The Crystalline and Molecular Susceptibilities of Triclinic Crystals with Application to Vanadyl Bisacetylacetonate

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Various methods of determining the principal molecular susceptibilities of triclinic crystals are discussed and the one outlined by Ghose is applied to the triclinic crystal vanadyl bisacetylacetonate between 300 and 90 K. It is shown that Ghose's method overcomes most of the difficulties encountered with previous methods. The principal molecular susceptibilities of vanadyl bisacetylacetonate so deduced between 300 and 90 K are then utilised in the assignment of its controversial electronic spectrum. We find that the sign of magnetic anisotropy even at room temperature favours the most recent assignments of its electronic spectrum by Valek *et al.*

SINGLE-CRYSTAL magnetic measurements have become a popular and powerful tool in the investigation of the electronic structure of a wide range of paramagnetic and diamagnetic materials.[1,2] The usual method of attack is to measure the principal crystalline susceptibilities (χ_i, $i = 1, 2,$ or 3) and then relate them by suitable transformations given by Lonsdale and Krishnan [3] to the principal molecular susceptibilities (K_i), the quantities of real interest to chemists. The symmetry of the crystal system determines the number of measurements needed to specify completely the crystalline susceptibility tensor and also the manner in which it is determined. If axial molecular symmetry is assumed the relations of Lonsdale and Krishnan reduce to a simple form and the principal molecular susceptibilities are easily calculated, in some systems with the aid of X-ray structural data. This procedure is used for all crystal systems except triclinic where, because of the lack of symmetry in the crystal, there is no obvious relation between the principal crystalline susceptibilities and the crystal axes a, b, and c. The determination of crystalline and molecular susceptibilities in the triclinic system is therefore considered a rather difficult problem, and the experimental studies so far have been restricted to copper sulphate (and selenate) pentahydrate.

The purpose of the present paper is two-fold. Methods used in the past to extract the principal values of susceptibility tensor in triclinic system are summarised and then a method originally suggested by Ghose [4] is applied to the triclinic vanadyl bisacetylacetonate [VO(acac)$_2$]. The

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measured principal molecular susceptibilities are then used to show that they are consistent with the presently accepted electronic structure of this fundamentally important compound.[5]

THEORY

The determination of the principal crystalline susceptibilities of triclinic crystals is not easy; six χ_{ij} (elements of the susceptibility tensor) are required. Krishnan and Mookherji [6] derived an approximate method which required measurements in eight different orientations. Subsequent methods [7-10] have not much reduced the tedium and the number of measurements.

Krishnan and Mookherji accomplished the transformation from the crystalline susceptibilities to the molecular susceptibilities of each ion by a method which was only applicable to copper sulphate pentahydrate. Ghosh and Mitra [11] pointed out that a better method would be to calculate the principal molecular susceptibilities directly without first finding the principal crystalline susceptibilities. However their method involved, besides magnetic anisotropy measurement, determination of maximum susceptibilities in different planes which made the method susceptible to large errors.[4]

Ghose [4] subsequently showed that for n magnetically inequivalent ions in the unit cell possessing principal magnetic susceptibilities K_i with direction cosines α_i, β_i, and γ_i with respect to an orthogonal set of axes x, y, and z, the measured crystalline anisotropy in the xy plane ($\Delta\chi$) is related to K_i by equation (1). Similarly

$$\{(K_2 - K_1)\Sigma(\alpha_2^2 - \beta_2^2) + (K_3 - K_1)\Sigma(\alpha_3^2 - \beta_3^2)\}^2 + 4\{(K_2 - K_1)\Sigma\alpha_2\beta_2 + (K_3 - K_1)\Sigma\alpha_3\beta_3\}^2 = n^2(\Delta\chi)^2 \quad (1)$$

if ($\Delta\chi'$) be the measured anisotropy in the (xz) plane, then we obtain equation (2)

$$\{(K_2 - K_1)\Sigma(\alpha_2^2 - \gamma_2^2) + (K_3 - K_1)\Sigma(\alpha_3^2 - \gamma_3^2)\}^2 + 4\{(K_2 - K_1)\Sigma\alpha_2\gamma_2 + (K_3 - K_1)\Sigma\alpha_3\gamma_3\}^2 = n^2(\Delta\chi')^2 \quad (2)$$

By solution of equations (1) and (2) $(K_2 - K_1)$ and $(K_3 - K_1)$ can be determined. There will in general be four alternative sets of solutions of which only one will be correct. Ghose has resolved this ambiguity by suggesting an approximate experimental determination of maximum susceptibility in working planes of the crystals which then leads to the correct solution. If axial molecular symmetry is assumed, *i.e.*, $K_1 = K_2 = K_\perp$ and $K_3 = K_\parallel$, then from equation (1) we obtain

$$(K_\parallel - K_\perp) = \frac{\pm n(\Delta\chi)}{\{[\Sigma(\alpha_3^2 - \beta_3^2)] + 4[\Sigma\alpha_3\beta_3]^2\}^{\frac{1}{2}}} \quad (3)$$

equation (3). Thus the principal axial molecular anisotropy can be calculated from a single measurement of the crystalline anisotropy in any conveniently chosen plane, the correct sign being determined by noting the sign of $\Sigma\alpha_3\beta_3$ and the direction of maximum susceptibility in the magnetic field. A further simplification can be made if all the ions are magnetically equivalent. Equation (3) then reduces to (4).

$$K_\parallel - K_\perp = \pm\frac{\Delta\chi}{\alpha_3^2 + \beta_3^2} = \pm\frac{\Delta\chi}{1 - \gamma_3^2} \quad (4)$$

Application to VO(acac)$_2$.—The crystals of VO(acac)$_2$ are triclinic with two magnetically equivalent molecules in the unit cell.[12] If axial molecular symmetry is assumed, equation (4) applies where now γ_3 is the cosine of the angle between the symmetry axis of the molecule and the normal to the plane in which the anisotropy is being measured. If the plane of measurement is perpendicular to a crystallographic axis, Ghose has shown that γ_3 is one of the direction cosines of $K_\parallel$ with respect to a, b, or c. Using the structural data of Dodge *et al.*[12] we found the direction cosines of $K_\parallel$ [defined by the V=O) direction] with respect to a, b, and c axes to be 0·8256, −0·0567, and 0·5399 respectively.

EXPERIMENTAL

VO(acac)$_2$ was prepared by the literature method [13] and analysed. Well developed single crystals were grown from ethanol. The magnetic anisotropy was measured by the apparatus described.[14] The average susceptibility was measured by the Guoy method.

The magnetic anisotropy was first measured with b axis vertical, and the results of measurement are given in Tables 1 and 2. With the b axis vertical, γ_3 is now −0·0567.

TABLE 1

Experimental average susceptibility and anisotropies of VO(acac)$_2$

T/K	$10^6\bar{\chi}$/cm^3 mol^{-1}	T/K	$10^6\Delta\bar{\chi}$/cm^3 mol^{-1}
291·5	1313	290·7	77
273·3	1408	267·4	82
244·0	1560	237·7	89
223·7	1681	220·6	94
195·2	1909	200·7	102
175·0	2104	167·0	117
154·0	2374	140·0	134
133·0	2731	128·1	152
113·4	3180	108·5	165
99·7	3575	93·0	191

Equation (4) shows that when $\gamma_3 = -0\cdot0567$, $(K_\perp - K_\parallel)$ becomes almost the same as $\Delta\chi$. So the crystalline anisotropy measured with b axis vertical is same (within 1%) as the molecular anisotropy $(K_\perp - K_\parallel)$. With the a axis vertical $\Delta\chi$ was found to be $25\cdot1 + 10^{-6}$ cm^3 mol^{-1}, which when transformed to the molecular frame gave 78×10^{-6} cm^3 mol^{-1} for the molecular anisotropy, in excellent agreement with the previous more direct measurement. The

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Table 2

Calculated and experimental molecular susceptibilities of VO(acac)$_2$

T/K	$10^6(K_\perp - K_\parallel)$	$10^6\bar{\chi}$	$10^6K_\perp$*	$10^6K_\parallel$*
	cm^3 mol^{-1}			
300	76	1260	1285 (1293)	1209 (1255)
260	83	1470	1498 (1477)	1415 (1437)
220	94	1690	1721 (1735)	1627 (1684)
180	109	2050	2086 (2105)	1977 (2037)
140	133	2620	2664 (2705)	2531 (2585)
100	178	3570	3629 (3765)	3451 (3580)

* The figures in parentheses are the calculated values.

sign of the anisotropy was decided by noting that at the ' setting ' position (when $\chi_{\text{max.}}$ in the working plane is parallel to the magnetic field direction) the (001) plane was inclined to the normal of the magnetic field direction at an angle of 19°. A calculation by use of Ghose's covarient matrix method showed that $K_\parallel$ was inclined to this normal at 14° in reasonable agreement with experiment and hence $K_\perp > K_\parallel$. The average susceptibility corrected for diamagnetism then allows the calculation of the principal molecular susceptibilities (Table 2).

A measurement of g-values gave $g_\parallel = 1{\cdot}93$ and $g_\perp = 1{\cdot}99$. No anisotropy was detected in the symmetry plane. This supports our assumption of axial ligand field above.

DISCUSSION

Although the optical spectrum of VO(acac)$_2$ arises from the d^1 configuration and hence is easy to deal with theoretically, the assignment of various bands is still being debated.[5] Basically there are two alternate energy level schemes for vanadyl complexes. In the Ballhausen and Gray scheme[15] band I (10,500—16,000 cm^{-1}) is assigned to the $d_{xy} \longrightarrow d_{xz},d_{yz}$ transition and band II (16,000—20,000 cm^{-1}) is assigned to the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition. Band III is variously assigned as a d–d ($d_{xy} \longrightarrow d_{z^2}$), charge-transfer, and/or spin-forbidden $n \longrightarrow \pi^*$ or $\pi \longrightarrow \pi^*$ transitions. In the present context however band III is irrelevant because none of the possible assignments affects the susceptibility. The ' cluster ' scheme of Selbin *et al.*[16,17] assigns band II to the $d_{xy} \longrightarrow d_{z^2}$ transition while the remaining d–d transitions are assumed to occur within the range of band I.

$$\frac{2N\beta^2\kappa_\perp{}^2}{\Delta_\perp(d_{xy} \longrightarrow d_{xy} \longrightarrow d_{xz,yz})} \tag{5}$$

$$\frac{8N\beta^2\kappa_\parallel{}^2}{\Delta_\parallel(d_{xy} \longrightarrow d_{x^2-y^2})} \tag{6}$$

The experimental g_i-values lead to low-frequency susceptibility values of 1160 and 1246 × 10^{-6} cm^3 mol^{-1} for $K_\parallel$ and $K_\perp$ respectively at 300 K. For $K_\perp > K_\parallel$ and since the high-frequency susceptibilities are given by expressions (5) and (6) respectively, only Ballhausen and Gray's scheme gives satisfactory agreement. With $\Delta_\parallel = 17{,}400$ cm^{-1} and $\Delta_\perp = 12{,}000$ cm^{-1},[5] and inclusion of the appropriate orbital reduction parameters,[18] the high-frequency contributions are 95 and 45 × 10^{-6} cm^3 mol^{-1} for $K_\parallel$ and $K_\perp$ respectively. In Table 2 the calculated values are given in parentheses. Ballhausen and Gray's scheme thus gives $K_\parallel < K_\perp$ and reproduces fairly well the temperature variation of $K_\parallel$ and $K_\perp$, the alternative assignments predicting $K_\parallel > K_\perp$.

Conclusion.—The problems of calculating the principal molecular susceptibilities in triclinic systems have been shown to be largely overcome if the method of Ghose is used. The errors to be expected from the use of assumed magnetic axes are minimised if the plane of measurement is chosen such that the measured crystalline anisotropy is a maximum. The sign of the molecular anisotropy of VO(acac)$_2$ even at room temperature favours the most recent assignment of the optical spectrum by Valek *et al.*[5]

We thank Professor R. L. Martin for encouragement.

[2/2159 *Received*, 27*th November*, 1972]

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