Spin Pairing and Variable Magnetic Defect Densities in the Maleic Anhydride Catalyst $(VO)_2P_2O_7$

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Spin pairing of the V^{4+} ions in the double chains of the bulk structure and variable magnetic V^{4+} defect densities in $(VO)_2P_2O_7$ are reflected in characteristic contributions to the magnetic susceptibility.

It is generally recognized that the compound $(VO)_2P_2O_7$ is the most active phase in the V–P–O system for the selective catalytic oxidation of butane and butene to maleic anhydride.[1—4] The activity and selectivity, however, depend sensitively on the details of the catalyst preparation procedure.[2] Very recently, Cavani *et al.*[5] showed that crystallographic disorder of a specific kind substantially increases the activity for oxidation of n-butane to maleic anhydride over that observed when this type of disorder is not present. Thus, this reaction is structure sensitive, although the physical origin of this effect is not yet clear.

In the work of Cavani *et al.* just cited, structural defects were implicated in enhancing the activity. Because the vanadium in $(VO)_2P_2O_7$ is in the +4 oxidation state, the vanadyl ions are paramagnetic with spin $S = \frac{1}{2}$. This suggests that structural defects might give rise to magnetic defects with a magnetic susceptibility $\chi(T)$ different than for bulk $(VO)_2P_2O_7$. One would then have a method for characterizing the defects which is independent of *X*-ray observations such as those used by Cavani *et al.* Indeed, the density of magnetic defects as probed by both e.s.r. and $\chi(T)$ measurements has recently been successfully correlated with the activity of

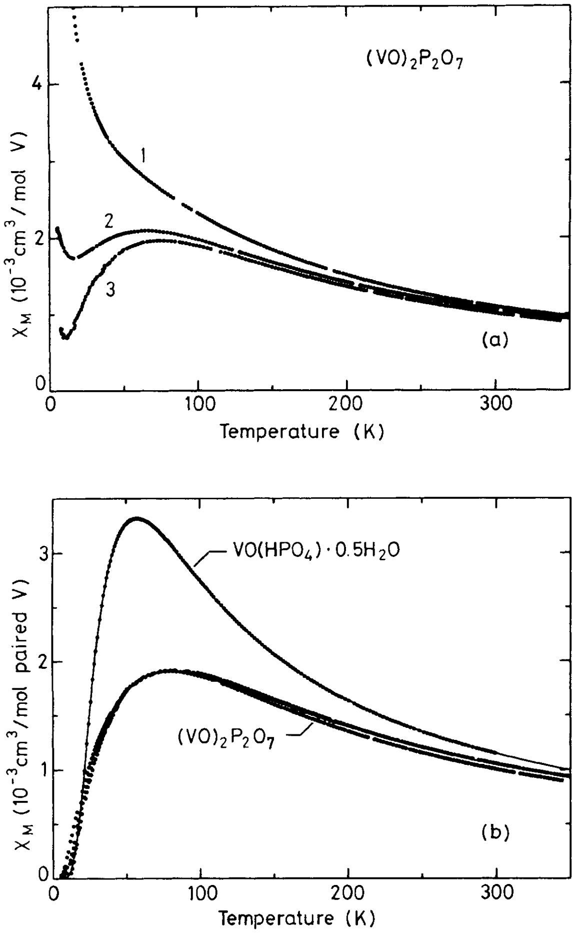

Figure 1. (a) Measured molar magnetic susceptibility χ_M (per mole of V) *vs.* temperature for three samples of $(VO)_2P_2O_7$ with different degrees of crystallinity; the crystallinity increases with sample number. (b) Magnetic susceptibility per mole of *paired* V for the three samples of (a), derived from the data in (a); data for $VO(HPO_4)\cdot 0.5H_2O$ from ref. 7 are included for comparison.

MoS_{2+x} hydrodesulphurization catalysts.[6] Herein, we report $\chi(T)$ data from 4 to 350 K for a set of $(VO)_2P_2O_7$ samples of varying crystallinity, and demonstrate the occurrence of a variable magnetic defect density in the samples which correlates with the degree of crystallinity.

The $(VO)_2P_2O_7$ samples were prepared by thermal decomposition of the crystalline precursor $VO(HPO_4)\cdot 0.5H_2O$ in flowing He as described previously.[7] Samples with different degrees of crystallinity were obtained by varying the severity of the heat treatment. Sample 1 was treated at 703 K for 19 h, sample 2 at 1063 K for 19 h, and sample 3 by annealing sample 2 in a sealed, evacuated quartz tube at 1048 K for 49 days.

$\chi(T)$ data were obtained using a George Associates Faraday magnetometer in a magnetic field H of up to 6.3 kG while sweeping the temperature T at less than 1 K/min. The contributions of ferromagnetic impurities (<20 p.p.m.) were measured independently from magnetization *vs.* H isotherms (0 to 8 kG) at selected temperatures, and are corrected for in the following. The $\chi(T)$ data for three samples are shown in Figure 1(a). For the least crystalline sample 1, χ decreases smoothly and monotonically with T, whereas the most crystalline sample 3 exhibits a rounded maximum near 75 K in addition to a small upturn below 14 K. Sample 2, with intermediate crystallographic order, shows intermediate magnetic properties.

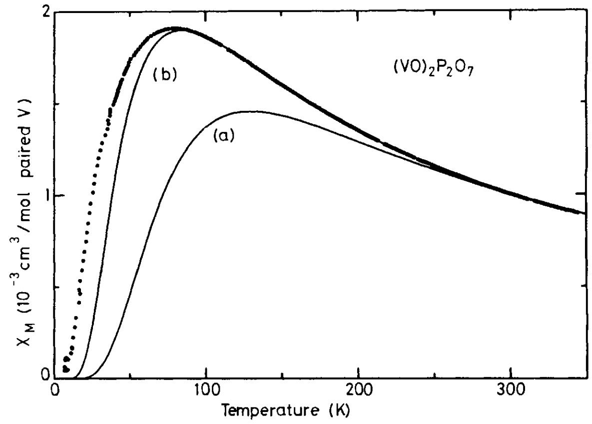

Figure 2. Comparison of the data in Figure 1(b) for sample 3 (· · · ·) with theoretical fits (—) assuming isolated V_2 spin coupled dimers (a) and V_2 dimers interacting in the Weiss molecular field approximation (b).

To understand the magnetic data in Figure 1(a), we first note that the structure[8] of the precursor $VO(HPO_4)\cdot 0.5H_2O$ contains isolated V^{4+}–V^{4+} dimers in which the V ions are antiferromagnetically coupled.[7] The magnetic properties of the precursor reflect this pairing, shown in Figure 1(b). The solid curve through the data points is a highly precise fit of the Bleaney–Bowers equation[9] to the data; see equation (1),

$$\chi^{BB} = \frac{C_d}{T}\,\frac{4}{3 + \exp(-2J/k_BT)} \qquad (1')$$

where C_d (= 0.374 cm^3 K/mol V) corresponds to the molar Curie constant for the paired V^{4+} and J/k_B (= −45.3 K) is the exchange constant in the interaction energy between the two spins in the dimer ($E = -2J\,\vec{S}_1\cdot\vec{S}_2$). When the precursor is heated to effect the topotactic[7,10] transformation to $(VO)_2P_2O_7$ accompanied by expulsion of H_2O, one expects many structural defects in the product initially. This is indeed found from our *X*-ray observations.[7] From Figure 1(a), these defects are probably (nearly) isolated V^{4+} or $(VO)^{2+}$ species which would give a Curie–Weiss contribution; equation (2) where θ is the Weiss temperature reflecting (weak) interactions with the other spins in the sample.

$$\chi^{CW} = C_i/(T - \theta) \qquad (2)$$

$$\chi(T) = \chi^{defect}(T) + \chi^{bulk}(T) \qquad (3)$$

As the severity of the annealing increases from sample 1 to 3, one would expect the defects to heal and the contribution to χ from the defects to decrease, as observed in Figure 1(a). More precisely, we assume that equation (3) holds for each sample, where $\chi^{defect}(T)$ is given by equation (2). From Figure 1(a) and keeping in mind $\chi(T)$ for $VO(HPO_4)\cdot 0.5H_2O$ in Figure 1(b), it appears that $\chi^{bulk}(T\rightarrow 0) = 0$ and $d\chi^{bulk}/dT(T\rightarrow 0) = 0$; these two assumptions are sufficient to determine uniquely the constants C_i and θ in equation (2) for each sample. We find that θ is small (−3 ± 2 K) for each sample. From the values of $C_i = Ng^2\mu_B{}^2S(S+1)/3k_B$, where $g = 2$ and $S = \frac{1}{2}$ are the Landé g factor and spin assumed for the defects, the defect spin densities N were computed to be 25, 7, and 2.3 mol% relative to vanadium for samples 1, 2, and 3, respectively. $\chi^{bulk}(T)$ is now simply obtained by subtracting $\chi^{defect}(T)$ from the observed $\chi(T)$ as per equation (3), and the results for the three samples are plotted in Figure 2(b). Remarkably,

χ^{bulk} is almost identical for each of the three samples even though, *e.g.*, there is no hint of a rounded maximum in the raw data for sample 1 in Figure 1(a). This agreement confirms that the isolated defects are indeed V^{4+} or $(VO)^{2+}$ cations and that equation (3) is valid for our analysis.

Qualitatively, the data for $(VO)_2P_2O_7$ and $VO(HPO_4)\cdot 0.5H_2O$ in Figure 1(b) are quite similar. In contrast to the data for the latter compound, however, the data for the former cannot be precisely fitted by equation (1), as shown by curve (a) in Figure 2 which was obtained by fitting equation (1) to the data near room temperature. A much better fit is obtained if a mean (or molecular) field interaction between the dimers is included; equation (4) where χ^{BB} is given in equation (1), C_d = 0.375 cm^3 K/mol V is the same Curie constant as in equation (1) and θ_1 reflects the magnetic interactions between the dimers. Using nonlinear regression, equation (4) was fitted to the data in Figure 1(b) for $(VO)_2P_2O_7$ sample 3 (shown separately in Figure 2) above 100 K, yielding $\theta_1 = -29.9$ K and $J/k_B = -67.5$ K. The fit is curve (b) in Figure 2, where the average deviation of the data from the fit is less than 0.2% from 100 to 350 K. At high temperatures $k_BT \gg |J|$, equation (1) is closely approximated by equation (2), with $\theta_2 = J/2k_B = -33.8$ K in this case. Thus, the strength of the interdimer interaction is comparable with that of the intradimer interaction in $(VO)_2P_2O_7$. This result is consistent with the known structure[11] which shows that $(VO)_2P_2O_7$ contains double chains of V^{4+} cations rather than isolated dimers as in $VO(HPO_4)\cdot 0.5H_2O$. The discrepancy between the data and curve (b) below 90 K in Figure 2 is not considered to be serious, since from preliminary calculations, it probably arises from quantum mechanical effects which were not taken into account in the mean field equation (4).

$$\chi^{MF} = (1/\chi^{BB} - \theta_1/C_d)^{-1} \quad (4)$$

In summary, our $\chi(T)$ data for $(VO)_2P_2O_7$ samples with different degrees of crystallinity are explained by the sum of two terms: the first is a Curie–Weiss term reflecting the presence of a variable density of (nearly) isolated V^{4+} or $(VO)^{2+}$ magnetic defects which may be associated with the crystallographic defects probed by *X*-ray diffraction, and the second is a bulk susceptibility term which reflects the interactions and spin pairing between the remaining V^{4+} cations residing in the double-chains of the bulk structure.

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