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Baker J M & Bleaney B. Paramagnetic resonance in some lanthanon ethyl sulphates. *Proc. Roy. Soc. London Ser. A* 245:156-74, 1958.
[Clarendon Laboratory, University of Oxford, England and Columbia University, New York, NY]

This paper reported electron spin resonance measurements, including hyperfine interactions, on ethyl sulphates of the lanthanons. Of particular interest were novel formulae for the "enhancement" of the nuclear Zeeman interaction through interactions with excited states. Enhanced magnetic cooling uses such substances with singlet ground states. [The *SCI*® indicates that this paper has been cited in over 190 publications.]

Enhanced Nuclear Zeeman Interaction

Brebis Bleaney
Clarendon Laboratory
University of Oxford
Oxford OX1 3PU
England

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The lanthanide ethyl sulphates form a complete series with similar hexagonal crystal structure; single crystals can readily be grown from aqueous solution. Their properties were investigated by electron paramagnetic resonance at the Clarendon Laboratory, University of Oxford, starting in 1950; well-resolved hyperfine structures made it possible to determine nuclear spins, with estimates of the nuclear moments. This paper by J.M. Baker and me reported further measurements, mainly on the non-Kramers ions of Pr, Tb, and Ho with an even number of electrons. Formulae were derived for novel interactions by which the nuclear Zeeman interaction is "enhanced" by admixture of some electronic moment through the hyperfine interaction. Another second order effect of the hyperfine interaction is similar in form to nuclear electric quadrupole terms.

Interactions between the lanthanide ions are so small that the ethyl sulphates remain paramagnetic down to temperatures well below 1 kelvin (K). They have been used for a variety of cryogenic experiments, including magnetic cooling and nuclear orientation. In the dysprosium compound, the electronic moments are large only along the symmetry axis; measurements on single crystals showed that, as expected, it becomes a dipolar ferromagnet[1] below 0.12 K, with long thin domains, magnetised in opposite directions to minimise the magnetic energy. Similar behaviour occurs in terbium ethyl sulphate.

Following a suggestion that such substances with ions in electronic singlet ground states could be used for hyperfine "enhanced" nuclear cooling, resonance measurements on a range of compounds were reviewed by M.A. Teplov.[2] Intermetallic compounds of praseodymium[3] became standard substances for reaching temperatures of order 1 millikelvin.

Nuclear magnetic resonance (NMR) has established the magnitude of the enhancement in a range of insulating compounds with the zircon structure. Holmium vanadate has a nuclear enhancement factor of over 150; as predicted from the NMR measurements, it enters an enhanced nuclear antiferromagnetic state below 5 millikelvin.[4] Thulium phosphate has been used for dynamic nuclear polarisation, and both substances have been investigated by means of enhanced nuclear acoustic resonance.

Laser spectroscopy has detected many similar nuclear effects in optically excited states. An exceptional case where the enhancement is only 3 parts in 10,000 was used to make a precise measurement[5] of the nuclear magnetic moment of the stable isotope (mass 141) of praseodymium. For a recent general review of electron spin resonance, hyperfine interactions and enhanced effects, see reference 6.

1. **Cooke A H, Edmonds D T, Finn C H P & Wolf W P.** Magnetic dipole interactions in dysprosium ethyl sulphate—III. Magnetic and thermal properties below the Curie point. *Proc. Roy. Soc. London Ser. A* 306:335-53, 1968. (Cited 20 times.)
2. **Teplov M A.** NMR study of singlet ground state systems. (Furrer A, ed.) *Crystal field effects in metals & alloys.* New York: Plenum Press, 1977. p. 318-29. (Cited 10 times.)
3. **Andres K.** Hyperfine enhanced magnetic cooling. *Cryogenics* 18:474-7, 1978. (Cited 25 times.)
4. **Bleaney B.** Properties of $HoVO_4$ below 1 K—I. Predictions from nuclear magnetic resonance. *Proc. Roy. Soc. London Ser. A* 370:313-30, 1980. (Cited 20 times.)
5. **MacFarlane R M, Burum D P & Shelby R M.** New determination of the nuclear magnetic moment of praseodymium[141]. *Phys. Rev. Lett.* 49:636-9, 1982. (Cited 10 times.)
6. **Bleaney B.** Microwave resonance spectroscopy and hyperfine interactions. (Gschneidner K A & Eyring L, eds.) *Handbook on the physics and chemistry of rare earths. Volume II. 200-year impact of rare earths on science.* Amsterdam, The Netherlands: North-Holland, 1988. p. 323-407.