Inadequacy of a simple Curie–Weiss approximation for nuclear magnetic resonance in paramagnetic transition-metal oxides

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A convenient test applied to published NMR data shows qualitatively that a simple Curie–Weiss approximation is often not adequate for NMR in paramagnetic transition-metal oxides.

In a recent communication,[1] Sananes and Tuel tried to show that a simple Curie–Weiss approximation can be used to interpret the temperature dependence of the (isotropic) shifts of the ^{31}P NMR data in vanadium phosphorus oxide catalysts and to deduce the corresponding Weiss temperature. Though the Weiss temperature so deduced agreed with that measured directly *via* magnetic susceptibility in the case of sample H [$VO(HPO_4)\cdot 0.5H_2O$], the other [sample P: $(VO)_2P_2O_7$] showed, however, a noticeable discrepancy beyond the range of experimental error. In this communication, an attempt is made to rationalise why a good agreement was obtained for one sample but not for the other and to show that a simple Curie–Weiss approximation is usually *not* adequate to analyse NMR data in transition-metal oxides.

The NMR shifts of nuclei of diamagnetic ions or ligands in paramagnetic materials such as transition-metal oxides are determined mainly by the hyperfine (Fermi contact, electronic spin–nuclear spin dipolar, and electronic orbital–nuclear spin) interactions between the observed nuclei and the unpaired electrons. The usual chemical shifts arising from the orbital contributions of all paired (core) electrons are generally much smaller in these cases and can therefore be safely neglected here. The unpaired electrons that are responsible for the large NMR shifts observed can be further divided into three categories: electrons localized at the (paramagnetic) metal ions, those delocalized (through covalent bonding) to the bridging elements (if any), and finally those delocalized further (from the bridging elements) to the observed nuclei.[2]

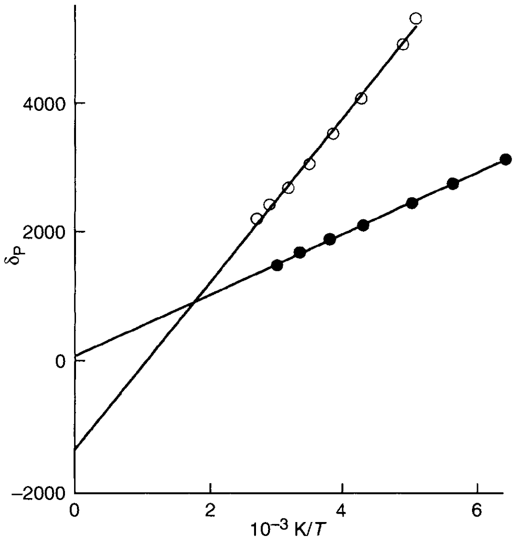

Fig. 1 δ_P *vs.* T^{-1} plots for the data taken from Fig. 2 in ref. 1. The straight lines are the linear fits of the data. The intercept at $T^{-1} = 0$ is δ 81 for sample H [$VO(HPO_4)\cdot 0.5\ H_2O$] (●) and δ −1350 for sample P [$(VO)_2P_2O_7$] (○). Note that the large intercept for sample P reveals the inadequacy of a simple Curie–Weiss approximation.

It is commonly understood[3] that the first *crucial* step towards a correct quantitative analysis of the NMR data of a 'diamagnetic' ion in transition-metal complexes (oxides here) is to have reliable information on the ground state of the paramagnetic metal ions which determines which kind of approximation is valid. For transition-metal oxides used as heterogeneous catalysts, one would expect that a Curie–Weiss approximation would be an exception rather than a rule. The real catalysts are often associated with a high degree of disorder and/or a mixture of different phases and therefore a poor local symmetry at the paramagnetic metal centres. Consequently, the susceptibility anisotropy and the zero-field splitting caused by such a poor local symmetry will make terms other than these described by the Curie-type approximation of significance,[2,3] *i.e.* terms other than T^{-1}-dependence appear.

In a recent paper, Acerete *et al.*[4] have elegantly demonstrated that an apparent linearity of δ (isotropic shift) *vs.* T^{-1} plots in the usually accessible temperature region is *not* sufficient to ensure a Curie-type approximation. A very simple test is to extrapolate the apparently linear experimental data of the δ *vs.* T^{-1} plot to $T^{-1} = 0$. If such an extrapolation has a zero intercept, then a Curie-type approximation is valid, otherwise other contributions that usually give a T^{-2} dependence should be taken into account.

We can apply such a simple test to the published data in ref. 1. Fig. 1 shows δ_P (in ppm with respect to H_3PO_4) *vs.* T^{-1} plots taken from Fig. 2 in ref. 1. The straight lines are the linear fits to the experimental data which give an intercept of δ 81 for sample H and δ −1350 for sample P. The very small intercept of sample H indicates the soundness of the Curie–Weiss approximation in giving the correct estimate of the Weiss temperature in this case, while the large intercept for sample P reveals the inadequacy of a simple Curie–Weiss approximation that leads to the discrepancy found in ref. 1.

It is thus concluded that no practical theory is available at present to permit a ready analysis of NMR signals in paramagnetic solids such as transition-metal oxides. This problem will be investigated in a forthcoming paper.

References

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