TiOCl, TiOBr-are these RVB d^1, S=1/2 materials? The results of scandium substitution set in the context of other S=1/2 systems of current interest for high-temperature superconductivity and the metal-insulator transition

TiOCl, TiOBr—are these RVB d^1, $S=\frac{1}{2}$ materials? The results of scandium substitution set in the context of other $S=\frac{1}{2}$ systems of current interest for high-temperature superconductivity and the metal–insulator transition

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Abstract. The title materials display anomalous electrical, magnetic and optical properties. They have the characteristics of Mott insulators showing high electrical resistance and ligand-field optical spectra, but at the same time they adopt a magnetic ground state which is neither of Curie–Weiss type nor indeed of some standard antiferromagnetically ordered condition. The observed state is one of lowish, isotropic, and almost temperature-independent paramagnetism. One solution in such circumstances would be some systematically distorted crystal structure in which the cation spins become paired up into chemical bonds. However, IR work shows that the TiOX structure is not distorted, at least not in a manner that breaks symmetry and/or increases the cell size. We have studied the magnetic properties of Sc-doped TiOX to cast light on the problem, seeking possible indications of the existence of the resonant valence bond or RVB state—the state currently suggested by some to be responsible for high-temperature superconductivity in the mixed-valence cuprates. It is necessary to distinguish between RVB and some extreme case of magnetic frustration in these $S = \frac{1}{2}$, 2D oxyhalide systems. In this paper we have tried to put the detailed behaviour of the oxyhalide materials in context with other $S = \frac{1}{2}$ systems. In many the $S = \frac{1}{2}$ quantum fluctuation problem is compounded by low dimensionality, by geometric frustration of antiferromagnetic order, and by the approach to the metal–insulator transition. The diversity of low-temperature behaviour is striking, but it is clear that RVB must constitute a rarely encountered ground state rather than the norm. Our tentative conclusion is that TiOX presents an RVB ground state which Sc doping renders glassy and static.

1. Introduction to the TiOX materials: promising systems for RVB

The low-valent halides and oxyhalides of titanium and vanadium with stoichiometries MX_2, MX_3 and MOX exhibit most interesting structural, optical and magnetic properties. However while those for the vanadium materials all are presently understandable, those for the titanium materials continue to pose serious problems of interpretation. In this paper we shall concentrate on the d^1 titanium oxyhalides, endeavouring to set our results in the context of those for the other halide families, upon which we have already reported [1]. The present work bears directly on current research into La_2CuO_4 and the various d^9 insulating cuprates, now of prime interest to the high-temperature superconductor field. In particular the work concerns the

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question of the possibility of the resonant valence bond or RVB state [2] as an alternative ground state to antiferromagnetic order, especially for crystal structures in which such order is geometrically frustrated.

The formal configurations with which we are involved in these uniformly non-metallic materials are $d^1 Ti^{3+}$, $d^2 Ti^{2+}$ and V^{3+}, and $d^3 V^{2+}$. Each family of compounds adopts some low-dimensional layer- or chain-type structure [3]. At MX_2 stoichiometry the hexagonal close-packed cation layers of the CdI_2 structure appear. By contrast for MX_3 stoichiometry (in the α sub-family) the cation layer is of honeycomb geometry (with stacking to give BiI_3, $FeCl_3$, and $AlCl_3$ structural polytypes). As in the MX_2 case, here too in α-MX_3 octahedral coordination units share edges to build up X–M–X sandwiches. In the alternative β-MX_3 sub-family (shown only by Ti—not V) the coordination units by contrast share faces and a c-axis chain structure results. The layered MX_2 and MX_3 materials are basically hexagonal, although certain of the van der Waals bonded stacking sequences can lead to an overall reduction in crystal symmetry (as in three-sandwich, monoclinic $AlCl_3$). More significantly, symmetry breaking may arise in titanium halides, as we shall see, from interactions within a single sandwich.

The crystal structure of the MOX materials (archetype FeOCl) is more complicated and less well known than those of the MX_2 and MX_3 materials. It is presented from several aspects in figure 1. Bond length information is given in table 1 [4]. (N.B. the axes are labelled here in accord with normal layer structure practice.) The structure is a bisandwich layer type, of orthorhombic symmetry, in which $Z = 2$. The halide ions once more mediate the van der Waals intersandwich interaction. Inside a sandwich the MO_4X_2 'octahedra' share edges, as in the MX_2 and α-MX_3 families, but now in more unusual and irregular fashion. Two (O–X) edge linkages produce chains parallel to the b axis while four further (O–O) edge linkages are shared with the second level of the double sandwich. The latter links are associated with a slightly shorter Ti–Ti separation (see table 1).

Table 1. Ti–Ti distances in the titanium oxyhalides. Space group D_{2h}^{13} ($Pmmm$); Ti site point group C_{2v}. All data from [3].

Compound	Ti–Ti (Å) ($\times N$)		
	Interlayer ($\times 4$)	a axis ($\times 2$)	b axis ($\times 2$)
TiOCl	3.10[a]	3.79	3.38
TiOBr	3.193	3.787	3.487

[a] Value calculated using TiOBr z parameter—see figure 1.

In all the above Ti and V materials the d states of interest essentially are of non-bonding t_{2g} geometry with respect to the coordinating ligands; i.e. the lobes of the cation wavefunctions are directed away from the ligands, and for the given edge-sharing structures they point towards similarly placed cations in neighbouring coordination units. In this the d^1 and d^2 ions differ from their d^8 and d^9 counterparts, say in NiX_2 or La_2CuO_4 [5] etc, where e_g-type pdσ^* orbital interaction is involved. This difference changes the ability of a material to undergo metal–metal bonding and also the details of the superexchange coupling in the case of a magnetic system.

Direct cation–cation interaction is promoted within early TM materials both by the above orientational aspect and additionally by the greater size (at set valence) of the ions of small d-electron count. In d^1 vanadium and titanium oxides direct M–M
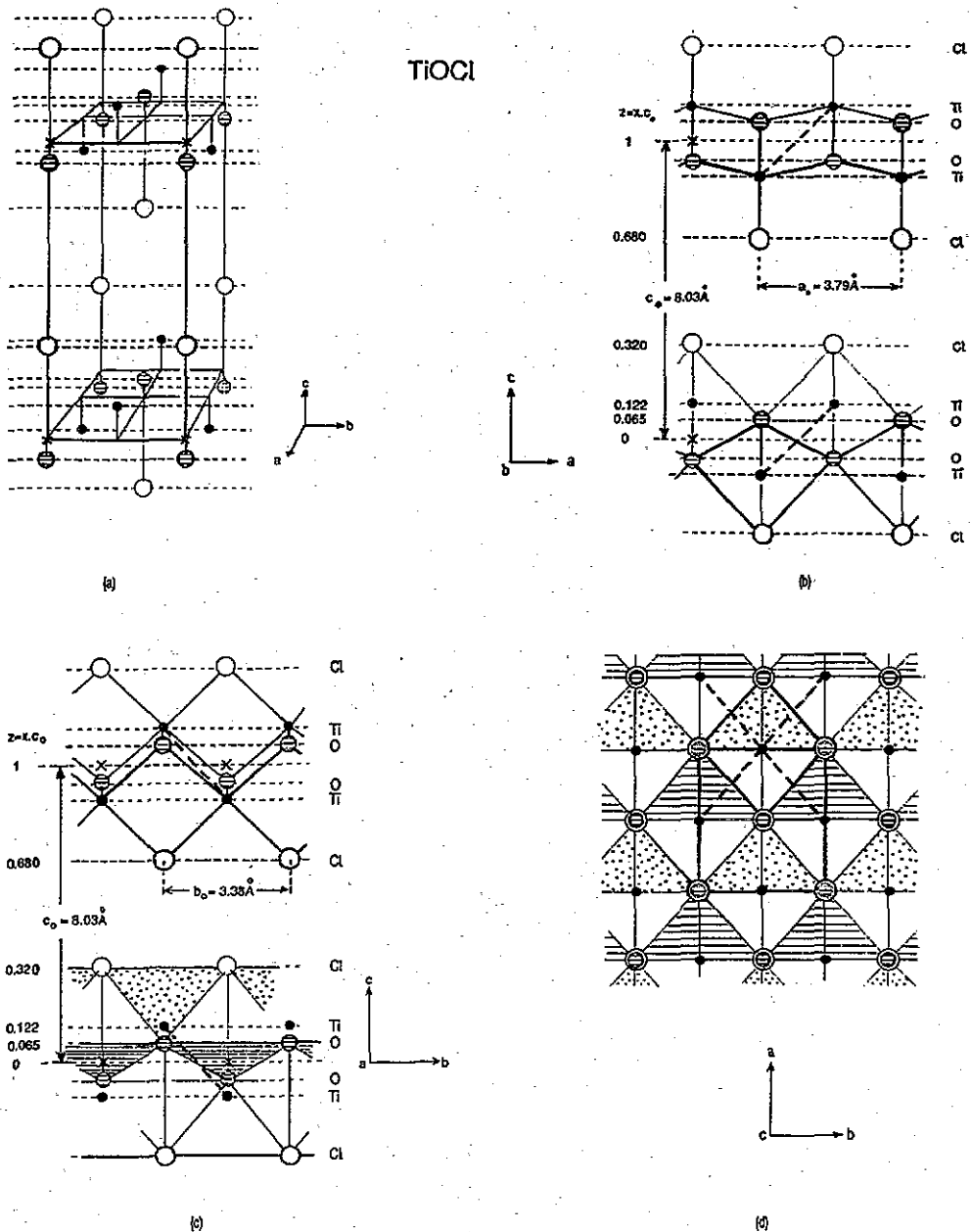
TiOCl

Figure 1. FeOCl-type, bisandwich layer structure of TiOCl. Orthorhombic, $Z = 2$, $D_{2h}^{13}-Pmmm$: full circles, Ti; hatched circles, O; big circles, Cl; crosses, unit cell corner. In projections (b) and (c) the bisandwich at the top of the cell shows bonds, while coordination units are highlighted in the bisandwich at the bottom. (d) The basal projection for a single bisandwich. Four potential M–M bonds are indicated by heavy broken lines.

interaction has traditionally been understood to be the source of the observed, weakly magnetic, non-metallic LT state. Dimerization proceeds via structural change which may be either discontinuous or continuous in form. Rutile-structured VO_2 (T_d 68 °C)

provides an example of the former [6], corundum-structured Ti_2O_3 of the latter [7]. Such (non-magnetic) metal–metal bonding becomes more prevalent and pronounced with the larger 4d and 5d cations. Thus $4d^1 NbO_2$ remains paired and insulating to over 1000 K. Pairing is also found among halides, as for example in $4d^1 NbI_4$ [8]. The latter compound could well become metallic too upon depairing, in probable contrast to $4d^5$ β-$RuBr_3$ [9] or $4d^3$ α-$MoCl_3$ [10]. It ought to be noted that among *lower*-valent binary halide systems (where the cations automatically are larger) there do in fact exist a few fully delocalized, non-magnetic, *metallic* materials from groups III and IV, such as $ZrCl$ [11] or LaI_2 [12], which manage to remain free of all symmetry breaking to very low temperature.

The sharp onset of metal–metal bonding in VO_2 at 68 °C is associated with a reduction in symmetry from tetragonal to monoclinic and a doubling in the atomic complement of the unit cell (from $Z = 2$ to 4) [6]. For Ti_2O_3 neither of these points is so, and, as stated above, c-axis Ti–Ti dimerization proceeds there steadily upon cooling [7]. A non-metallic ground state is gained when the anti-bonding states generated no longer overlap their bonding (and non-bonding) counterparts within the 't_{2g}' manifold. Thus, while for zig-zag chain-structured $5d^2 WTe_2$ slight overlap and a semi-metallic state are obtained [13], for similarly structured $4d^2 ZrI_2$ a semiconducting state [14] is gained, in consequence of the now narrower, much less hybridized bands of the halide. ZrI_2 shows an alternative insulating Zr_6Cl_{12}-type cluster form [15] and few cluster structures exist also among early 3d halides, e.g. Ti_7Cl_{16} with its trimers based on $Ti^{2+}(d^2)$ [16]. Trimers appear again in cation-layered, rocksalt-based $d^2 LiVO_2$ below 450 °C [17] in preference to chain formation. In a ternary system it often proves possible for the lattice to be braced against such deformation by inclusion of a larger 'counter-cation'; $d^1 LaTiO_3$ [18] and $LaTiS_3$ [19] are examples. These two will offer interesting comparison with TiOCl. Likewise $d^1 BaVS_3$ [20] will afford useful comparison with β-TiI_3 [21], since in neither chain structure is there simple dimerization, yet neither is metallic (see section 5).

With titanium and vanadium halides and oxides delocalization is primarily governed by the degree of direct metal–metal overlap, rather than by d–p cation–anion hybridization [1]. This is the converse of what is true with d^8 nickel chalcogenides or the d^8 and d^9 copper oxides, as the d shell approaches closure [22]. In consequence within the titanium halide families all the various transition temperatures *fall* through the sequence (F)–Cl–Br–I of increasing anion size, while the opposite occurs in the corresponding Ni or Cu materials (whether here, or similarly through the sequence O–S–Se–Te) as admixture of anion p states into the states near E_F rises rapidly.

Within the above context what sort of materials are the TiOX family?

It should first be noted that we are dealing with TiOCl and TiOBr alone: only a single early report of TiOI exists [23]. We have tried several times by several routes to produce the oxyiodide, but without success. Since the p $\rightarrow$ d charge transfer gap will still be large in the oxyiodide, it should in fact lie no closer than does TiOBr to metallization. Both TiOCl and TiOBr are Mott insulators—and so it would seem they remain up to 60 kB [24]. The Mott condition is in line with a critical spacing for delocalization in Ti^{3+} oxides as determined by Goodenough [25] of 3.05 Å. It may be seen from table 1 that the smallest Ti–Ti separation in TiOCl is 3.10 Å. In accord with the Mott status the d^1 TiOX show no Drude edge in the IR. Likewise they display a single sharp ligand-field-like transition near $1\frac{1}{2}$ eV, appropriate to a Ti^{3+} ionic system [1]. The intensity of the latter spectral feature however is high, indicating

delocalization is not too far distant. Indeed to immediately higher energies there is evident an 'unexpected', quite strong, and steadily rising (d → d) absorption edge. This edge is responsible for the brown colouring even of very thin flakes. $LaTiO_3$ falls apparently into the same borderline category, the very much lower resistivity of the perovskite material being probably attributable to a defective oxygen stoichiometry [18].

Table 2. Ti–Ti NN distance in the titanium compounds related to the titanium oxyhalides.

Compound	Ti–Ti NN (Å) ($\times N$)
Ti_2O_3	2.579 ($\parallel c$) ($\times 1$)
	2.997 ($\perp c$) ($\times 3$)
α-$TiCl_3$	3.533 ($\perp c$) ($\times 3$)
α-$TiBr_3$	3.729 ($\perp c$) ($\times 3$)

All d^1 α-TiX_3 and d^2 TiX_2 binary halides are automatically embedded further into the Mott-insulating régime than TiOX [22]. Nonetheless, as observed by direct structural measurement and also by the indirect evidence of IR phonon spectra and magnetic susceptibility data, the materials of both these binary halide families are found to pass via first-order transitions into low-temperature, metal–metal bonded, distorted conditions, whereupon the susceptibilities fall strongly [1]. While there is increase in the number of molecules per unit cell, decrease actually occurs here in the molar volumes (by $1\frac{1}{2}$% for the case of α-TiX_3 and 6% for TiX_2). The TiOX family, somewhat surprisingly (considering the far closer Ti–Ti approach), somehow manages to escape such behaviour. This is evident in for example the IR phonon spectrum, which remains simple [24] and much as for VOX (though appreciably down-shifted in energy). The susceptibility at low temperature for the TiOX [1] likewise is little changed from its value at room temperature; viz. a paramagnetism $\sim 500 \times 10^{-6}$ cgs per mole†. This, it should be noted, is considerably greater than that observed under the M–M bonded conditions prevailing in Ti_2O_3 [7] or the TiX_3 and TiX_2 halides at low temperatures [1]. There, following correction for core diamagnetism, the values are $\approx 200 \times 10^{-6}$ cgs mol^{-1}. Such values customarily have been ascribed to van Vleck inter-d-state excitation in a d-band manifold now containing a small gap.

The above susceptibility for the TiOX of 500×10^{-6} cgs per mole is even less likely to emerge from some more standard filled-band situation. Although the basic unit cell of TiOX does actually contain two molecules, for the stated space group symmetry it is not in fact possible for a single band to drop off from the bottom of the t_{2g} complex throughout the entire Brillouin zone. The ligand–field spectrum and Mott-insulating electrical character of the TiOX must encourage one instead to consider the substantial paramagnetism from a more localized perspective. Clearly the susceptibility is much larger than the temperature-independent paramagnetism (TIP) encountered in some filled 3d sub-band systems like $t_{2g}^6 FeS_2$ or $t_{2g}^4 FeAs_2$.

One has then to examine more closely the TIP of d^1 TiOX, paying due regard to the observed magnetic behaviour of the d^2 VOX and d^3 CrOX families. Three topics are of significance for TiOX at this point, namely (i) the $S = \frac{1}{2}$ quantum fluctuation problem, (ii) low structural and magnetic dimensionality, and (iii) geometrical frustration of simple antiferromagnetic order. These three features make the TiOX

† N.B. $\chi_{SI}^M = \chi_{cgs}^M \times 4\pi \times 10^{-6}$ (units; m^3 mol^{-1} and cm^3 mol^{-1} respectively).

materials (which, as we have seen, manage to escape simple *distortive* M–M bonding) prime cases for study of these questions, and accordingly for the quest for the proposed RVB state. The scandium doping experiments which we report in the next section were undertaken to see if the RVB state might be induced and identified, and whether, in consequence, any high-temperature superconductivity might then be found.

2. Experimental details and results

The (Ti/Sc)OX single crystal samples used in our experiments were grown by a three-zone vapour transport technique at growth temperatures of $\approx$ 600–700 °C [26]. The starting material is produced by pre-reaction at $\approx$ 300–400 °C of stoichiometric amounts of Ti (metal), TiO_2 (powder) and the required halogen X_2 (X:Cl, Br) in an evacuated silica tube. All constituents used were of high purity and had been dried by exposure to P_2O_5 prior to sealing. The Sc substitution levels in the products were found to be within 1–2% of nominal composition by measurement of the EDX spectra for a selection of crystals using a scanning electron microscope.

The crystals produced have the same morphology as the pure titanium oxyhalides, although they are of slightly smaller size ($\approx$ 2×3 mm versus 3×5 mm) and a somewhat paler orange-brown colour. Despite the substituted crystals seemingly being less air sensitive than the pure oxyhalides (a white patina forms only after an exposure of 2–3 weeks) the samples were stored and mounted within an argon 'dry box'.

The magnetic susceptibility measurements were carried out using a semi-automated Faraday balance controlled by a (BBC B+) microcomputer [27]. The system allows measurements to be made quasi-continuously over the temperature range 10–320 K and for magnetic fields up to $\approx$ 0.8 T.

The introduction of Sc into TiOCl at levels of 5 and 10%, and into TiOBr at 10%, was in each case found to cause the emergence of large tails in χ at low T (figures 2 and 3: N.B. core diamagnetic contributions have been subtracted using values from Selwood, etc. [28]). An attempt to fit the tails to a Curie–Weiss expression

$$\chi_{cgs}^{mol} = C/(T + \theta_p) + \chi_0 \qquad (1)$$

produced good fits at low temperatures, where the data for the pure TiOX would suggest the intrinsic susceptibility has become virtually temperature independent (namely –OCl, $T < 60$ K; –OBr, $T < 35$ K). The fitting parameters are given in table 3. Extending these fits to data beyond the above low-temperature ranges produces increasingly unsatisfactory overall fits (as determined by chi tests), indicating the presence there of additional temperature-dependent contribution besides the Sc-induced Curie tail. Since a 'free' Ti^{3+} ion in the titanium oxyhalides is in an approximately octahedral coordination, its μ_{eff} may be taken to be close to the spin-only value of 1.73 μ_B (of simple circumstances and low spin-orbit coupling). When a typical experimental value of $\mu_{eff} \approx 1.8$ μ_B [29] is employed, the sizes of the fitted C parameter become consistent with effective concentrations of 'free' Ti^{3+} ions (per mole of (Ti/Sc)OX) liberated on a 'one-for-one' basis with the nominal Sc dopant level (see table 3).

After subtraction of these fitted tails the $\chi(T)$ plots of the doped materials recover the general shape of the plot for the corresponding pure TiOX (figures 2 and 3); namely a gradual fall below a very weak maximum. However for both doped-OCl
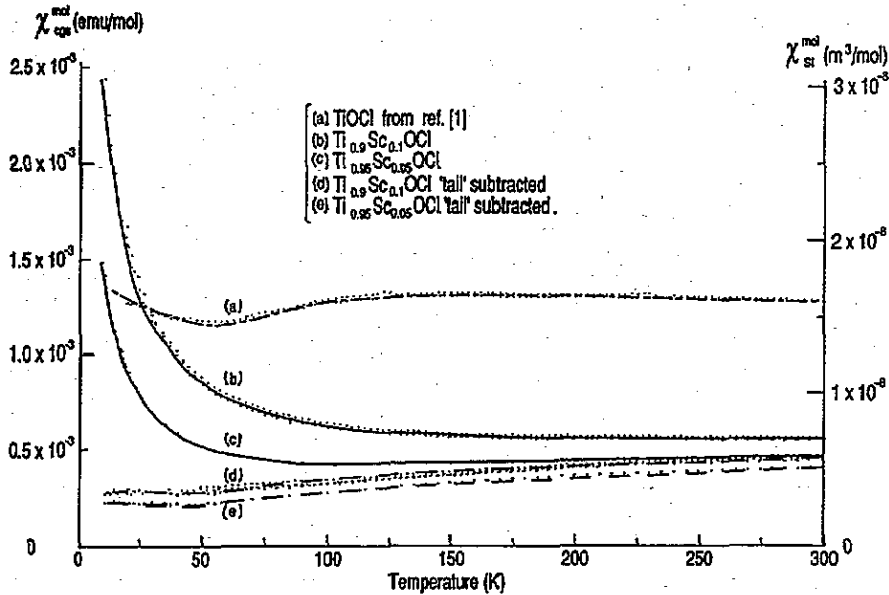
Figure 2. Molar magnetic susceptibilities for (Ti/Sc)OCl. (Details as key, and table 3.) Note $\chi_{SI}^{M} = \chi_{cgs}^{M} \times 4\pi \times 10^{-6}$ (units: $m^3\ mol^{-1}$ and $cm^3\ mol^{-1}$ respectively).
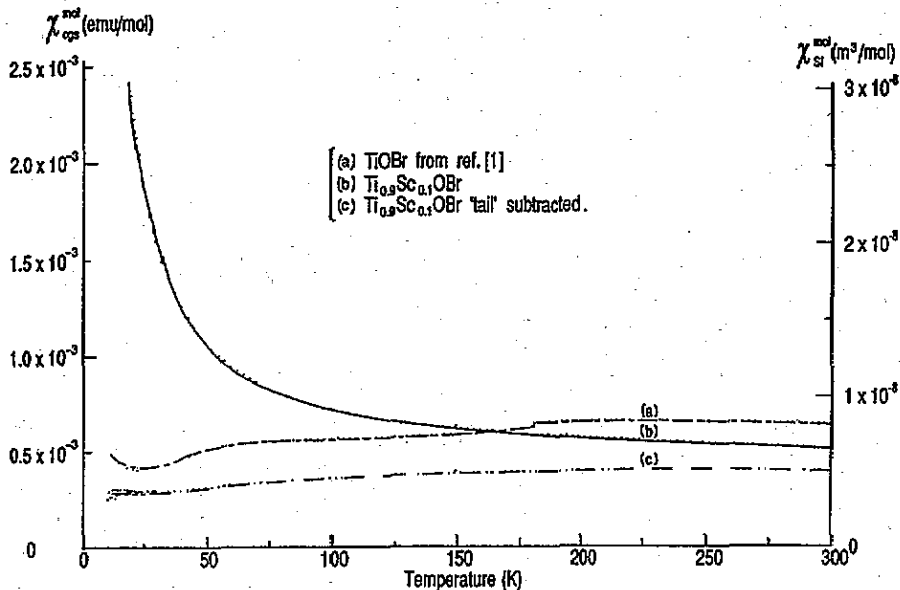

Figure 3. Molar magnetic susceptibilities for (Ti/Sc)OBr. (Details as key, and table 3.)

concentrations the positions of the maxima in χ appear now shifted above 300 K. The absolute magnitude of χ is initially lowered considerably, but χ_{sub} might subsequently rise a little with increased Sc level. In the –OBr system subtraction of the LT tail again reveals a gradual fall in the underlying susceptibility from room temperature, with χ near its maximum at 300 K. The LT fall is less marked than in the oxychloride system,

Table 3. Fit coefficients from equation (1) for (Ti/Sc)OX data.

Sample	$C(\times 10^{-2}$ emu mol^{-1} K$^{-1})$	$\chi_0(\times 10^{-4}$ emu mol$^{-1})$	θ (K)	% Ti^{3+} ions ($\mu_{\text{eff}} = 1.8$)
Ti$_{0.95}$Sc$_{0.05}$OCl	1.56 ± 0.15	2.25 ± 0.3	3 ± 1	4 ± 0.5
Ti$_{0.9}$Sc$_{0.1}$OCl	3.05 ± 0.1	2.85 ± 0.2	4 ± 1	8.5 ± 0.5
Ti$_{0.9}$Sc$_{0.1}$OBr	3.6 ± 0.05	2.9 ± 0.25	-2 ± 1	9 ± 0.2

Note: $\chi_{\text{SI}}^{\text{M}} = \chi_{\text{cgs}}^{\text{M}} \times 4\pi \times 10^{-6}$ (units: m^3 mol^{-1} and cm^3 mol^{-1} respectively).

as too is the lowering of χ_{sub} below the pure TiOBr value. The small sharp transition at 180 K present only in the TiOBr data is now seen as having come from trace surface contamination by α-TiBr$_3$, which has a strong first-order pairing transition at this temperature [1]. In all cases χ remains isotropic.

3. The magnetic behaviour of $S = \frac{1}{2}$: d^1, (LS) d^5, (LS) d^7, and d^9 systems

Because of the especial significance of quantum fluctuations for $S = \frac{1}{2}$ magnetic systems [30], Anderson queried in 1973 [2] whether standard antiferromagnetic ordering could ever provide the ground state there. Anderson explored the possibility that though a material might avoid static, distortive, local-pair bonding, would not a resonant valence bond condition always be on hand of lower energy than the alternative $S = \frac{1}{2}$ Néel state? More recent theoretical examination has shown that the generality of the original argument was flawed [2]. Antiferromagnetic order does in fact sometimes arise in $S = \frac{1}{2}$ systems. Examples of recent interest for example have been provided by certain insulating cuprates with fairly isolated Cu^{2+} ion centres, such as Y$_2$Cu$_2$O$_5$ ($T_{\text{N}} = 11.3$ K) [31] and 'green phase' Y$_2$BaCuO$_5$ ($T_{\text{N}} = 31$ K) [32]. Indeed, early examples were known, such as TiF$_3$ ($T_{\text{N}} = 52$ K) [33,50] and VF$_4$ ($T_{\text{N}} = 28$ K) [34].

Prior to ordering some cases of fairly standard spin-only ($g = 2$) Curie–Weiss behaviour have been reported for which $\mu_{\text{eff}} \simeq 2\sqrt{S(S+1)}\mu_{\text{B}} = \sqrt{3}\mu_{\text{B}}$, examples being TiF$_3$, perovskites BaVO$_3$ and CdVO$_3$ [35], 'green phase' Y$_2$BaCuO$_5$ [32], and Bi$_2$CuO$_4$ [36]. In the latter material the unusual chain structure of staggered individual square-planar units produces a Néel temperature of only 42 K: (NB the direct Cu–Cu distance in the chain at 2.9 Å is too great for dimerization). Just above T_{N} the Curie susceptibility in Bi$_2$CuO$_4$ is correspondingly large, and is $1\,100 \times 10^{-6}$ cgs units mol^{-1} even at 300 K; from the $1/\chi$ versus T plot a μ_{eff} value of 1.5 μ_{B} is extracted. Curie–Weiss and Néel behaviour like this contrasts with the magnetic behaviour of the still simpler, flat chain compound CaCuO$_2$ [37], which looks to be an extreme Bonner–Fisher-type system, with low, temperature-independent susceptibility and no sign of any long-range magnetic order. Chain-structured d^1(β) TiI$_3$ possibly has this character too, but there are problems (see section 5).

With *layered* compounds magnetic SRO, as reflected in the Bonner–Fisher behaviour, is less extreme, not *normally* being extended through to such low temperature without the appearance of LRO. For cuprates, as discussed below, the exchange interactions can be particularly strong. In the now well known 2D chequer-board layer structures of La$_2$CuO$_4$ and YBa$_2$Cu$_3$O$_6$, with their highly effective 180° superexchange paths, a very high degree of 2D short-range magnetic coupling is evident above the Néel points for full 3D order [38]. Furthermore the Néel points themselves are remarkably high, being 325 K for stoichiometric La$_2$CuO$_4$ [39],

415 K for $YBa_2Cu_3O_6$ [40] and 540 K for $(Ca_{0.85}Sr_{0.15})CuO_2$ [41]. Some cuprates correspondingly remain EPR silent above T_N [42].

When such d^9 cuprates order magnetically the actual site moments measured by neutron scattering reveal a clear depression as expected because of the pronounced quantum fluctuations incurred in the spin $S = \frac{1}{2}$ situation. Instead of 1 μ_B, values for site moment of 0.60, 0.65 and 0.67 μ_B have been determined for La_2CuO_4 [43], $YBa_2Cu_3O_6$ [44] and CuO [45] respectively. (N.B. for CuO the strongest exchange coupling is actually between 'chains', making this system magnetically of higher dimensionality than $CaCuO_2$– and T_N (commensurate) = 212 K below an initial incommensurate ordering at 231 K [46, 26].)

These reduced ordered moments together with the often rather low susceptibilities above T_N (resulting from the SRO existing there in these magnetically as structurally low-dimensional systems) must not be allowed to conceal the fact that for the cuprates extremely large superexchange couplings are in play. Thus for La_2CuO_4 [47], although χ at 350 K is only 60×10^{-6} cgs units mol^{-1}†, the superexchange constant parallel to the plane, J, is ≈ 1500 K or 125 meV [48] (yielding a magnetic exchange anisotropy here well in excess of 10^3). These high superexchange couplings come in consequence of the earlier noted degeneracy of the Cu e_g states with the O p states, so that heavy mixing characterizes the relevant $pd(e_g)\sigma^*$ hybrid states.

Another consequence of that degeneracy is to confer upon copper materials their many unique crystal structures. CuO for example is much more complex in structure than the preceding TM rocksalt monoxides, it being formed of mutually inclined and canted interleaving chains [49]. Often the structural situation is made worse for d^9 Cu^{2+} by the effect of strong Jahn–Teller distortion (from the e_g^3 configuration) with highly deformed structures being brought to Cu^{2+} halides as to more delocalized materials (e.g. CuF_2 [50], $CuCl_2$ [50], and the novel 1D structures of α- and β-$KCuF_3$ [51]—the latter two show 1D Heisenberg order at 22 and 39 K respectively.)

The reason why full Néel order is gained at a lower temperature in La_2CuO_4 than in $YBa_2Cu_3O_6$ is that 3D magnetic ordering in the essentially body-centred tetragonal (BCT) structure of La_2CuO_4 encounters total geometric frustration, given the staggered stacking of its successive chequer-board Cu-O planes. Antiferromagnetic ordering then is totally dependent upon spin anisotropy effects [39]. The situation becomes partially relieved by the orthorhombic distortion under octahedral tilting which onsets in stoichiometric La_2CuO_4 in second-order fashion at 530 K [52]. One should note that in the corresponding fluoride K_2CuF_4, which retains the BCT structure, 3D magnetic order is only finally attained at 6.25 K [53].

While this same confluence of spin $S = \frac{1}{2}$, low dimensionality and geometrical frustration of magnetic order may be encountered just as readily at d^1 as at d^9 above (or again in a low-spin (LS), octahedral d^7 system such as $Ni^{3+}(t_{2g}^6e_g^1)$ in $LiNiO_2$ [54]), it must be noted that the details of the resulting behaviour are *not* equivalent. With materials such as $LiNiO_2$ and La_2CuO_4 the magnetically active states are of e_g symmetry, and the hybrid wavefunctions involved are strongly antibonding under the heavy p/d mixing of these *high*-d^n-count cations. Hence for those t_{2g}^1 systems which escape M–M bonding, it ought not to be expected that their magnetic characteristics will be always analogous to those displayed by d^9 or even low-spin d^7 systems.

Binary t_{2g}^1 Ti_2O_3 and VO_2 as we have seen dimerize out from metallic high-temperature conditions to a low-χ state [6, 7]. By contrast metallic Pauli

† Making the diamagnetic correction this value becomes 160×10^{-6} cgs mol^{-1}.

paramagnetism is retained to the lowest temperatures for (well formed), ternary, cubic, perovskite-structured $SrVO_3$ [35,55]. The PPM susceptibility of $SrVO_3$ (corrected for diamagnetism) is 250×10^{-6} cgs mol^{-1}, or about only half the susceptibility of TiOCl. With $CaVO_3$ [35] χ is again temperature independent but here has jumped (when stochiometric) to 1100×10^{-6} cgs mol^{-1}. The latter material now is not highly metallic if well formed. The difference compared with $SrVO_3$ appears in the main due to its orthorhombic distortion, which from the lattice parameters is likely to be of the $Z = 4$ $GdFeO_3$ type. It is possible then that, because of the enlarged $Z = 4$ cell, the various t_{2g} subbands could provide van Vleck susceptibilities of the observed magnitude. $LaTiO_3$ [18] seems very similar to $SrVO_3$ prior to a ferromagnetic ordering that sets in at 125 K. The flat susceptibility of the rhombically layered rocksalt $NaTiO_2$ [56] suggests it too could be viewed likewise; certainly this particular material of edge-sharing octahedra is expected to be in the delocalized régime. Accordingly $NaTiO_2$ ought not to be grouped (as it has been) with isostructural but Mott-insulating LS d^7 $LiNiO_2$ as an example of strong antiferromagnetic frustration on a hexagonal net [54]. High-temperature Ti_2O_3 is the proper point of reference.

One does with K_2NiF_4-structured Sr_2VO_4 [57] reach the d^1 Mott-insulating condition. Strong Curie–Weiss behaviour is evident, with χ_M climbing to $23\,000 \times 10^{-6}$ cgs mol^{-1} at 10 K, just prior to what seems to be the onset of antiferromagnetism—though it proved not possible to confirm this using polarized neutrons. Recently it has been found that an alternative, molecularized, K_2SO_4-related form of Sr_2VO_4 also exists [58]. For this, by contrast, $s = \frac{1}{2}$ dimer modelling proves appropriate. The susceptibility now rises to a broad maximum around 60 K at the much lower value of 3000×10^{-6} cgs mol^{-1}. Such behaviour is reminiscent of that in d^1 vanadyl pyrophosphate, $(VO)_2P_2O_7$ [59], where there occur pre-existing structural pairs [60].

The recently examined Sr_2RhO_4 [61] offers added contrast to the behaviour of the TiOX materials. This low-spin $S = \frac{1}{2}$ $t_{2g}^5Rh^{4+}$ material displays the La_2CuO_4 type orthorhombic distortion of the K_2NiF_4 layer-perovskite structure. Similar to orthorhombically distorted $CaVO_3$ [35] and $LaTiO_3$ [18] (ABO_3 perovskites) the distortion appears to be responsible, somewhat unexpectedly, for rendering the 4d material non-metallic (bearing in mind the rutile-structured binaries $t_{2g}^5RhO_2$ and IrO_2 are delocalized, as is $t_{2g}^4RuO_2$) [22]. The susceptibility of Sr_2RhO_4 at 1000×10^6 cgs mol^{-1} is appreciably higher than for $NaTiO_2$ or $LaTiO_3$ and indeed the TiOX (by factors of three and two respectively). Accordingly the general shape of the $\chi(T)$ plot for Sr_2RhO_4 with its very broad maximum at 250 K is perhaps to be viewed rather as a striking example of magnetic frustration of 3D antiferromagnetic LRO in this magnetically 2D system. Note the susceptibility of Sr_2RhO_4 in fact is much higher than that for isostructural and also Mott-insulating $3d^9$ La_2CuO_4 (where χ is only 160×10^{-6} cgs mol^{-1} even after making the diamagnetic correction) [47]. This illustrates the very strong, short-range, e_g-based coupling prevailing above T_N in La_2CuO_4, much stronger than in the 4d material with its t_{2g}-based superexchange pathways. Appropriately when cuprates lose this order (whether short-range or long-range) as say within the $(La_{2-x}Sr_x)CuO_4$ [47] or $YBCO_{6+\delta}$ [62] systems, the susceptibility *rises* appreciably, despite entry into the 'metallic' (mixed-valent) régime.

Above its distortion temperature of 180 K α-$TiBr_3$ provides still further illuminating contrast with TiOX. The honeycomb cation sublattice of the α-MX_3

structure does not (unlike the full MX_2 hexagonal net) cause primary geometrical frustration of antiferromagnetic order. Indeed the d^2 VX_3 [1, 27] show standard Curie–Weiss behaviour passing into antiferromagnetism for VCl_3 and VBr_3, and ferromagnetism for VI_3, at 30 K, 35 K, and 55 K respectively. In the α-TiX_3 the abnormal, somewhat low (1000×10^{-6} cgs mol^{-1}) and rather temperature-independent behaviour of the susceptibility in the α-TiX_3 in the vicinity of 300 K is therefore an expression of the $S = \frac{1}{2}$ situation, plus the general tendency toward SRO well in advance of LRO as one approaches the metal–insulator transition. Whether that SRO is with respect to antiferromagnetic order or to dimerization is the question here. Ultimately for the α-TiX_3 crystallographic dimerization wins, although because of the large Ti–Ti distance (> 3.5 Å) the origins of the 'dimerization' have also been discussed from points of view other than homopolar M–M bonding [63]. Recall indeed even in the β chain form of the TiX_3 family [21], for which the M–M distance is much reduced, distortive M–M bonding is not proven, though the paramagnetic susceptibility is there very low (TiI_3: 150×10^{-6} cgs mol^{-1}—or only half that in the *low*-temperature condition of the α-family). For the β-materials, neutron diffraction shows no antiferromagnetism and IR phonon work no extra lines, a situation we shall return to in section 5.

From the above we see the TiOX being squeezed among d^1 compounds between somewhat more delocalized systems such as $LaTiO_3$ [18], $NaTiO_2$ [56] and $CaVO_3$ [35] on the one hand, and somewhat more Mott-insulating materials like the α-TiX_3 [1] on the other, while distortive M–M bonding is attendant both from within the delocalized and the localized régimes, as in Ti_2O_3 [7] and α-TiX_3 [1] respectively.

4. TiOX: the view from within the MOX family

IR phonon work on the TiOX shows them to hold to the same $Z = 2$ structure as the d^2 VOX, although the lines in the TiOX IR spectra do appear substantially down shifted in energy [1]. Neutron diffraction from VOCl [64] reveals low-temperature antiferromagnetic order (T_N, 80 K). The rather flat, though high, isotropic paramagnetic susceptibility of VOCl (2000×10^{-6} cgs mol^{-1} at 300 K) can be fitted quite closely above T_N by the Lines quadratic 2D Heisenberg expression for 'NN' antiferromagnetic coupling. T_N however is clearly significantly depressed by the high degree of frustration presented to antiferromagnetic order by the FeOCl structure. Indeed FeOCl itself [65], despite having $S = \frac{5}{2}$, has a RT susceptibility of less than 3000×10^{-6} cgs mol^{-1}, this already dropping away towards the value of 2500×10^{-6} reached at its Néel point of 90 K. Such behaviour contrasts markedly with the situation in the t_{2g}^3 CrOX family [66], where the exchange couplings are shifting towards ferromagnetism (as in CrX_3) and Curie–Weiss plots are obtained which display standard gradients. Susceptibilities in excess of $20\,000 \times 10^{-6}$ cgs mol^{-1} are then reached by 100 K prior to LRO.

Turning to the situation in t_{2g}^2 VOCl *below* T_N, neutron measurements [64] reveal a site moment likewise significantly depressed of only 1.5 μ_B (at 4 K). Clearly the situation is set to become much more marked in TiOX when compounded by the advance to delocalization and the $S = \frac{1}{2}$ problem. The delocalization will effect a more rapid growth in J, the 'direct' M–M coupling between the two levels of the bisandwich structure, relative to J_a and J_b, the superexchange couplings in the axial directions. Of the latter J_a (through the quasi-linear O bridge (see figure 1)) probably

dominates J_b (through the '90°' O and Cl bridges). (J_a upon going slightly positive moved the CrOX into helical rather than collinear antiferromagnetic structures.)

In VOCl the ordered moments are determined to align parallel and antiparallel to a_0 [64]. However because of the total geometric frustration inherent between the upper and lower halves of the XMO′OM′X′ bisandwich towards *mutual* antiferromagnetic order, there emerge, as regards AFLRO, two completely decoupled *magnetic sublattices.* *The order developed in VOCl within either sublattice is of the very simplest form, involving cell doubling in all three axial directions.* However the coupling between the sublattices is selected in random fashion equally between two options. The latter misleadingly have been termed 'ferromagnetic' and 'antiferromagnetic' in [64], relating the choice to a single cation sub-cell and to the moment at its origin. Figure 4(*b*) and (*c*) shows that what is actually specified with this choice is a symmetry-breaking handedness, leading to twinning in the magnetic order. A final result on VOCl in [64] calling for comment here is that the fitting of the magnetic order parameter leads to a critical exponent which fairly closely mimics the 2D Ising model for $S = \frac{1}{2}$, when $S = 1$ behaviour might have been anticipated for d^2 VOCl. Recall too that the neutron observed ordered moment is refined as only 1.48 μ_B. An even more strongly reduced moment of 1.2 μ_B was earlier encountered in $d^2 V_2O_3$ in its insulating AF state [22]. Such behaviour was there attributed to geometrical inequivalence between the two electronic orbitals (half) occupied under the given, strongly uniaxial, ligand field.

5. Discussion of the (Ti/Sc)OX results and the possible RVB nature of TiOX. Comparison with β-TiX$_3$, Ba(V/Ti)S$_3$ and Mg$_{3/2}$Ti$_{3/2}$O$_4$

Three features are of importance in the data obtained on the (Ti/Sc)OX systems. Firstly the materials all remain insulating despite the now inhomogeneous d^1/d^0 electron count on the cation array. This is akin to the situation encountered for the d^9/d^{10} mix in (Nd/Cu)$_2$CuO$_4$ with $x < 0.15$ [67] (or in YBCO$_6$ [68]). Delocalization is somewhat more difficult to secure here than for a d^9/d^8 mix as in (La/Sr)$_2$CuO$_4$ [69] or the d^1/d^2 mix of (Sr/La)VO$_3$ [70]. The state energies at the d^0 and d^{10} counts are sufficiently different from d^1 and d^9 respectively that localized states are more strongly pulled out of the band for these terminal cases. In (Ti/Sc)OX delocalization is further impeded by the electron counts not being controlled by a counter-ion as in the above cases, instead being directly associated with the change of primary cation. Such disorder leads to difficulty even in somewhat more delocalized circumstances, such as (V/Ti)$_2$O$_3$ [71] or Ba(V/Ti)S$_3$ [72]. Similarly, as was noted above, M–M bonded, non-metallic Ti$_2$O$_3$ does not yield free carriers when substituted with Sc [73]. From the lattice details TiOCl itself clearly remains at some distance from the Mott transition, as was earlier demonstrated by taking the material to 60 kbar without metallization being observed [24]. Such being the case it is felt that delocalization will not be encountered in the d^1/d^2 mix of (Ti/V)OX either.

The second feature of note in the (Ti/Sc)OX data is the appearance of local moments as substitution of d^0Sc^{3+} disrupts the coherent homogeneity of the condition presented by the pure TiOX materials. The fact that the number of Ti^{3+} moments freed emerges as being equal, within experimental assessment, to the number of substitions made (rather than, say, to the number of nearest neighbours of each substituent site) could indicate that the disruption involved is to pairings of cations.
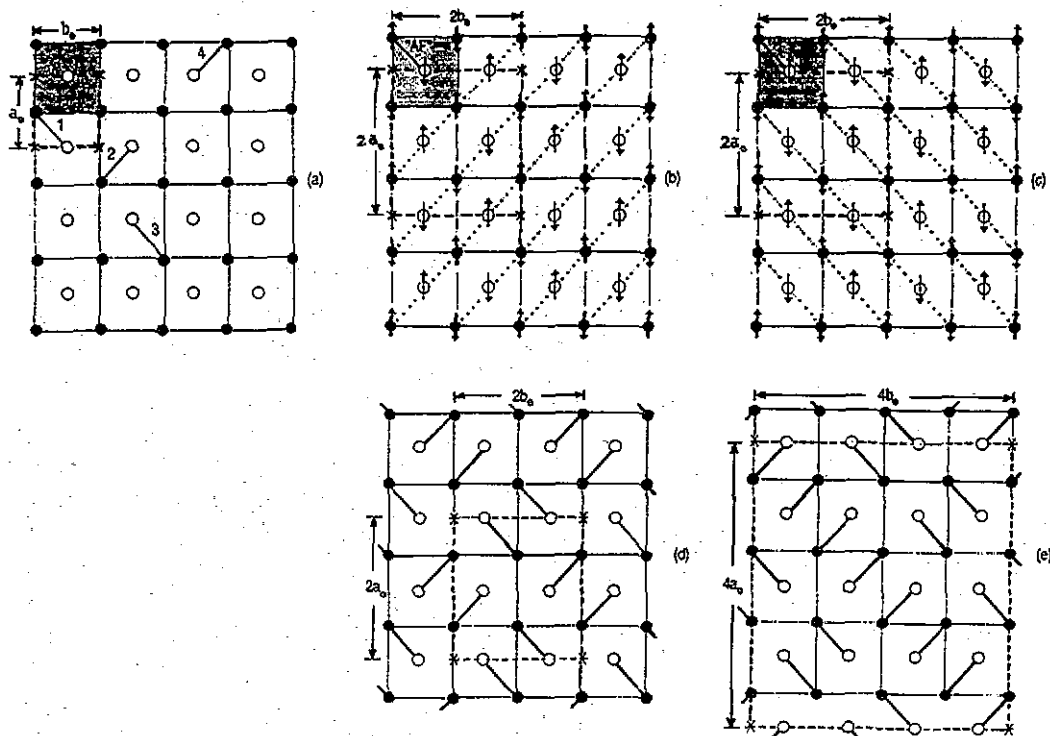
Figure 4. M atom arrays for single MOCl bisandwich: ●, level 1; ○, level 2. (a) four M–M inter-level bond orientations; (b), (c) two orientations for antiferromagnetic ordering in VOCl; (d) $2a_0 \times 2b_0$ symmetric M–M bond superlattice; (e) asymmetric $4a_0 \times 4b_0$ striped order.

Any such pairing must at the outset be dynamic, since as we have seen there is no clear indication of static pairing either crystallographically or in the IR phonon spectrum. It should be recalled, however, that there is a marked down-shift in the energies of the TiOX IR phonon lines and some broadening when compared with VOX [1, 24], as if in response to a dielectric constant/polarizability increase [74]. This then may reflect a dynamic instability towards pairing, which ought to show up in the Debye–Waller factors for the cations positions. There is no possibility of doing full single-crystal, soft-mode neutron work with specimens of the size currently available.

The third feature of significance is that the *underlying*, flat, isotropic susceptibility of the (Ti/Sc)OX system progressively *falls* with Sc substitution, and to such a degree that, even prior to the induced Curie tails being stripped away, the total susceptibility is decreased. This would suggest that the original coherent homogeneous state actually is being stabilized within the residue of 'unaffected' micro-regions. What appears a feasible scenario here is that the unsubstituted system represents a resonant (RVB) state which the scandium substitution rapidly converts into a glassy, frozen pattern of residual pair bonding. The sooner this configurational freezing occurs and the more reasonable it would be for the Ti^{3+} moments to appear on a one-for-one basis with the number of scandium atoms added, as seem to be the case.

The way in which the scandium substitution produces free moments from within the coherent state resembles in part the effect of Zn (d^{10})-substitution upon (d^9)

Mott-insulating La_2CuO_4 [75] as the LRO Néel state is destroyed. Note there, however, that above T_N the susceptibility remains virtually unchanged. Still more striking contrast emerges with the recent data from Zn-substituted $YBa_2Cu_4O_8$ [76] where the susceptibility is driven up to *higher* values at *all* temperatures. In '124' this very rapid seeding out of free moments on the Cu planes is coupled to an equally rapid suppression both of the normal-state metallicity and of the superconducting state itself [77]. Conversely in (Ti/Sc)OX the pairing postulated would appear to be enhanced over the situation prevailing in the pure TiOX.
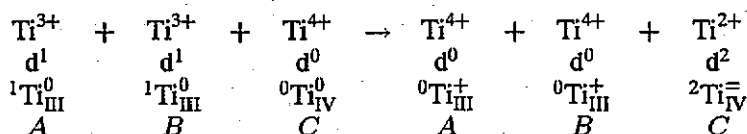
Comparable disordered M–M pairing could also be in evidence in two previously introduced $S = \frac{1}{2}$ chain systems; namely the β-MX$_3$ trihalides of group IV (archetype TiI$_3$) [13, 21, 22] and BaVS$_3$ [20, 72] (which is of the same one-third filled hexagonal close-packed (HCP) form, but with the interchain spaces now occupied by Ba^{2+} ions). It long has been known that even $5d^1$HfI$_3$ [78] is not metallic despite the close M–M distance along the c axis (which should surely secure delocalization given the metallic nature of LaI$_2$ [12]). However there is some indication of weak basal-plane cell doubling and orthorhombicity [21, 79], as could come in response to 'frustrated', pair-deformation phasing between neighbouring chains in hexagonal packing. With the Hf material it is known that some cation vacancies are present which would help to promote a disordered pair state. Certainly one finds a very low TIP $\simeq 150 \times 10^{-6}$ cgs mol^{-1}, in conjunction with no evidence of magnetic order [80].

By contrast AFLRO does appear in BaVS$_3$ [72] below 70 K (from a Curie–Weiss state above), associated with transfer to an insulating condition. At higher temperatures the material is semimetallic. Both circumstances are however rather fragile, because partial substitution of V by Ti quickly suppresses both the AF state and also the metallicity above T_N. What is still more significant is that (as with Sc doping of TiOX) this substitution also steadily suppresses the magnetic susceptibility, so that by 20% substitution of Ti only a TIP of 200×10^{-6} cgs mol^{-1} remains. The loss of moments is accompanied by loss of structural orthorhombicity, as would match disordered pairing. The resulting observed $\rho \propto \exp(T^{-1/2})$ behaviour, plus a Seebeck coefficient of 78 μV K^{-1}, serve further to reflect that disorder.

The above results from (Ti/Sc)OX and Ba(V/Ti)S$_3$ suggest that substitution of the parent phase in these t_{2g} systems leads to disordered M–M pairing in contrast to the e_g system La_2CuO_4, where, whether under Cu/Zn [75] or La/Sr [69] mixing, 'spin-glass' behaviour is found following suppression of AFLRO [81]. Both for BaVS$_3$ and La_2CuO_4 there is clear AF order to displace, but for TiOX the nature of the parent state clearly is ambiguous. There certainly is no magnetic LRO. The susceptibility indeed remains strictly isotropic at all temperatures [27]. The slight drop off in susceptibility to low temperatures mimics Bonner–Fisher behaviour, but the magnitude of χ is low for a 2D system. Clearly the approach to delocalization, the frustrated exchange coupling, and the t_{2g} orbital geometry in the given crystal structure all promote M–M bonding at the expense of an oriented spin, 'magnetic' ground state. The susceptibility of the TiOX materials is appreciably lower than that of the somewhat more 3D-like $S = \frac{1}{2}$ systems Sr_2RhO_4 [61] $CaVO_3$ [82] and $LiNiO_2$ [54] where a magnetic solution to the problems they raise may look more probable.

Like TiOX, most of the $S = \frac{1}{2}$ systems mentioned in this paper are relatively little explored. New $S = \frac{1}{2}$ systems are regularly being added to the list. It is evident that the $S = \frac{1}{2}$ situation can present problems for the development of AFLRO especially in low-dimensional and structurally frustrated geometry, but it is equally evident that

there are many routes of escape from the dilemma presented. RVB certainly does not present the principal one of these. Rather the question is, as with the Mott transition [22], can one system be identified with the possibility to fit the requirements? Of all systems examined it would appear that the TiOX offer that possibility. Further phonon work, NMR and neutron work should now be undertaken on vanadium- as well as scadium-substituted material. Present indications are that—RVB or not—this system does not support superconductivity, although as $(Nd/Ce)_2CuO_4$ [67] shows superconductivity is not always directly to hand. Where some indication of high-temperature superconductivity at d^0/d^1 has recently been reported is in the B-site mixed-valence spinel approximating to $Mg^{2+}(Mg^{2+}_{1/2}Ti^{4+}_{1/2}Ti^{3+})O_4$ [83]. In this system strong sharp resistance loss is repeatedly detected at temperatures in excess of 40 K over a *very* narrow range of stoichiometry for which the average Ti valency is $3\frac{1}{3}+$, corresponding to the above formula. This value is precisely the one required to favour the operation (rather than RVB) of the inter-site, electron-pair-producing, 'seeded' dynamic disproportionation

$$
\begin{array}{ccccccccccc}
Ti^{3+} & + & Ti^{3+} & + & Ti^{4+} & \rightarrow & Ti^{4+} & + & Ti^{4+} & + & Ti^{2+} \\
d^1 & & d^1 & & d^0 & & d^0 & & d^0 & & d^2 \\
{}^1Ti^0_{III} & & {}^1Ti^0_{III} & & {}^0Ti^0_{IV} & & {}^0Ti^+_{III} & & {}^0Ti^+_{III} & & {}^2Ti^=_{IV} \\
A & & B & & C & & A & & B & & C
\end{array}
$$

This situation would then parallel that described in [84] for the suggested pair-producing fluctuation procedure operative in the cuprate and bismuthate HTSC materials. What feature now however confers added stability and $-U$ characteristics upon the configuration $^2Ti^=_{IV}$ is not clear. Perhaps the uniaxial potential produced by the contiguous B-site Mg^{2+} ion promotes the double-loading fluctuation by stabilizing a local d_{z^2} orbital from the t_{2g} set. Remember in the above the key process is a *seeded*, dynamic disproportionation. Pure $d^1Ti_2O_3$ (like TiOX—and unlike TiI_3) is stable at least to 700 °C against ordinary, static disproportionation.

6. Summary

We have taken a new look at TiOCl and TiOBr in the light of the magnetic data reported here on scandium-substituted material. We were interested to discover the contrasts and parallels between $d^0/d^1/d^2$ systems and the HTSC $d^8/d^9/d^{10}$ cuprate systems. Since one interpretation of the HTSC phenomenon is based on resonant valent bond behaviour we wished to see whether such a material could be positively identified anywhere. The TiOX have the requisite $S = \frac{1}{2}$ configuration, and moreover possess 2D geometry and a cation array for which simple AF order is frustrated. Additionally making the TiOX favourable candidates for establishment of the RVB state is their t_{2g} symmetry and their proximity to the metal–insulator condition. Static dimerization is known to occur to either side of the Mott boundary in $t^1_{2g}Ti^{3+}$ materials, e.g. Ti_2O_3 and α-$TiCl_3$. Static dimerization is not shown by the TiOX, but the results of the action of scandium substitution suggest static random pairing may result. There is no evidence for increase in size of the unit cell of the TiOX, of the type represented in the symmetrized pairing arrays of figure 4(d), (e). The phonon spectrum does however indicate a much enhanced polarizability over d^2 VOX.

It is clear the $S = \frac{1}{2}$ condition can create serious problems for the establishment of a simple AF Néel ground state. However systems denied the Néel condition opt

for a very wide range of alternative behaviours. To cope with this, theory will have to incorporate far more detail regarding crystal structure, covalency, and the specific electronic configurations. Clearly whether d^1, d^9, or low spin d^5 and d^7, there are many unusual $S = \frac{1}{2}$ systems such as $BaVS_3$, $NaTiO_2$, $BaCuO_2$, Sr_2RhO_4 and $LaNiO_3$ demanding further investigation. Among these TiOX should now figure prominently. High-resolution IR work, electron microscopy, neutron and NMR work would be most valuable in resolving whether the TiOX are possibly unique in adopting an RVB ground state. Current indications are that 'as suspected' the state does not appear to support HTSC upon 'doping': however for those intent on researching superconductivity in addition to RVB there is the strange phenomenon of $Mg_{3/2}Ti_{3/2}O_4$.

Acknowledgments

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