

noncollinear form factor increases in this way. Finally, we note that the noncollinearity due to spin-orbit coupling in free atoms can never be observed with \mathbf{K} parallel to \hat{n} . This type of density contributes to the scatter-

ing amplitude only in conjunction with the collinear part.

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Low-Temperature Magnetic Susceptibilities of $\text{Al}_2\text{O}_3:\text{V}^{3+}$ †

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Previous measurements of the magnetic anisotropy of single-crystal $\text{Al}_2\text{O}_3:\text{V}^{3+}$ in the temperature range 1–5°K have already been used to obtain more accurate values for the zero-field splitting δ and for the perpendicular splitting factor g_1 . The results of measurements by the Faraday method of χ_{11} and χ_1 are reported here along with some new anisotropy measurements. The results for all the parameters agree very well between the two experiments, and the values found are $\delta = 8.06 \pm 0.15 \text{ cm}^{-1}$, $g_1 = 1.720 \pm 0.003$, and the spin-orbit parameter $\lambda = 91 \pm 1 \text{ cm}^{-1}$.

SEVERAL years ago, Brumage, Quade, and Lin^{1,2} reported results of magnetic-susceptibility measurements on vanadium-doped Al_2O_3 in the temperature range 4–300°K. From these results, they were able to determine the zero-field splitting δ of the trigonal ground state, the perpendicular g factor g_1 , the trigonal field splitting Δ_T , and the spin-orbit coupling parameter λ . Later, Brumage, Seagraves, and Lin³ extended some of these measurements to 1000°K to make a more direct determination of Δ_T . More recently, Smith⁴ has measured the magnetic anisotropy of this crystal system using one of Brumage's samples in the temperature range 1–5°K, a region in which the susceptibility expressions are most sensitive to δ and g_1 . Reported here are results of measurements by the Faraday method of the parallel and perpendicular susceptibilities, χ_{11} and χ_1 , respectively, in the same low-temperature range. For consistency, however, the measurements have been extended up to 300°K. Also, new anisotropy results are included and, not only are they compatible with the Faraday results, but they are believed to be more accurate than those reported in Ref. 4 for two reasons: (i) The sensitivity of the torsion balance has been greatly improved, and (ii) a new method of analysis of the data has been used which is independent of the reference value.

To obtain a more direct determination of g_1 and the zero-field splitting of the trigonal ground state of the V^{3+} ion in the octahedral field of the Al_2O_3 host

crystal, measurements by the Faraday method have been made down to about 1°K for the magnetic field parallel and perpendicular to the c axis of the crystal. The apparatus was similar to that used in magnetic studies⁵ of V_2O_5 but equipped with a low-temperature Dewar and manifold for pumping on the liquid-He vapor. Helium gas at a pressure of about 2–3 cm of Hg was inserted in the sample chamber when the system was at 77°K for the purpose of exchanging heat between the liquid He and the sample. However, in selected temperature ranges less exchange gas was used, but a longer time between temperature changes was allowed so that the sample could reach thermal equilibrium with its environment. The same procedure

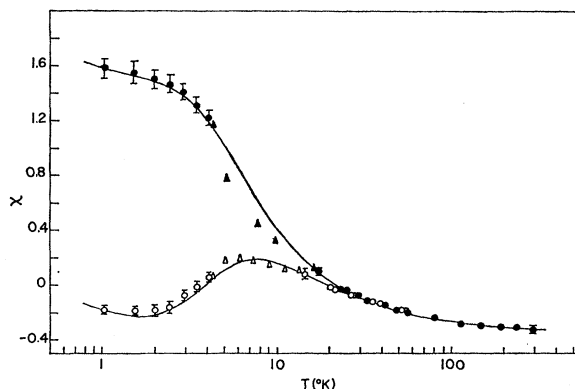


FIG. 1. Measured magnetic susceptibilities of $\text{Al}_2\text{O}_3:\text{V}^{3+}$ in units of 10^{-6} cgs emu. Only the circles, both filled (χ_1) and unfilled (χ_{11}), were used in the data analysis. The solid curves represent the theoretical values (including $C/T + \chi_{\text{dia}}$) obtained using the parameters in Table I. Above 80°K, filled circles represent both χ_{11} and χ_1 .

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² W. H. Brumage, C. R. Quade, and C. C. Lin, *Phys. Rev.* **131**, 949 (1963).

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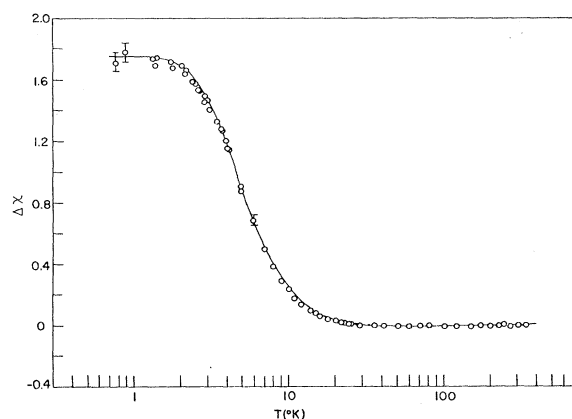


FIG. 2. Magnetic anisotropy of $\text{Al}_2\text{O}_3:\text{V}^{3+}$ in units of 10^{-6} cgs emu. Circles represent data points and only those below 12°K were used in the data analysis. Solid curve is the theoretical expression using the parameters in Table I.

was used in making the new anisotropy measurements where the torsion balance was the same as in Ref. 4 except for some refinements, as mentioned above. The sample in both cases was a 266.4-mg piece of Brumage's sample *B* which had a reported V^{3+} concentration of 0.092%. The results for the susceptibility measurements are shown in Fig. 1 and the anisotropy results are shown in Fig. 2. In both figures, typical errors are shown on the graph for the low-temperature points. For the higher-temperature points, these errors are smaller than the circles used to represent the data and so they are not shown. In Fig. 1, both the filled and unfilled triangles represent very low-pressure drift points and almost certainly the sample and its surroundings were not in thermal equilibrium so these points were not used in the data analysis. Above about 15°K , the sample chamber drifted up in temperature much more slowly and the instabilities arising from convection currents were much less violent, thus allowing for the use of more exchange gas and longer time intervals between measurements. Therefore, these points were believed to be good data and were used in the analysis.

The torsion datum is of the form $\Delta\chi_{T_1}/\Delta\chi_{T_2}$ as shown by Eqs. (3) and (5) of Ref. 2. For $T_2=4.12^\circ\text{K}$, these ratios were fitted with ratios of the expression for $\Delta\chi(\equiv\chi_{\perp}-\chi_{\parallel})$ given by Eq. (30) of Ref. 2 for data below 12°K , where the Van Vleck term $(\Delta\chi)_{vv}$ is negligible and was omitted. The expressions for g_{\perp} from Eq. (21) and for δ from Eq. (35) of Ref. 2 were also used to reduce $\Delta\chi$ to an expression containing only the two parameters $N\mu_0^2$ and λ , and when the ratio of $\Delta\chi$'s is used, $N\mu_0^2$ drops out leaving only λ . This, of course, assumes a knowledge of all the other parameters appearing in the equations, and we have used Brumage's values for them, including 1100 cm^{-1} for Δ_T . The technique of Eq. (31) of Ref. 2 was also applied to the

TABLE I. Parameters used to fit experimental magnetic susceptibilities of $\text{Al}_2\text{O}_3:\text{V}^{3+}$.

Parameter	This work	From Brumage, Ref. 2
$N\mu_0^2$ (cgs emu)	$(2.39 \pm 0.10) \times 10^{-6}$	2.72×10^{-6}
λ (cm^{-1})	91 ± 1	95 ± 5^a
δ (cm^{-1})	8.06 ± 0.15	8.3 ± 0.2
g_{\perp}	1.720 ± 0.003	1.720 ± 0.005

^a The $\pm 5\text{-cm}^{-1}$ uncertainty is taken from Ref. 3.

ratio data. As described, this method is independent of the particular value of δ . By restricting g_{\perp} to reasonable values and averaging over the spread of values, results completely consistent with the least-squares analysis were obtained.

The susceptibility data were fitted by least squares to Eq. (23) of Ref. 2 using λ and $N\mu_0^2$ as parameters as was done in the torsion data analysis. The data were corrected for the diamagnetism of the host and for a small concentration of an unwanted isotropic Curie-type of impurity whose contribution to $\chi_{\parallel,\perp}$ could not be neglected at the low temperatures. The presence of such an impurity was confirmed by an electron spin resonance spectrum taken on the same sample. Thus, to the Eq. (23) of Ref. 2 a term of the form $C/T + \chi_{\text{dia}}$ was added. χ_{dia} was determined by measuring the temperature dependence of the susceptibility of an undoped Al_2O_3 single crystal resulting in a value of -0.339×10^{-6} cgs emu. These data were isotropic within our experimental error and while this value is slightly smaller in magnitude, it is believed to be more accurate than the previously accepted value of -0.363×10^{-6} cgs emu.⁶ The value of C was determined from χ_{\parallel} at low temperature and was found to be 0.16×10^{-6} cgs emu $^\circ\text{K}$. This corresponds to approximately 6 ppm of sample weight of an impurity with $g=2$, $S=\frac{5}{2}$ and is consistent with the undoped sample and with guaranteed purity specifications supplied with other crystals by the manufacturer.

The quantitative results of our experiments are given in Table I. $N\mu_0^2$ is smaller than Brumage reported for the same crystal. This is most likely due to the difference in the temperature range over which it was determined but another possibility is that we have now used only a piece of the original crystal, and the V^{3+} concentration may not have been distributed uniformly throughout. The solid curves in Figs. 1 and 2 are plotted using our new parameters, and it can be seen that they fit the data points exceptionally well over the entire temperature range.

⁶ G. Föex, *Constantes Selectionnees Diamagnetisme et Paramagnetisme Relaxation Paramagnetique* (Masson and Co., Paris, 1957), Vol. 7.