

**Bleaney B & Rubins R S.** 'Forbidden' transitions in paramagnetic resonance.  
*Proc. Phys. Soc.* 77:103-12. 1961.  
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This paper provided an explanation for the abnormal intensity of "forbidden" hyperfine transitions in electron spin resonance. These appear for ions in which the electronic ground state has more than twofold degeneracy and arise from combinations of off-diagonal terms in the electronic and nuclear spin Hamiltonians. [The *SCI*<sup>®</sup> indicates that this paper has been cited in more than 195 publications.]

## "Forbidden" Hyperfine Transitions

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Hyperfine structure in the electron spin resonance spectrum of  $Mn^{2+}$ ,  $3d^5$ , was first observed<sup>1</sup> by David Ingram, now vice chancellor of the University of Kent at Canterbury, England, and me. The sixfold electronic multiplicity is slightly split by crystal field effects; together with the hyperfine structure, they were analysed for two single crystals, each diluted with diamagnetic ions to reduce broadening by the random magnetic fields of neighbouring ions. The strong hyperfine lines correspond to electronic transitions in which the nuclear magnetic quantum number  $m_I$  does not change; weak lines, clearly from transitions in which  $m_I$  changes by  $\pm 1$ , appeared when the external magnetic field was at an angle to the symmetry axes, with inexplicably large intensity.

In early work, highly anisotropic crystals such as cobalt compounds were secured

from rotation in the applied magnetic field by fixing them in plasticine (modelling clay). Once, a student burst into my room with the news that the nuclear spin of  $^{59}Co$  was  $I = 5/2$ ; I pointed out that it was well known to be  $I = 7/2$ . What he had discovered was a manganese impurity spectrum in plasticine; for many years its hyperfine structure was used to calibrate the modulation field in electron spin resonance experiments at low temperatures.

The high intensity of the "forbidden" lines was only explained many years later. In the electron spin resonance spectrum of divalent vanadium in a single crystal of zinc fluosilicate, Roy Rubins had determined and fitted the orientation dependence of their intensity, but not the magnitude. I then realised the importance of cross terms between the electronic splitting and the hyperfine interaction and derived formulae for the intensity of such transitions, together with their positions in the spectrum, including small displacements arising from the nuclear Zeeman interaction. This paper contains photographs of the extra lines in this substance (figure 2) and in modelling clay (figure 4). There are also weaker transitions where  $m_I$  changes by  $\pm 2$ .

Similar transitions occur<sup>2</sup> in crystals of MgO with a different angular dependence of intensity, since the cubic crystal field is involved, and in powdered samples.<sup>3</sup> A "far-out" observation is reported<sup>4</sup> in calcite from a crater caused by a nuclear explosion on Eniwetok Atoll. Generally such "forbidden" transitions are mentioned, but are not central to the paper. However, in  $ZnTiF_6 \cdot 6H_2O$ , their intensity increases<sup>5</sup> below 180 K in a phase-change from trigonal to monoclinic structure.

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2. Rubins R S & Drumheller J E. "Forbidden" hyperfine transitions in the electron paramagnetic resonance spectrum of  $Mn^{2+}$  in cubic MgO. *Phys. Rev. A-Gen. Phys.* 133:199-1103. 1964.
3. Rubio J, Munoz E P, Boldu J O, Chen Y & Abraham M M. EPR powder pattern analysis for  $Mn^{2+}$  in cubic crystalline fields. *J. Chem. Phys.* 70:633-8. 1979. (Cited 15 times.)
4. Vizgirda J, Ahrens T J & Fund-Dow Tsay. Shock-induced effects in calcite from cactus crater. *Geochim. Cosmochim. Acta* 44:1059-69. 1980. (Cited 10 times.)
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