low- or high-spin behaviour  $(E/\zeta=\pm\infty)$  are seen only when  $|E|/\zeta<1$ . The resulting curves are not, however, notably different in shape from those obtained in other situations where  $\mu$  is temperature dependent. In this connexion it is worth remarking that one is likely, in practice, to be able to observe a portion only of the  $\mu(T)$  curve, since thermal decomposition and phase changes invariably impose an upper

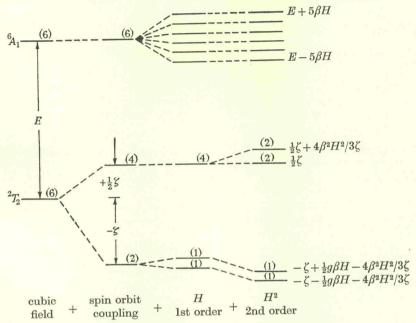


Figure 3. Energy levels (not to scale) of configuration  $d^5$  in the crossover region.

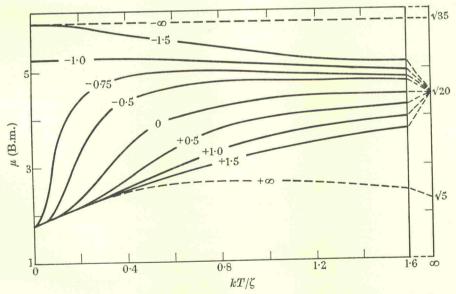


Figure 4. Calculated values of the effective magnetic moment  $\mu$ , assuming g=2, and values of  $E/\zeta$  as given on the curves.

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temperature limit on measurements. Further, which portion of the  $\mu(T)$  curve is being seen is also uncertain, since  $\zeta$  is not known a priori;  $\zeta$  can only be regarded as a parameter whose value probably lies somewhere between 300 and 440 cm<sup>-1</sup> (see Figgis 1961).

The exceptional nature of the magnetic behaviour is better revealed by the temperature dependence of the reciprocal molar susceptibility,  $\chi_M^{-1} = 3kT/N\beta^2\mu^2$ . From figure 4 are derived the full-line curves of  $\chi_M^{-1}$  in figure 5. As Guha (1963) has pointed out, under certain conditions a  $\mu(T)$  dependence of the kind shown in

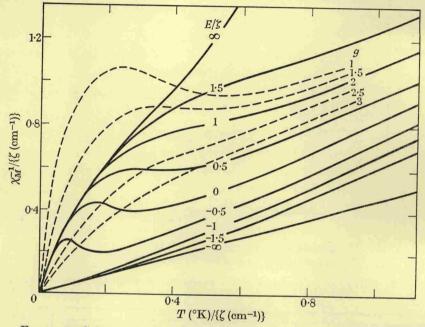


FIGURE 5. Calculated values of  $\chi_M^{-1}$ . Full lines: g=2 with various values of  $E/\zeta$ . Broken lines:  $E/\zeta=1$  with various values of g.

figure 4 may produce maxima and minima in curves of  $\chi_M(T)$  and  $\chi_M^{-1}(T)$ . Such maxima and minima are of obvious diagnostic value, and they are predicted in the present instance when  $|E|/\zeta < 1$ .

The generality of this last inequality requires some qualification. The parameter g was introduced into figure 3 and equation (1) as one of the many possible ways of distorting a doubtless idealized model. The broken curves in figure 5, in which we have assumed a constant value of  $E/\zeta$ , namely +1, and various values of g, shows that the maximum and minimum in  $\chi_M^{-1}$  may develop, for  $|E|/\zeta > 1$ , if g differs sufficiently from 2. On the other hand, g-values differing from 2 by more than 0.5 for a low-spin octahedral complex would be unexpected. We conclude that an experimental observation of a maximum and minimum in  $\chi_M^{-1}(T)$  is a sensitive test for nearly coincident  ${}^2T_2$  and  ${}^6A_1$  states. At the same time, the precise details of the model assumed in figure 3 are seen not to be critical. Indeed, calculations show that maximum-minimum behaviour could be produced in this system even if spin-orbit interaction were neglected entirely, provided one admitted a sufficiently low value