CHAPTER IV
STUDY OF $\text{YBa}_2(\text{Cu}_{0.98-x}\text{V}_x\text{Fe}_{0.02})_3\text{O}_{7-\delta}$ SYSTEM USING X-RAY ABSORPTION SPECTROSCOPY
IV.1. Introduction

The tetragonal-orthorhombic phase transition has been of central concern in studies on superconducting YBa$_2$Cu$_3$O$_{7-\delta}$(123). As we have already discussed in Chapter III, the orthorhombic phase contains one more oxygen per unit cell than the tetragonal phase. The transformation depends on the diffusion of oxygen and is accompanied by lattice parameter changes. The problem of partial replacement of Cu has also been studied exhaustively in the 123 system. The situation is complicated by the presence of two inequivalent sites for copper, Cu(1) and Cu(2) and the dopant ion occupies either one of the sites or both depending on its preferential coordination number. Since the ionic radii of all the 3d elements are close to that of Cu, they can easily substitute for the latter. All the 3d elements depress the T$_c$ relative to that of the undoped material but some dopants, such as Fe$_2$O$_3$, have a much greater effect than others, such as V$_2$O$_5$.

X-ray absorption spectrum has traditionally been divided into a low energy region, the so-called X-ray absorption near edge structure (XANES), in which the transitions are to bound states [1-3], and a high energy region, the so-called extended X-ray absorption fine structure (EXAFS), where the transitions are to free electron states [4-5]. Recently, as mentioned in Chapter I, high intensity X-ray sources have become available whose intensities are about $10^6$ times higher than those previously available. This results in improved signal to noise ratios, which allow meaningful measurements to be made even on dilute systems [5-6].

In this Chapter we present our measurements, made with X-rays from Rigaku X-ray generator, on K X-ray absorption spectra of superconducting oxides containing vanadium and several model vanadium compounds. The model compounds which we have studied in the present work are CrVO$_4$, GdVO$_4$, BiVO$_4$, Cd$_2$V$_2$O$_7$, Ca$_3$Fe$_2$GeVO$_{12}$, Pb$_5$(VO$_4$)$_3$Cl, Zn$_3$(VO$_4$)$_2$, NaVO$_3$, VO(acac)$_2$, VO(bzac)$_2$$^1$, (NH$_4$)$_4$[VO—dd—tar]$_2$2H$_2$O$^2$, VOSO$_4$.3H$_2$O, VO(acen), VOPc$^3$, VOTPP$^4$,

$^1$bsac = benschylacetonate (C$_{10}$H$_{9}$O$_2$)
$^2$tart = tartarate (C$_4$H$_8$O$_6$)
$^3$Pc = phthalocyanine
$^4$TPP = tetraphenyl porphyrin
VOMoO₄, V₂O₅, VO, (NH₄)₂SO₄·VSO₄·6H₂O, V₂O₅, SmVO₃, V₂S₃, VN, VO₂, V₄O₇, VC, VO(hshed)(acac)₁₆, PbV₂O₆ and Ca₃V₂O₁₂·18H₂O. The superconducting oxides of vanadium include compounds of composition YBa₂(Cu₀.₉₈₋ₓVₓFe₀.₀₂)₃O₇₋₄ where x = 0.04, 0.05, 0.06. Electronic transitions from 1s to 3d, 4s and 4p states, in the model compounds as well as in superconducting oxides have been assigned to different spectral features observed in the vanadium K-edge spectra on the basis of atomic model of Shulman et al [7] and others [8-11].

IV.2. Experimental

YBa₂(Cu₀.₉₈₋ₓVₓFe₀.₀₂)₃O₇₋₄ (x = 0.04, 0.05, 0.06) samples were prepared from raw materials consisting of Y₂O₃, CuO, BaCO₃ and V₂O₅ and Fe₂O₃ added individually as dopants. The powders were mixed with 123 as the parent composition in the required proportions and the compounds were prepared according to the procedure described in Chapter III. Direct-current resistance measurements were made by the conventional four-probe technique. X-ray powder diffraction patterns were recorded at room temperature with Ni-filtered CuKα radiation on a Rigaku DMAX-II C wide angle goniometer x-ray diffractometer.

IV.3. Results and Discussion

The zero of the energy scale of the XANES spectra was taken with respect to the first inflection point of the vanadium metal in the first derivative spectrum at 5465.0eV, which, according to Bearden and Burr [12], marks the threshold or onset of photoejection of the 1s electron in vanadium metal. All the spectra were normalized by fitting a linear function to the pre-edge data and fitting cubic spline to the EXAFS region of the data up to 400 eV, extrapolating both functions to the zero of energy i.e. the inflection point energy [and taking the difference (the edge step height)], subtracting the pre-edge data function from each point in the experimental spectrum, and dividing by the step height. This procedure results in a normalization

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⁵tutton's salt
⁶hashed = N-salicylidine-N’-(2-hydroxyethyl)-ethylenediamine
of the data to the unit step height. The energy positions of the important spectral features in all the compounds studied in this work are given in Table IV.1.

IV.4. Assignment of Electronic Transitions

Before discussing our results on X-ray absorption measurements, it would be interesting to mention here that in the case of X-ray absorption spectra of transition metal compounds studied by various authors [13-21], the K-absorption edges exhibit a weak low-energy peak at the threshold followed by a shoulder on a rising absorption curve that culminates in a strong peak. Through an examination of X-ray absorption spectra of a series of cubic perovskites of first-row transition metals, KMF$_3$ (where M = Mn, Fe, Co, Ni, and Zn), Shulman et al [7] assigned the lowest energy features in such edges as 1s → 3d transitions, the intermediate feature as a 1s → 4s transition, and the dominant peak as 1s → 4p transition. It is observed by these authors that the experimentally measured energies of these features agree rather well with the spectroscopic energy levels of the Z+1 (where Z is an atomic number) ions. Similar assignments have been made previously by other authors [8-11].

The assignments, 1s → 3d, 1s → 4s and 1s → 4p, although useful in a qualitative sense, are unsatisfactory in one respect. They are based on an atomic model for the available orbitals that does not allow for covalent bonding. Clearly, the final orbitals for the lower energy transitions cannot be of pure d or s character, since the angular momentum selection rules forbid 1s → nd or 1s → (n+1)s transitions. Shulman et al [7] have claimed that vibronic mixing of s, p and d characters makes the low energy transitions allowed. However, in many complexes covalent interactions between metal and ligands could also cause such mixing, in which case a molecular orbital (MO) description of the electronic transitions would be more desirable. In section IV.4, the MO scheme has therefore been used for interpretation of X-ray absorption spectra.

Most of the studies on the near-edge structure so far carried out by various authors have been primarily experimental in nature. Comparisons were made only with calculated molecular energy level spacings; no transi-
tion strengths were included. However, more quantitative calculations for the near-edge structure in transition-metal compounds have been done and few results have been published. Bair and Goddard [22] have carried out ab initio self-consistent field calculations on the excited states of the CuCl₂ molecule involving excitations of the Cu 1s orbital into bound valence and unbound virtual orbitals. These authors have calculated both the absolute excitation energies and the transition strengths, and considered the presence of a fully relaxed core hole, in their theoretical method based on a multielectron model utilizing a Hartree-Focks configuration-interaction approach. They have found that the weak pre-edge peak is indeed due to a transition to a partially unoccupied orbital of a primarily metal 3d character, in agreement with the above discussion. The main absorption peak at 8993 eV is assigned as a transition to the orbitals that are primarily of a metal 4p character (1s → 4pₓ) again in agreement with some of the above studies. However, the shoulder (the lower energy feature at 8986 eV) is not assigned to any single-electron transition. The 1s → 4s monopole transition strength is found to be far too weak to be observed and appears at the wrong energy to fit the shoulder peak data. Rather, this feature is reassigned by these authors to a "shake down" satellite transition involving a Cu 1s → 4pₓ transition simultaneous with ligand-to-metal charge transfer.

A similar interpretation has recently been proposed [23,24] for the polarized spectra of CuCl₂.2H₂O and (creat)₂CuCl₂. Satellite peaks, which are pronounced in inner-shell XPS studies of many transition-metal complexes [25-29], are predicted to be significantly reduced in intensity in X-ray absorption edge studies due to the shielding of the valence electrons when the photoelectron is in the low-energy threshold region. A previous study [30] comparing the XPS and X-ray absorption spectra of FeCl₂, MnCl₂ and CoCl₂ found low intensity satellites to the high energy side of the principal absorption maxima at energies corresponding to those expected on the basis of the prominent satellite splittings found in XPS. More rigorous calculations have been reported by Kutzler et al [31] who have performed self-consistent field Xα multiple scattering wave calculations for the near-edge of iron, chromium and molybdenum compounds. Like Bair and Goddard, they calculated one-electron transition strengths into bound and continuum states including the fully relaxed core hole. The results of these numerical studies indicate that a molecular cage defined by the first shell
Fig. IV.1 X-ray absorption spectrum of vanadium metal
Fig. IV. 2 X-ray absorption spectra of VO, V$_2$O$_3$, V$_4$O$_7$, V$_2$O$_4$, V$_2$O$_5$ and NH$_4$VO$_3$
Fig. IV.3 X-ray absorption spectra of $\text{CrVO}_4$, $\text{GdVO}_4$, $\text{Zn}_3(\text{VO}_4)_2$, $\text{Ca}_3\text{Fe}_3\text{VGeO}_{12}$, and $\text{Pb}_5\text{Cl}(\text{VO}_4)_3$.
Fig. V. 4 X-ray absorption spectra of VOPc, VOTPP, (NH₄)₄[VO tart]₂·2H₂O, VO(bzac)₂, VO(acac)₂ and VOMoO₄.
Fig. IV.5 X-ray absorption spectra of Tutton's salt, PbV$_2$O$_6$, Ca$_3$V$_{10}$O$_{28}$·16H$_2$O, [VO(hshed)(acac)], SmVO$_3$, V$_2$S$_3$, and VN.
Fig. IV.6. X-ray absorption spectra of $\text{YBa}_2(\text{Cu}_{0.98-x}\text{V}_x\text{Fe}_{0.02})_3\text{O}_{7-\delta}$ Where $x=0.04$, 0.05 and 0.06.
of ligands, which breaks the inversion symmetry at the metal atom site, can make transition from a $1s$ electron state to a bound state of a mainly nd character possible via admixture with $p$ orbitals from liganding atoms. They also show that the shoulder or kink, which has been assigned by several authors to a $1s \rightarrow (n+1)s$ transition, appears to be an inherent feature of the continuum and that the principal absorption maximum corresponds to a $1s \rightarrow (n+1)p$ transition. However, it is worth noting that the results of Kutzler et al. fail to predict the various shoulder-peak splittings observed in the measured spectra of transition-metal compounds [32-35]. These authors speculated that many-electron processes (such as shake-down transition considered by Bair and Goddard) may be involved but they have not attempted to incorporate such effects into their calculations.

From the above studies we see that the interpretation and calculation of the near-edge structure for the transition-metal compounds is much less clear cut. Many-electron effects due to an incompletely screened core hole appear to be sufficiently important to alter the simple molecular orbital or symmetry-based transition scheme invoked by various investigators. Although it appears that we are safe in labelling the pre-edge peak and main absorption maximum as $1s \rightarrow 3d$ and $1s \rightarrow 4p$ transitions, respectively, more corroborating calculations are needed before a definite assignment of the shoulder peak is possible.

Vanadium K-absorption spectra in vanadium metal and typical vanadium compounds are shown in Figs. IV. 1, 2, 3, 4 and 5. In Fig. IV. 6 are given the near-edge absorption spectra of vanadium in superconductors of the composition $YBa_2(Cu_{0.88-x}V_xFe_{0.02})_3O_{7-\delta}$ ($x = 0.04, 0.05, 0.06$). These spectral curves were obtained by averaging the results of a very large number of spectra recorded for each sample. For the superconductors, 10 scans of each were recorded in order to confirm all the fine structure peaks.

It is observed from Fig. IV. 1 that the K absorption edge of vanadium metal splits into three components. In the case of the vanadium compounds the absorption discontinuity is seen to split into three or more components. Our results in this respect are in good agreement with those obtained by Wong et al. [36] for vanadium metal and some of the compounds studied. For compounds viz. $Zn_2V_2O_7$, $PbV_2O_6$, $(NH_4)[VO-\text{dd}-\text{tart}]_2.2H_2O$, $Ca_3Fe_3GeVO_{12}$, $GdVO_4$, etc., no experimental data are available for comparison.
We shall first discuss our results on the near edge structure in model compounds having vanadium ions at tetrahedral, square pyramidal and octahedral sites and then we shall use these results to extract structural information in the superconducting oxides of vanadium. The relevant structural data on model compounds are presented in Table IV.2 [37-61].

IV.4.1. Vanadium K-edge in model compounds

The K-absorption near edge spectra of transition metal compounds are rich in information from which details on the coordination environment can be deduced. The profiles of the vanadium K-absorption edge in Figs. IV. 1, 2, 3, 4 and 5 show a pre-edge feature at the threshold followed by a shoulder on the rising absorption curve which culminates in a strong absorption peak. The pre-edge peaks are due to the transitions of the photoelectron to final states that are essentially vanadium 3d bound states. These transitions are quite sensitive to the crystal field [62-63] due to ligands around vanadium and hence the number, position, and intensity of these pre-edge peaks give information about the coordination environment of vanadium.

The main reason for this can be found in the d°, d¹, d², d³ electronic configurations of V⁵⁺, V⁴⁺, V³⁺ and V²⁺ ions respectively. All the d symmetry molecular levels are vacant completely or partially depending on the oxidation state of vanadium and available to receive the photoelectron to give (1s)¹(3d)¹, (1s)¹(3d)², (1s)¹(3d)³ and (1s)¹(3d)⁴ excited electronic configurations. The symmetry of the final state is that of the d levels since the 1s core hole is totally symmetrical and all other shells below the valence band are filled. Taking into account only the dipole electron transitions (\(\hat{\mathcal{O}}\) dipole operator), the transition moment is given by the general Fermi golden rule [64]

\[
M \propto <\psi_{\text{ground}}|\hat{\mathcal{O}}_{\text{dip}}|\psi_{\text{excited}}>^2 [N(E)]\delta(h\nu - E_{\text{ground}} + E_{\text{excited}})
\]

In this expression, \(N(E)\) is the number of vacancies in the excited states. This number is 0 or 1 or 2 in a molecular orbital description of a filled, singly occupied, or vacant orbital; \(\delta\) is a Dirac function, and the matrix element is a complex quantum function quite difficult to be computed exactly in the present state of the art [22,31,65].
In a pure tetrahedral symmetry, the pre-edge absorption is an outstanding feature in the K-edge XANES spectra of vanadium compounds, as can be seen from Fig. IV. 3. In every spectrum of Fig. IV. 3, an intense single pre-edge peak is observed. It corresponds to a dipole-allowed transition from the 1s level to admixed state formed from the 3d and 4p metal orbitals and from the 2p orbitals of neighbours.

In an octahedral symmetry, a weak pre-edge feature is observed (see Fig. IV. 2 and 5), the intensity of which is rather low due to the presence of an inversion centre at the V site \( T_1 \). The weakness of the intensity is due to the absence of \( A_{1g} \) in the direct product and there is no more 3d-4p mixing. The presence of such weak transitions may be assigned [3] to some relaxation of the Laporte selection rules, by vibronic coupling, or to the interference of a quadrupolar mechanism, as already demonstrated in a square planar \( \text{CuCl}_2^- \) complex [66].

The assignment of the first peak after threshold i.e. shoulder on the rising absorption curve (and other weak peaks between this shoulder and 1s \( \rightarrow \) 3d peak) is still controversial [67-68]. As mentioned earlier, according to the self-consistent X\( _a_ \) multiple scattering wave calculations of Kutzler et al [31], this feature, which has been assigned by several authors to a 1s \( \rightarrow \) 4s transition, appears to be an inherent feature of the continuum, while, according to the ab initio self-consistent field calculations of Bair and Goddard [22], this feature cannot be assigned to any single electron transition. Rather, this feature is reassigned by these authors as a 1s \( \rightarrow \) 4p transition plus simultaneous shakedown. It appears always much below the main transition with weak intensity and it will not be discussed further. Nevertheless, its presence in the spectra of liquid samples studied by Sonaye [69] allows us to rule out any interpretation of this transition based only on 3d solid-state interactions. The remaining peak, i.e., the main absorption maximum can be assigned to the transition of 1s electron to the 4p state. Since it is a dipole-allowed transition (\( \Delta l = +1 \)), its intensity is expected to be more as compared to the intensities of the pre-edge and shoulder peaks.

As mentioned earlier, the profiles of the X-ray absorption spectra of tetrahedrally coordinated vanadium compounds given in Figs. IV. 1 and 3 show a very intense pre-edge peak. The intensity of this pre-edge feature (in Fig. IV. 4) is slightly lowered for compounds in which vanadium ion has square-pyramidal coordination and its intensity is the least for octahedrally
coordinated vanadium compounds as can be seen from Figs. IV. 2 and 5.

**IV.4.2. XANES spectra and Superconducting Oxides**

YBa$_2$Cu$_3$O$_{7-\delta}$ is a well established oxide superconductor with $T_c \approx 92\text{K}$ for $\delta \leq 0.1$. This system is extensively investigated for its superconducting behaviour as a function of ionic substitution on the various sites. The 3d character of the ionic substitution into the Cu-site has been observed to influence the superconducting behaviour in a significant manner. Several transport and susceptibility studies have been reported [70-72] in literature on this aspect. These studies, however, do not reveal the relative site occupancy of the substituted 3d-ion on the two inequivalent copper sites present in the crystal structure of this superconducting material. Some techniques [73,74] like Neutron diffraction, Mössbauer, NMR etc., have been fruitfully employed to get an insight into the structural and site occupancy aspects. It has been seen that Fe$_2$O$_3$ dopant inhibits the tetragonal to orthorhombic phase transition in the 123 compound on the cooling part of the sintering cycle. However for YBa$_2$Cu$_3$O$_{7-\delta}$ the orthorhombic phase was dominant. V$_2$O$_5$ dopants in 123 do not change its orthorhombic structure up to $x = 0.06$ [75].

It is possible to discern the role of iron in blocking superconduction. Fe is presumed to substitute for Cu on either Cu(1) site or the Cu(2) site. In the sintered material Fe is trivalent, while for charge balance in orthorhombic 123, Cu must be trivalent or divalent. If Fe$^{3+}$ substitutes for Cu$^{3+}$ on the Cu(1) site, the half filled shell in the former ion would block the chains of small Cu$^{3+}$ ions and inhibit superconduction. However the structure would then be orthorhombic instead of tetragonal which is in fact found. Thus Fe must substitute on the alternative Cu(2) site. Mössbauer studies on Fe substituted 1-2-3 systems have shown [74] that the Fe substitutes Cu on both, the pyramidal-coordinated Cu(2) and 4-oxygen coordinated Cu(1) chain sites in varying proportions depending upon the amount of Fe substitution. However little work seems to have been done on vanadium substituted 1-2-3 compounds in order to see whether vanadium ion occupies Cu(1) or Cu(2) site. We have undertaken this investigation of K-edge of vanadium in the superconducting system of composition YBa$_2$(Cu$_{0.9-x}$V$_x$Fe$_{0.02}$)$_3$O$_{7-\delta}$, where $x = 0.04, 0.05$ and 0.06.
The vanadium K-edge spectra in superconducting oxides are shown in Fig. IV. 6. The spectra of the samples containing 4 and 5 at.% of vanadium are more or less similar to each other. For these two samples, the intensity of the pre-edge peak corresponding to the $1s \rightarrow 3d$ transition is nearly the same, whereas it is considerably small for the 6 at.% sample. The relative intensities of the $1s \rightarrow 3d$ peak for 4 at% and 5 at% samples are almost similar to those observed in pentavalent vanadium compounds.

The principal absorption maximum observed at $22.5 \pm 0.5$eV, which is attributed to the $1s \rightarrow 4p$ transition, is sharp in all the three superconducting compounds. The energies of both, the pre-edge as well as the principal maxima, as can be seen from Table IV. 1, are well within the energy range of these features in the model pentavalent vanadium compounds.

Both the above observations lead us to suggest the presence of $V^{5+}$ ions in the 4 at% and 5 at% samples in a square pyramidal coordination. It indirectly means that these ions occupy pyramidal Cu(2) sites and in turn drives Fe ions to occupy the chain sites in the Y123 structure. A tentative explanation on the basis of ionic radii can be given for the above inference. It is not at all surprising that $V^{5+}$ ions, which have ionic radii 0.59Å, could prefer to occupy the smaller interstitial pyramidal Cu(2) sites. In fact the vanadium site occupancy can be studied by different techniques like Mössbauer spectroscopy, neutron diffraction technique etc. However, to our knowledge no such studies have been hitherto reported.

For $x = 0.06$, the slightly lower intensity of the $1s \rightarrow 3d$ transition and the energies of this peak and the principal maximum seem to suggest the presence of $V^{5+}$ ions having lower coordination number, probably four (or considerably distorted penta-coordinated $V^{5+}$ ions). This means that these ions can occupy Cu(1) chain sites. It is well known, in the Y123 structure, Cu(1) ions are at chain sites and are coordinated by four oxygen atoms in square-planar configuration. This leads us to conclude that pentavalent vanadium ions are coordinated to oxygen atoms in a four fold coordination or a square planar configuration and the Fe ions are forced to occupy pyramidal Cu(2) sites. However to our knowledge no compound of vanadium is reported in literature wherein vanadium ions are coordinated to four oxygen atoms in a plane. This needs to be confirmed by single crystal X-ray diffraction or neutron diffraction analysis.
Vanadium Orbitals  Molecular Orbitals  Oxygen Orbitals

$4p(t_{1u})$

$4s(a_{1g})$

$3d(t_{2g} + e_g)$

$4p(t_{1u})$

$3a_{1g}$

$2t_2^g$

$3e_g$

$2p(\Pi(t_{2g} + t_{1u} + t_{1g} + t_2^g))$

$2p\sigma(a_{1g} + e_g + t_{1u})$

$2s(a_{1g} + e_g + t_{1u})$

$1s\frac{1}{2}$

$K$ - Absorption

$\bullet = \text{Electron pair}; \circ = \text{Vacant state}; \odot = \text{Unpaired electron}$

$a = \text{Anti-Bonding}; n = \text{Non-Bonding}; b = \text{Bonding}$

$\Delta_o = \text{Crystal field splitting}$

Fig. IV.7. Molecular orbital energy level scheme for octahedral vanadium compound.
IV.5. Molecular-Orbital approach and V-edge Structure

It is well known [2,3] that the fine structure within about 20 to 25eV of an absorption edge in a compound is characteristic of chemical bonding. Literature survey shows that the molecular orbital theory has been successfully employed by many workers to explain fine structure observed in the absorption edges of compounds. Fischer [34,35], Pendharkar and Mande [76], Obashi [77,78], Chetal and coworkers [79-81], Sarode and Pendharkar [82] have assigned the spectral features of X-ray absorption edge to the transition of core electrons to the partially or completely vacant molecular orbitals of appropriate symmetry formed from the interaction of ligands with central metal atoms.

In the present work, a qualitative molecular orbital diagram for octahedral compounds like VO, V2O3 and VO2, adapted from a book by Ballhausen and Gray [83] is shown Fig. IV. 7. This diagram takes into account the interactions of the metal 3d, 4s and 4p orbitals and the 2s and 2p(\(\sigma, \pi\)) orbitals of the ligand. In this figure, solid, half open, and fully open circles represent electron pairs, unpaired electron and fully vacant states respectively. For octahedral group such as \(\text{VO}_6\), which exists in a compound like VO, vanadium atom contributes five electrons (3d\(^5\)4s\(^2\)) and six oxygen ligands contribute 36 electrons (2s\(^2\)2p\(^4\)) to the formation of molecular orbitals. However, the VO\(_6\) ion has ten more electrons because of its negative charge if vanadium is in 2\(^+\) state. [For trivalent and tetravalent compounds, there are nine and eight electrons respectively]. Therefore total number of electrons of \(\text{VO}_6\) cluster that contributes to the formation of the molecular orbitals is 51. After distributing all these electrons in the various molecular orbitals as shown in Fig. IV. 7, one finds that the orbitals below 2t\(_{2g}\) are completely filled. The antibonding orbital 2t\(_{2g}\) is partially vacant (half-filled) and the higher energy orbitals above 2t\(_{2g}\) are completely vacant. The partially vacant antibonding orbital 2t\(_{2g}\) and completely vacant 3e\(_g\) orbital have d symmetry and the empty antibonding orbital 3a\(_{1g}\) has s symmetry and the outermost empty antibonding 4t\(_{1u}\) level has p symmetry.

In VO, V\(_2\)O\(_3\), VO\(_2\) and other transition metal oxides, where transition metal ion is octahedrally coordinated to oxygen, the 3d band splitting is
less than 2 eV \[84\]. It is difficult to see two transitions from 1s core level to 3e_g and 2t_2g levels as the resolution of our spectrometer is \(~4\) eV. Therefore, the pre-edge peak can be attributed to the 1s electron transition to (3e_g, 2t_2g) levels. The shoulder and the main absorption maximum in Figs. IV. 2 and 5 can be assigned to the transitions of the 1s electrons of the K shell to the vacant 3a_1g and 4t_1u molecular orbital levels respectively.

It may be noted that the 1s \(\rightarrow (3e_g, 2t_{2g})\) and 1s \(\rightarrow 3a_{1g}\) transitions are dipole forbidden. However, as can be clearly seen from the molecular orbital diagram (Fig. IV. 7) some amount of the p character from oxygen orbitals mixes up with metal orbital to form these molecular orbitals, making these two electronic transitions allowed. If the liganding atom is nitrogen or carbon or sulphur instead of oxygen, the same molecular orbital picture is valid. Furthermore, in some compounds like VOTPP and VO(hshld)(acen) vanadium has six ligands comprising nitrogen and oxygen atoms, the molecular orbital picture in this case will remain, to the first approximation, the same. Therefore, the absorption fine structure in such compounds can be interpreted in a similar way.

For vanadium compounds like GdVO_4, BiVO_4, wherein the vanadium ion is tetrahedrally bonded to the oxygen ligand, the molecular orbital picture is shown in Fig. IV. 8. It takes into account the interaction of metal 3d, 4s and 4p orbitals and 2s and 2p(\(\text{\sigma, \pi}\)) orbitals of oxygen ligands. The vanadium atom contributes 5 electrons and 4 oxygen atoms contribute 24 electrons to the formation of molecular orbitals. Taking into consideration the charge on the VO_4 cluster, the total number of electrons is 32. After distributing these electrons in various molecular orbitals of VO_4 ion as shown in Fig. IV. 8, one observes that the antibonding orbital 2e and the other antibonding orbitals viz. 4t_2, 3a_1 and 5t_2 are completely vacant. The 2e molecular level is formed from the interaction of 3d metal orbitals and 2p orbitals of oxygen atom. The antibonding levels 4t_2 and 5t_2 have d + p admixture of metal character and s+p admixture of ligand. The 3a_1 level has the s character from metal and s+p character from ligand. Hence the electrons from the K level can go, in the X-ray absorption process, to all these levels without violating the dipole selection rules. Thus, like electron transitions in octahedral compounds, the pre-edge absorption peak can be attributed to the transition of 1s electron to the (2e, 4t_2) molecular orbitals, since the 3d level splitting is very small. The shoulder peak and
the main absorption maximum can be assigned to the transition of the 1s electrons to the 3a_1 and 5t_2 molecular levels respectively. It may be interesting to note here that the relative intensity of 1s → 3d transition in tetrahedrally coordinated vanadium ions is relatively large as compared to that of vanadium compounds wherein vanadium ions are octahedrally coordinated. The reason is obvious. If we compare the transitions of 1s electron to (2t_2g, 3e_g) and (2e, 4t_2) levels in the octahedral and tetrahedral compounds respectively. The level 2t_2g or 3e_g has little p(σ, π) contribution from oxygen and hence the intensity of 1s → (2t_2g, 3e_g) transition is very small in octahedral compounds. However, the level 4t_2 (or 2e) has relatively large amount of p contribution from metal 4p and p(σ, π) contribution from ligand. It means that the 4t_2 MO level has more p-contribution and therefore the pre-absorption peak corresponding to the transition 1s → (2e, 4t_2) is more intense. This is the reason why many workers [8,32,85-88] have observed a very intense 1s → 3d transition in vanadium, chromium and manganese compounds.

For pentacoordinated (square pyramidal) vanadium compounds viz. VO(bzac)_2, V_2O_5 the qualitative molecular orbital diagram is not available in literature. According to Figgis [87], a probable splitting pattern for the d-orbitals in a square-pyramidal complex is similar to that in a square-planar complex, wherein the d level splits into four components. A similar thing is expected to happen in a square-pyramidal complex. In an order of increasing energy, the sequence of molecular orbitals given by Figgis [87], is b_2(d_x^2), e(d_x^2-d_y^2), a_1(d_y^2), b_1(d_2-y_2). All these antibonding orbitals are empty if the vanadium ion is pentavalent. If it is tetravalent, the b_2 orbital will have one electron. The next empty antibonding orbitals will be a_1g, a_2g and e_u which have 4s + 2p_x, 4p + 2p_y and 4p + 2p_z characters respectively. As mentioned earlier, since the d band splitting is very small, the pre-edge peak would be attributed to 1s electron transition to the empty molecular orbital (b_2, e, a_1, b_1). The shoulder of the K-edge and the principal absorption peak may be assigned to the transition of 1s electron to the vacant antibonding a_1g orbital and (a_2g, e_u) orbitals respectively. The relatively large intensity of the pre-edge peak is difficult to explain unless a full description of MO diagram is available.
Fig. IV. 8 Molecular orbital energy level scheme for tetrahedral Vanadium compound.

- Electron pair; ○ = Vacant state; Δ₀ = Crystal field splitting
IV.6. Bond Length determination from V K-edge Structure

As mentioned earlier, there is a growing interest in understanding the X-ray absorption near-edge structure (XANES) part of X-ray absorption spectra for local-structure determination in complex systems [88-90]. According to Bianconi et al [89], XANES of transition metal compounds can be separated into two parts:

(a) the discrete part below the continuum edge, where the weak features are usually called pre-edge peaks (or prepeaks), due to transitions to unoccupied bound antibonding orbitals [89] and

(b) the continuum part where the peaks are due to multiple-scattering resonances of the photoelectron, which are sensitive to both coordination geometry and interatomic distances [91,92].

The effect of the interatomic distance $R$ has been shown to shift the multiple-scattering resonances in diatomic molecules, with a given geometry, following the rule [93] $k_r R = \text{constant}$, where $k_r$ is the wave vector of the photoelectron at resonance for small variation ($< 20\%$) of $R$. The shift of the multiple-scattering resonances with distance variation in diatomic molecules of low-$Z$ elements has been applied in chemisorption studies [94] but the main limitation in the bond-distance determination is in the determination of $\tilde{V}$, the average interstitial potential, which is necessary for the definition of $k$ because $k$ is related to $\tilde{V}$ by the relation, $k = \hbar \omega E_0 - \tilde{V}$, where $E_0$ is the continuum threshold.

The correlation between the energy position of the multiple-scattering resonances in the continuum and the interatomic distances has been recently demonstrated by Bianconi, Natoli and others [92-96]. In the framework of the $X_\alpha$ - multiple-scattering theory, the absorption cross section can be shown to be determined by the multiple-scattering matrix $M$ of the photoelectron with kinetic energy $(\hbar k)^2/2m = E = E^* - \tilde{V}$ where $E$ is the energy of the resonance above the threshold and $\tilde{V}$ is the average muffin-tin interstitial potential as mentioned above. The maxima in the absorption correspond to the $\det(M) = 0$ condition. In this formalism, Natoli derived the following relation between continuum resonance energy, $E_r$, and the first coordination shell distance,
where \( C_r \) is the constant corresponding to \( E_r \). However, \( C_r \) being unknown and \( \tilde{V} \) being experimentally undeterminable, the above equation was found to be of little use in practice. Natoli also obtained a similar expression for the bound state resonance energy, \( E_b \), with a different constant \( C_b \), i.e.,

\[
(E_r - \tilde{V})R^2 = C_r
\]

Combination of the above two relations eliminates \( \tilde{V} \) and leads to the following equation

\[
(E_r - E_b)R^2 = C_r - C_b
\]

or

\[
\Delta E_{3d-4p} \approx \frac{C_r}{R^2}
\]

This is a relation containing only measurable quantities and of immediate application.

By the term "bound or excitonic resonances" we mean those spectral pre-edge features due to transitions to truly bound state in molecules (e.g., the \( \pi^* \) transition in diatomic molecules [97] or to antibonding states of 3d character in metal oxides [94]). Both have in common the feature that they fall in an energy region where atomic resonances of the constituent atoms occur and, so to speak, are driven by them.

When applied [98] to free molecules, the above equation states that the energy difference between the \( \sigma^* \) and the \( \pi^* \) resonance depends only on the bond length, provided initial state differences, like more or less covalence or polarity of the bond, have the same effect on the two excited states. For chemisorbed molecules one is led to the same conclusions, provided the two resonances are affected by the metal substrate shielding in the same way. Under these assumptions [98], the constant should be transferable from one phase to another. If applied to metal oxides or in general, metal compounds, this equation, according to Natoli [98] implies that the energy separation between the pre-edge excitonic feature and the first strong absorption maximum after rising edge is a function of the bond length. This
Fig. IV.9. A plot of $\Delta E_{3d-4p}$ versus $1/R^2$ for vanadium compounds.
relation has been employed by Natoli [98] and other researchers [99,100] to
determine the bond distances in the transition metal compounds.

This relation is the equation of a straight line passing through the origin
and having a slope $C_{rb}$. In order to determine the value of constant $C_{rb}$, we
have plotted in Fig. IV. 9 the energy separations ($\Delta E_{3d-4p}$) between the
multiple - scattering resonances in the continuum ($1s \rightarrow 4p$ transition) and
bound ($1s \rightarrow 3d$ transition) states versus the reciprocal of square of the
interatomic distances ($R$) for a number of vanadium compounds covering
a wide range of structures. The least-squares analysis of the data using all
the 26 points was carried out on PC-486. As can be seen from Fig. IV. 9,
Natoli's simple relation at first glance, does not seem to hold true for these
compounds. However, when these compounds are classified according to
the coordination number of vanadium and $\Delta E_{3d-4p}$ vs $1/R^2$ graphs were
plotted for 4-fold, 5-fold, and 6-fold coordinated compounds separately, a
fairly good linear relation was found to exist between $\Delta E_{3d-4p}$ and $1/R^2$ in
each case as shown in Fig. IV. 9. For tetrahedrally coordinated compounds,
the correlation coefficient and standard error of estimates are found to be
0.983 and 0.095 respectively. For penta coordinated compounds, if we take
into account the data for all eight compounds for regression analysis, we
get the values of correlation coefficient and standard error of estimates as
0.656 and 2.994 respectively. However, for two complexes, namely VOPc
and VOTPP, the deviation for the least-squares line is very large. Such
large deviations for these two compounds have also been observed in the
plots of intensity of pre-edge peaks versus average bond lengths of first shell
ligands in various ligand geometries in the work of Wong et al [36]. If we
perform the analysis excluding the data points for VOPc and VOTPP, the
values of correlation coefficient and standard error of estimates are found
to be 0.943 and 0.207 respectively. In the case of octahedrally coordinated
compounds, the regression analysis gives the values of correlation coeffi-
cient and standard error of estimates as 0.747 and 1.405 respectively. By
examining the experimental and calculated energy separations for the oc-
tahedral compounds, it is seen that the residues are large for VN, $V_2S_3$ and
VC. That is why a relatively large value of standard error of estimates is ob-
tained. However, the analysis carried out, excluding the data for VN, $V_2S_3$
and VC, yields the values of the correlation coefficient and standard error
of estimates as 0.879 and 0.692 respectively. Thus, we can see that there
is a lot of improvement. Although it is difficult to give any satisfactory explanation for the large deviation observed for these three compounds, the nature of bonding seems to have some role to play in the large energy separations in the X-ray absorption spectra of these compounds. For example, the V-S and V-N bonds are strongly covalent and strongly ionic in nature respectively whereas all other compounds have mixed bond character. Barring such exceptions, we may conclude that Natoli's relation is valid for a series of compounds wherein the metal ions have the same coordination geometry. i.e., \( \Delta E_{3d-4p} \times R^2 = \text{constant} \) for a particular coordination polyhedron of ligands around metal ions. The constants for tetrahedral, square pyramidal and octahedral coordination geometries were determined from the least-squares fitting of the data to a linear equation of the form \( \Delta E_{3d-4p} \times R^2 = C \), where \( C \) is the constant for each coordination geometry and are given in Table IV. 3. Once the constants are known it is easy to use this formula to predict coordination geometry and bond distance from the profiles and energy positions of the XANES peaks. We have employed this method to predict the interatomic distances in superconducting compounds for which the values of \( \Delta E \) have been determined from the XANES spectra.

**IV.6.1 Test of Transferability of Structural constants**

As a first test of the transferability of these constants, we have chosen three compounds. These compounds are CrVO\(_4\), (NH\(_4\))\(_4\)[VO – dd – tart]\(_2\).2H\(_2\)O and PbV\(_2\)O\(_6\), whose structures had been elucidated previously by X-ray crystallography [37,45,60]. The absorption spectra of these three vanadium compounds have been recorded and the normalized spectra are presented in Figs. IV. 3, 4 and 5. To obtain structural information, the profiles of the edges of these compounds were first compared with those of the model compounds. The comparison suggests that vanadium ions are four fold coordinated in CrVO\(_4\), five-fold coordinated in (NH\(_4\))\(_4\)[VO – dd – tart]\(_2\).2H\(_2\)O and six-fold coordinated in PbV\(_2\)O\(_6\). Therefore using the constants \( C_{\text{tetra}} \), \( C_{\text{sqpyr}} \) and \( C_{\text{octa}} \), we have calculated the V-X (X = ligand) bond distances in these compounds. The bond lengths 1.791\( \text{Å} \), 1.975\( \text{Å} \) and 1.979\( \text{Å} \) in CrVO\(_4\), (NH\(_4\))\(_4\)[VO – dd – tart]\(_2\).2H\(_2\)O and PbV\(_2\)O\(_6\) respectively determined in this work are in good agreement with those reported in literature.
The close correlation of both the coordination geometry and bond distances lends confidence to our ability to predict the coordination numbers and distances in compounds of unknown structures by XANES spectroscopy.

IV.6.2 Determination of Bond Distances in Superconductors

The XANES spectra of the superconducting oxides containing 4, 5 and 6 at% vanadium are shown in Fig. IV.6. Comparison of the K-edge profiles of the superconductors containing 4 and 5 at% vanadium with those of the model compounds suggests the presence of square-pyramidally coordinated V$^{5+}$ ions in the superconducting oxides. Therefore, using the structural constant corresponding to square-pyramidal geometry, C$_{\text{sq.pyr.}}$, we have estimated the V-O bond distances for the two compounds containing 4 and 5 at% vanadium as 1.863Å and 1.852Å respectively from the energy separations 17.6 and 17.8 eV. For the sample containing 6 at% vanadium, it is difficult to calculate the V-O bond distance since the structural constant for square-planar configuration is not obtained from the XANES analysis. This is because, as mentioned earlier, the compounds of vanadium in which the vanadium ion is ligated to four oxygen atoms in a plane are not known. However, if we use C$_{\text{sq.pyr.}}$, the bond distance is obtained as 1.714Å and if we use C$_{\text{teta}}$ (since we do not have C$_{\text{sq.planar}}$), we get a bond distance as 1.760Å. Since we have not done Mössbauer spectroscopy measurements, it is difficult to comment on the site occupancy of V$^{+5}$ ions in 6% compound.
Table IV.1. Energy positions of various Spectral Features in Vanadium K-edge Spectra in vanadium compounds ± 0.5 eV

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Absorber</th>
<th>Pre-edge peak(eV)</th>
<th>Main absorption peak(eV)</th>
<th>Energy separation ΔE_{3d-4p}(eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>V metal</td>
<td>-</td>
<td>19.3</td>
<td>-</td>
</tr>
<tr>
<td>2.</td>
<td>CrVO₄</td>
<td>4.3</td>
<td>24.8</td>
<td>20.5</td>
</tr>
<tr>
<td>3.</td>
<td>GdVO₄</td>
<td>3.9</td>
<td>24.7</td>
<td>20.8</td>
</tr>
<tr>
<td>4.</td>
<td>BiVO₄</td>
<td>4.7</td>
<td>26.4</td>
<td>21.7</td>
</tr>
<tr>
<td>5.</td>
<td>Cd₂V₂O₇</td>
<td>4.6</td>
<td>26.4</td>
<td>21.8</td>
</tr>
<tr>
<td>6.</td>
<td>Ca₅Fe₃GeVO₁₂</td>
<td>4.1</td>
<td>25.7</td>
<td>21.6</td>
</tr>
<tr>
<td>7.</td>
<td>Pb₅(VO₄)₃Cl</td>
<td>3.9</td>
<td>25.1</td>
<td>21.2</td>
</tr>
<tr>
<td>8.</td>
<td>Zn₃(VO₄)₂</td>
<td>3.9</td>
<td>25.8</td>
<td>21.9</td>
</tr>
<tr>
<td>9.</td>
<td>NaVO₃</td>
<td>4.1</td>
<td>25.6</td>
<td>21.5</td>
</tr>
<tr>
<td>10.</td>
<td>VO(acac)₂</td>
<td>3.9</td>
<td>20.9</td>
<td>17.0</td>
</tr>
<tr>
<td>11.</td>
<td>VO(bzac)₂</td>
<td>4.1</td>
<td>20.8</td>
<td>16.7</td>
</tr>
<tr>
<td>12.</td>
<td>(NH₄)₄[VO − dd − tart]₂.2H₂O⁺</td>
<td>3.5</td>
<td>20.6</td>
<td>17.1</td>
</tr>
<tr>
<td>13.</td>
<td>VOPc</td>
<td>3.9</td>
<td>27.3</td>
<td>23.4</td>
</tr>
<tr>
<td>14.</td>
<td>VOTPP</td>
<td>4.0</td>
<td>25.6</td>
<td>21.6</td>
</tr>
<tr>
<td>15.</td>
<td>VOMoO₄</td>
<td>4.4</td>
<td>21.4</td>
<td>17.0</td>
</tr>
<tr>
<td>16.</td>
<td>V₂O₅</td>
<td>4.8</td>
<td>23.0</td>
<td>18.2</td>
</tr>
<tr>
<td>17.</td>
<td>VOSO₄.3H₂O⁺</td>
<td>4.8</td>
<td>21.0</td>
<td>16.2</td>
</tr>
<tr>
<td>18.</td>
<td>VO(acen)⁺</td>
<td>4.0</td>
<td>20.6</td>
<td>16.6</td>
</tr>
<tr>
<td>19.</td>
<td>VO</td>
<td>3.2</td>
<td>21.2</td>
<td>18.0</td>
</tr>
<tr>
<td></td>
<td>Compound</td>
<td>X</td>
<td>Y</td>
<td>Z</td>
</tr>
<tr>
<td>---</td>
<td>---------------------------------</td>
<td>---</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td>20.</td>
<td>((\text{NH}_4)_2\text{SO}_4\text{VSO}_4\cdot6\text{H}_2\text{O})</td>
<td>3.4</td>
<td>20.4</td>
<td>17.0</td>
</tr>
<tr>
<td>21.</td>
<td>(\text{V}_2\text{O}_3)</td>
<td>3.5</td>
<td>22.9</td>
<td>19.4</td>
</tr>
<tr>
<td>22.</td>
<td>(\text{SmVO}_3)</td>
<td>3.3</td>
<td>23.9</td>
<td>20.6</td>
</tr>
<tr>
<td>23.</td>
<td>(\text{V}_2\text{S}_3)</td>
<td>3.1</td>
<td>23.1</td>
<td>20.0</td>
</tr>
<tr>
<td>24.</td>
<td>(\text{VN})</td>
<td>4.8</td>
<td>20.0</td>
<td>15.2</td>
</tr>
<tr>
<td>25.</td>
<td>(\text{VO}_2)</td>
<td>4.5</td>
<td>25.8</td>
<td>21.3</td>
</tr>
<tr>
<td>26.</td>
<td>(\text{V}_4\text{O}_7)</td>
<td>4.1</td>
<td>25.2</td>
<td>21.1</td>
</tr>
<tr>
<td>27.</td>
<td>(\text{VC})</td>
<td>5.2</td>
<td>20.5</td>
<td>15.3</td>
</tr>
<tr>
<td>28.</td>
<td>([\text{VO(hshed)}\text{(acac)}])</td>
<td>3.8</td>
<td>23.8</td>
<td>20.0</td>
</tr>
<tr>
<td>29.</td>
<td>(\text{PbV}_2\text{O}_5)</td>
<td>4.6</td>
<td>24.9</td>
<td>20.3</td>
</tr>
<tr>
<td>30.</td>
<td>(\text{Ca}<em>3\text{V}</em>{10}\text{O}_{28}\cdot16\text{H}_2\text{O})</td>
<td>4.1</td>
<td>25.7</td>
<td>21.6</td>
</tr>
<tr>
<td>31.</td>
<td>4 at% sc sample</td>
<td>4.8</td>
<td>22.4</td>
<td>17.6</td>
</tr>
<tr>
<td>32.</td>
<td>5 at% sc sample</td>
<td>4.8</td>
<td>22.6</td>
<td>17.8</td>
</tr>
<tr>
<td>33.</td>
<td>6 at% sc sample</td>
<td>4.1</td>
<td>24.9</td>
<td>20.8</td>
</tr>
</tbody>
</table>

* Test compounds
+ Data taken from unpublished work of B. H. Sonaye
### TABLE IV.2. Structural Parameters for vanadium compounds

<table>
<thead>
<tr>
<th>Sr. No.</th>
<th>Compound</th>
<th>Q^a</th>
<th>Bond Type</th>
<th>No. of Bonds</th>
<th>R[^b]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>V metal</td>
<td></td>
<td>V-V</td>
<td>8</td>
<td>2.622</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Tetrhedral</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>CrVO₄</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.765</td>
<td>37(a), 37(b)</td>
</tr>
<tr>
<td>3.</td>
<td>GdVO₄</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.760</td>
<td>38</td>
</tr>
<tr>
<td>4.</td>
<td>BiVO₄</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.730</td>
<td>39</td>
</tr>
<tr>
<td>5.</td>
<td>Cd₂V₂O₇</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.718</td>
<td>40</td>
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<tr>
<td>6.</td>
<td>Ca₃Fe₃VGeO₁₂</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.724</td>
<td>41</td>
</tr>
<tr>
<td>7.</td>
<td>Pb₂(VO₄)₃Cl</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.740</td>
<td>42</td>
</tr>
<tr>
<td>8.</td>
<td>Zn₂(VO₄)₃</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.715</td>
<td>43(a)</td>
</tr>
<tr>
<td>9.</td>
<td>NaVO₃</td>
<td>5</td>
<td>V-O</td>
<td>4</td>
<td>1.723</td>
<td>43(b)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Square pyramidal</td>
<td></td>
<td></td>
<td></td>
</tr>
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<td>10.</td>
<td>VO(acac)₂</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>1.889</td>
<td>44</td>
</tr>
<tr>
<td>11.</td>
<td>VO(bzac)₂</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>1.894</td>
<td>44</td>
</tr>
<tr>
<td>12.</td>
<td>(NH₄)₄[VO – dd – tart]₂.2H₂O</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>1.886</td>
<td>45(a)</td>
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<td></td>
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<td></td>
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<td>45(b)</td>
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<td>13.</td>
<td>VOPc</td>
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<td>V-O</td>
<td>5</td>
<td>1.937</td>
<td>46</td>
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<td>V-N</td>
<td></td>
<td></td>
<td></td>
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<tr>
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<td>VOTPP</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>2.006</td>
<td>47</td>
</tr>
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<td></td>
<td></td>
<td></td>
<td>V-N</td>
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<td></td>
<td></td>
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<td>15.</td>
<td>VOMoO₄</td>
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<td>V-O</td>
<td>5</td>
<td>1.913</td>
<td>48</td>
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<td>V₂O₅</td>
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<td>V-O</td>
<td>5</td>
<td>1.840</td>
<td>49(a)</td>
</tr>
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<td>VO₅SO₄.3H₂O</td>
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<td>V-O</td>
<td>5</td>
<td>1.936</td>
<td>49(b)</td>
</tr>
<tr>
<td>18.</td>
<td>VO(acen)</td>
<td>4</td>
<td>V-O</td>
<td>5</td>
<td>1.922</td>
<td>49(c)</td>
</tr>
<tr>
<td>Entry</td>
<td>Formula</td>
<td>Octahedral</td>
<td>V-O</td>
<td>Bond distance</td>
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</tr>
<tr>
<td>-------</td>
<td>---------</td>
<td>------------</td>
<td>-----</td>
<td>---------------</td>
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<td></td>
</tr>
<tr>
<td>19.</td>
<td>VO</td>
<td>2</td>
<td>V-O</td>
<td>2.050</td>
<td></td>
<td></td>
</tr>
<tr>
<td>20.</td>
<td>(NH₄)₂SO₄VSO₄.6H₂O</td>
<td>2</td>
<td>V-O</td>
<td>2.140</td>
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</tr>
<tr>
<td>21.</td>
<td>V₂O₃</td>
<td>3</td>
<td>V-O</td>
<td>2.010</td>
<td></td>
<td></td>
</tr>
<tr>
<td>22.</td>
<td>SmVO₃</td>
<td>3</td>
<td>V-O</td>
<td>1.929</td>
<td></td>
<td></td>
</tr>
<tr>
<td>23.</td>
<td>V₂S₃</td>
<td>3</td>
<td>V-S</td>
<td>2.080</td>
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</tr>
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<td>24.</td>
<td>VN</td>
<td>3</td>
<td>V-N</td>
<td>2.070</td>
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<td></td>
</tr>
<tr>
<td>25.</td>
<td>VO₂</td>
<td>4</td>
<td>V-O</td>
<td>1.930</td>
<td></td>
<td></td>
</tr>
<tr>
<td>26.</td>
<td>V₄O₇</td>
<td>3,4</td>
<td>V-O</td>
<td>1.982</td>
<td></td>
<td></td>
</tr>
<tr>
<td>27.</td>
<td>VC</td>
<td>4</td>
<td>V-C</td>
<td>2.091</td>
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<td>28.</td>
<td>[VO(hshed)(acac)]</td>
<td>5</td>
<td>V-O</td>
<td>1.973</td>
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<td>V-N</td>
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<td>29.</td>
<td>PbV₂O₆</td>
<td>5</td>
<td>V-O</td>
<td>1.962</td>
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<td>30.</td>
<td>Ca₃V₁₀O₂₈.16H₂O</td>
<td>5</td>
<td>V-O</td>
<td>1.920</td>
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</table>

### Superconducting samples

<table>
<thead>
<tr>
<th>Entry</th>
<th>At%</th>
<th>Sample Details</th>
<th>V-O</th>
<th>Bond distance</th>
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<tbody>
<tr>
<td>31.</td>
<td>4</td>
<td>5 (1.863)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>32.</td>
<td>5</td>
<td>5 (1.852)</td>
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<td></td>
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<tr>
<td>33.</td>
<td>6</td>
<td>4 (1.760)</td>
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Q = Oxidation state  
R = Bond distance
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<tr>
<th>Coordination polyhedron</th>
<th>Notation for the constant</th>
<th>Numerical Value of the constant</th>
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<tbody>
<tr>
<td>Tetrahedron</td>
<td>$C_{\text{tetra}}$</td>
<td>64.46</td>
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<tr>
<td>Square Pyramid</td>
<td>$C_{\text{sq.pyr}}$</td>
<td>61.08</td>
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<tr>
<td>Octahedron</td>
<td>$C_{\text{oct}}$</td>
<td>77.62</td>
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</table>
References


