a sudden drop near 150 K, then again a semiconductor-like behavior down to 90 K.

The present paper deals with a comparative study of stoichiometric V_6O_{13} and

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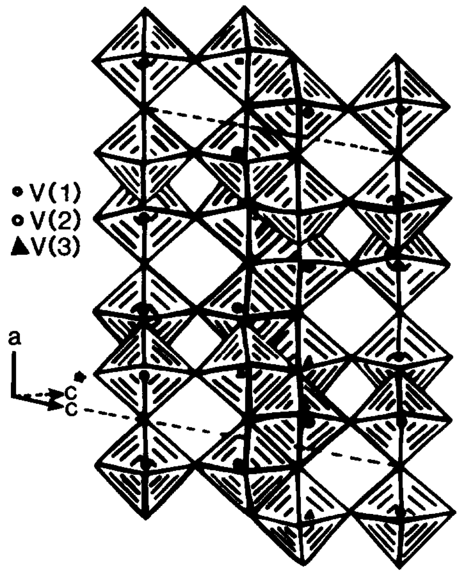

FIG. 1. Crystal structure of V_6O_{13}.

$V_6O_{13.27}$, particularly to see how excess oxygen atoms modify the V_6O_{13} lattice and its properties. These systems have been investigated by both a macroprobe magnetic susceptibility and a microprobe ^{51}V NMR.

Experimental

Nonstoichiometric $V_6O_{13.27}$ was prepared by the decomposition of NH_4VO_3 in a long-necked glass ampoule (*7*). The extent of nonstoichiometry of the oxide was measured by measuring the weight gain of the specimen during its oxidation in air in a thermal analyzer (Stanton Redcroft, STA 780 UK) and the exact formula was found to be $V_6O_{13.27}$ (*8*). Susceptibility measurements were carried out with a Squid magnetometer over the temperature range 2–400 K and in fields of 0.5–5 T. The NMR spectra were taken at 15 MHz on a Varian WL 210 NMR spectrometer with a Varian low-temperature accessory. The ^{51}V shifts reported are with reference to Na_3VO_4 in solution.

Results and Discussion

Figure 3 sums up the susceptibility results of the system. The sharp break in χ in pure V_6O_{13} at 150 K is considerably rounded off even in $V_6O_{13.05}$ (*9*) and vanishes altogether in $V_6O_{13.27}$; a plateau has been observed near this temperature. There is a steady increase in χ below 150 K, where it follows the Curie–Weiss law. The results in the case of $V_6O_{13.27}$ are similar to those observed by Jhans and Honig (*10*) in the case of nonstoichiometric cation deficient V_2O_3 ($V_{2-y}O_3$). Here the cation deficiency causes the lattice to distort (contract), counteracting the high-temperature lattice expansion. As such, one can infer that an excess of oxygen in the case of $V_6O_{13.27}$ possibly causes the lattice to distort and hence flattening is seen in the χ–T plot.

^{51}V NMR

^{51}V NMR of polycrystalline V_6O_{13} at 300 K (Fig. 4) simulates the V_6O_{13} single-crystal spectrum (*5*) but obviously is not as sharp and not all satellites corresponding to $I = \frac{7}{2}$

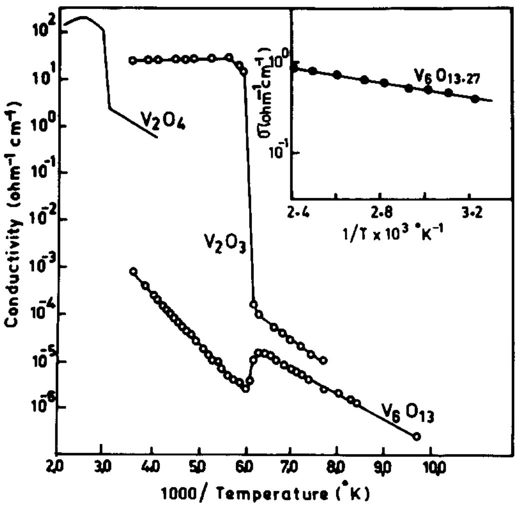

FIG. 2. Electrical conductivity vs temperature for oxides of vanadium.

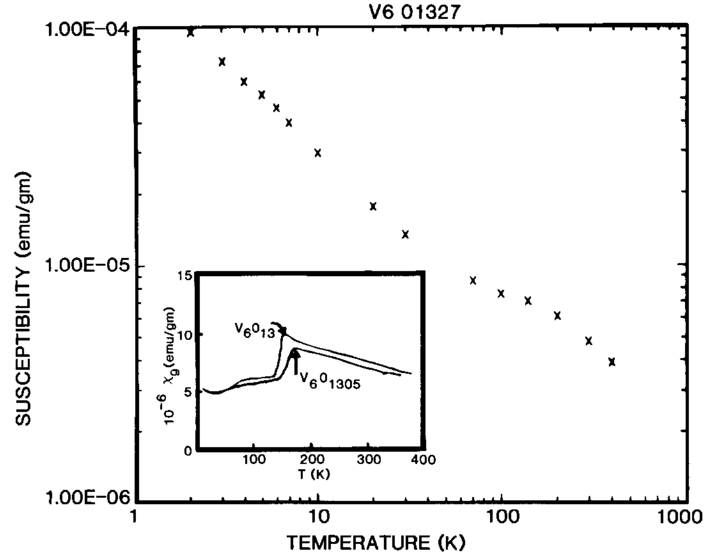

FIG. 3. χ–T plot of $V_6O_{13.27}$.

are clearly resolved. But the spectrum does clearly reveal three nonequivalent sites in the shifts, viz. V_1 (−1.4%) at highest field, V_3 (−1%) in the middle, and V_2 (−0.09%) at the extreme left. These shifts parallel the charge distribution of 4.16, 4.34, and 4.6 for

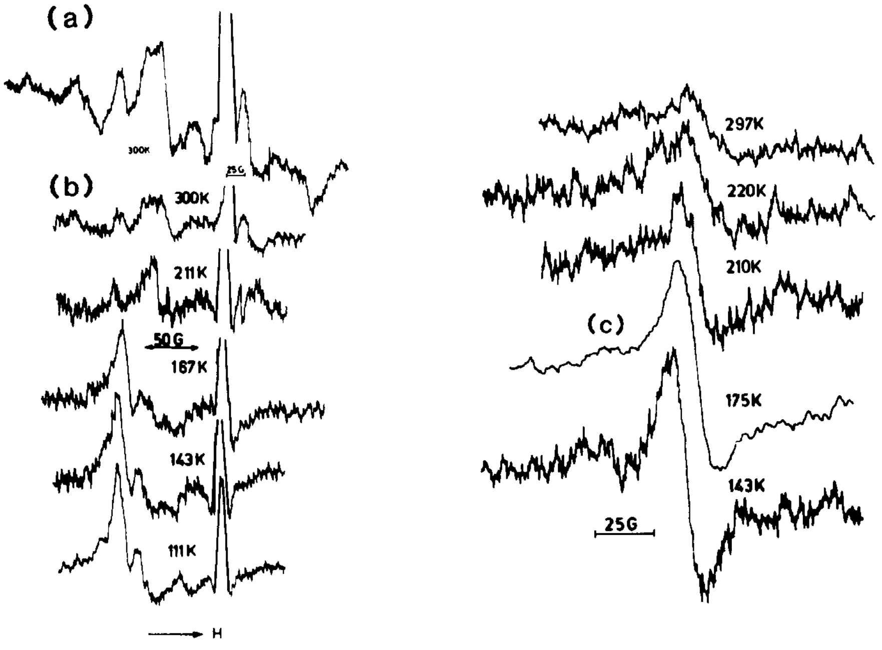

FIG. 4. ^{51}V spectra at 15 MHz. (a) V_6O_{13} with signal averager at 300 K; (b) V_6O_{13} with single scan; (c) $V_6O_{13.27}$.

V_1, V_3, and V_2, respectively, obtained from X-ray data (*4*). Across the phase transition at 150 K, the charge distribution changes to 4.4, 4.4, and 4.2 for V_1, V_2, and V_3, respectively (*4*). The NMR shifts, viz. V_1 (0.1%) and V_3 (−1.3%), corroborate this changed charge distribution. Thus, one observes an intense low-field line from overlapping V_1 and V_2 and a high-field wide line from V_3 (which has become most V^{4+}-like). NMR shifts and X-ray data indicate that V_1 spins are preferentially paired in V_6O_{13} at 150 K, whereby the charge distribution changes drastically from 4.16 to 4.4. Thus it is the V_3 spins which become antiferromagnetic at 50 K.

In the case of $V_6O_{13.27}$ no satellites are present in ^{51}V NMR at 300 K and a single broad asymmetric line is obtained, indicating a distortion of the V_6O_{13} lattice itself. But X-ray values for $V_6O_{13.27}$ agreed well (*8*) with the values for V_6O_{13} reported in the literature (*4*). However, NMR as a more sensitive probe is able to detect subtle distortions, particularly in the quadrupolar interaction. On lowering the temperature, the ^{51}V line increasingly narrows and becomes more intense and at 143 K an almost symmetric intense narrow central line along with two broad (weak) lines appear on either side. Frequency variation study from 15 to 8 MHz shows the line positions to be frequency-dependent. However, the narrowing of the broad line at 300 K, with lowering of temperature, indicates spin-pairing. Though a structural transition at 150 K as in V_6O_{13} may not occur, narrowing leads to reemergence of the three lines corresponding to three vanadium sites V_1, V_2, and V_3, broadened by the distortion due to extra oxygen at 300 K.

Conclusion

From the χ–T diagram (Fig. 3) it is evident that the spin-paired state at 150 K causing the so-called *M–I* transition is present in V_6O_{13}. This is not disturbed even by the antiferromagnetic transition at 50 K. But so far no mechanism for such spin-pairing has been suggested. Goodenough (*11*) already established a critical overlap criterion for predicting localized vs collective electron behavior. In 3*d* metal oxides, the critical separation R_c (max) is 2.97 Å and as such spin-pairing results in *M–I* transition of VO_2, where the *V–V* distance is 2.85 Å. As pointed out before, the V(1)–V(1) separation in V_6O_{13} is 3.049 Å, which is significantly larger than R_c. So, considering the V–V distances, the susceptibility peak in χ–T diagram, and intensification of NMR lines with narrowing, it is suggested here that this strong spin-paired state at 150 K arises from the same type of "bipolaronic mechanism" (*12–17*) that has been postulated in β-$Na_{0.4}V_2O_5$, β-$Li_{0.4}V_2O_5$, and $Pb_xV_2O_5$ (*18*). Moreover, the X-ray data (*4*) of V_6O_{13}, which indicates that V_1 is displaced away from the mirror plane at T_c, may be cited as an indication of phonon-mediated distortion in the bipolaronic state. It thus appears that though the structural distortion in the oxygen enriched $V_6O_{13.27}$ flattens out χ–T peak, the non-Curie behavior of χ, and also the appearance of three lines near 150 K, points to the same type of bipolaronic spin-pairing mechanism as in V_6O_{13}.

Acknowledgments

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