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A Reinterpretation of the Anisotropy in the Magnetic Susceptibility of $VO(acac)_2$. A Reply

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Very recently Lukins and Stiles [1] have reinterpreted our magnetic susceptibility data [2] on bis-(pentan-2,4-dionato)oxovanadium(IV), $VO(acac)_2$. On the basis of a single calculation of the paramagnetic anisotropy at one temperature the authors conclude that a quite large diamagnetic anisotropy in $VO(acac)_2$ must be present. The details of their calculation were not exactly clear, the orbital reduction parameters (k) in the effective magnetic moment operator $\beta H(kL + 2.0023S)$ were ignored, and comparison of the experimental data with their theory over the published range of temperature was not attempted. It is well known that orbital reduction parameters are necessary for the precise fitting of experimental magnetic and EPR data to theory and no matter what their precise interpretation they are empirically not normally exactly one [3, 4]. It has also been recognized for a long time that a much more stringent test of a magnetic model is to test its validity over a range of temperature.

In this system there are four anisotropic susceptibility quantities ($\Delta\chi = K_\parallel - K_\perp$) of interest. There is the anisotropy in the first order Zeeman term, $\Delta\chi^z$, and the temperature independent anisotropy in the second order Zeeman term, $\Delta\chi^{tip}$; the sum of these two is then the paramagnetic contribution $\Delta\chi^P$ to the anisotropy of the system. Lukins and Stiles show that a diamagnetic anisotropy $\Delta\chi^D$ should also be considered so the total anisotropy is the sum of $\Delta\chi^P$ and $\Delta\chi^D$. [In the absence of any available diamagnetic analogue the correction for the diamagnetic *anisotropy* could not be made in the original measurements [2]].

We have reanalysed our experimental data taking account of all these considerations and find that Lukins and Stiles are correct in showing that a significant diamagnetic anisotropy exists in $VO(acac)_2$. However their magnetic parameters do not reproduce well the available experimental data. We have used our computer program VVLH [5] to generate the eigenvalues and eigenfunctions of the complete matrix for the ^2D state under the Hamiltonian including crystal field effects, spin–orbit coupling and the applied magnetic field. If E_i is the energy of the i^{th} level and H is the applied magnetic field then $\partial E_i/\partial H$ is the magnetic moment of the i^{th} level. The magnetic properties of the ion are then calculated from the values of $\partial E_i/\partial H$ which are generated by the program. The single d electron problem is complicated because there are off-diagonal matrix elements of the magnetic moment operator (both $k_\parallel L_z$ and $k_\perp L_x$) which connect the ground state and some excited states (using the standard strong field $\{l\, s\, m_l\, m_s\}$ basis set [6]). We first generated magnetic moment as a function of temperature and verified the g-values and $\Delta\chi^P$ (26×10^{-6} cm^3 mol^{-1}) at 300 K (with λ = 150 cm^{-1}, $k_\parallel = k_\perp = 1.0$) reported by Lukins and Stiles. However the experimental temperature variation of $\Delta\chi^{exp}$ is not the same as predicted by them,even taking account of the diamagnetic anisotropy; for example their predicted anisotropy is approximately 50% low at 300 K and about 12% low at 100 K (using the Ballhausen and Gray energy level scheme). Further, the magnitude and sign of $\Delta\chi^P$ at 300 K is extremely sensitive to the value of λ (we prefer not to separate $\Delta\chi^{tip}$ and $\Delta\chi^z$ because when calculated numerically *as a function of H* the first and second order Zeeman terms lose their meanings.) For example if the free-ion value of λ is used (250 cm^{-1}) [7] then $\Delta\chi^P$ changes sign, so that at 300 K $\Delta\chi^P = -15 \times 10^{-6}$ cm^3 mol^{-1}. The temperature variation of $\Delta\chi^P$ is also extremely sensitive to the magnitude of the orbital reduction parameters, particularly $k_\parallel$.

We then used our least squares computer program VVLE [5] to fit $\Delta\chi^{exp}$ to the expression $[\Delta\chi^P + \Delta\chi^D]$ where $\Delta\chi^D$ was assumed to be a constant and independent of temperature and $\Delta\chi^P$ was calculated from the ^2D state in terms of *H, Dq, Ds, Dt,* λ (the spin-orbit coupling constant in the complex), $k_\parallel$ and $k_\perp$. We have taken H = 3000 Oe (the experimental value used in the magnetic anisotropy work [2]), and *Dq, Ds,* and *Dt* from the Balihausen and Gray and Selbin energy level schemes [1]. λ is an extremely difficult quantity to estimate but in this quite anisotropic system we will assume [3, 4] that $\lambda_\parallel = k_\parallel\lambda_o$ and $\lambda_\perp = k_\perp\lambda_o$, λ_o (the free-ion value) = 250 cm^{-1} [7]. The two orbital reduction parameters $k_\parallel$ and $k_\perp$ were too strongly correlated for reliable fits so $k_\perp$ was held constant at 1.0 and 0.9 (from the structure we expect $k_\parallel < k_\perp$). The two variables were then $\Delta\chi^D$ and $k_\parallel$.

Extremely good fits were obtained for both energy level schemes and for both values of $k_\perp$, the differences in $k_\perp$ being absorbed by small differences in $k_\parallel$. In each case $\Delta\chi^D = -68 \times 10^{-6}$ cm^3 mol^{-1} and $k_\parallel$ varied from 0.72 to 0.80. Both energy level

schemes gave similar calculated g-values which depended slightly on the exact values of $k_\parallel$ and $k_\perp$, but to within 0.004, $g_\parallel = 1.926$ and $g_\perp = 1.968$.

Our conclusions are therefore that there is a diamagnetic anisotropy present in $VO(acac)_2$ [$\Delta\chi^D \cong -68 \times 10^{-6}$ cm^3 mol^{-1}] and the paramagnetic anisotropy is extremely sensitive to λ and the orbital reduction parameters and can be of either sign. Further, the temperature variation of the experimental anisotropy requires $k_\parallel \cong 0.8$ and $\lambda_\parallel \cong 200$ cm^{-1} in both energy level schemes and so neither magnetic nor EPR measurements can distinguish between them. The difficulties arise in this d^1 system because λ is small, the ligand field splittings are large and so the paramagnetic anisotropy is small and extremely sensitive to parameter variation. In part this arises because of the relatively large anisotropic temperature independent contributions to the principal susceptibilities which are best calculated exactly using numerical techniques.

References

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