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Magnetic resonance, nuclear orientation and antiferromagnetism

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A small range of compounds contain ions from two transition groups, 3d and 4f. Most of these enter an ordered antiferromagnetic state only at liquid helium temperatures, and the internal fields are 1 tesla or less. Experiments are suggested on various single crystals. Measurements by electron spin resonance on impurity ions in antiferromagnetic dysprosium phosphate show that similar compounds could be used for experiments on nuclear orientation with nuclear magnetic resonance.

1. Introduction

The properties of antiferromagnetic (AF) compounds have been studied by a variety of methods, but little work has been carried out on the nuclear orientation of paramagnetic impurities in such compounds. One problem is that in a substance such as the classic antiferromagnet manganese fluoride, with Néel temperature 67 K, the spin–lattice relaxation time is extremely long at low temperatures. Cooke and Edmonds [1] found that thermal contact with the nuclear spins of the manganese ions was lost below about 0.5 K. Also, the internal field of the manganese ions is so large that the electron resonance frequency for many impurity ions would lie in the infrared.

For most other AF substances of the 3d group the internal field is also large, except in hydrated compounds, which are more dilute. These usually order only at liquid helium temperatures and the internal field in the AF state is correspondingly smaller. Nevertheless, at the millikelvin temperatures required for a nuclear orientation experiment, spin–lattice relaxation rates are very slow.

This problem has been overcome by applying an external field sufficient to pass through spin-flop. Kotlichi and Turrell [2], and Allsop *et al.* [3] have shown that the rapid reversal of the hyperfine field produces almost instantaneous thermal contact with the lattice. This made it possible to detect nuclear magnetic resonance of ^{54}Mn ($I = 3$), a radioactive isotope with half-life about 290 days, by nuclear orientation (NMRON). Similar experiments on this isotope have been carried out on single crystals of the quasi-one-dimensional antiferromagnet $CsMnCl_3,2H_2O$, for which $T_N = 4.89$ K [4].

2. Lanthanide compounds

In the lanthanide (4f) group, a number of compounds become antiferromagnetic at liquid helium temperatures. The problem of thermal contact is less acute, and the internal fields are of the order of 1 tesla or less, so that spin-flop or spin-flip can be reached readily. Examples of such compounds with the zircon structure, where the crystal field has tetragonal symmetry, are listed in table 1, which also contains the values of the Néel temperature and estimates of the internal field.

These compounds become simple antiferromagnets, with two sublattices and magnetic moments along the *c* axis. The ion Gd^{3+} has a half-filled 4f shell, and an octet S-state with $g = 1.992$ (isotropic). Gadolinium vanadate orders at 2.49 K, and spin-flop occurs [5] at 1.08 T. In $DyPO_4$, the levels of the trivalent dysprosium ion, $4f^9$, $^6I_{15/2}$, are split by the tetragonal crystal field [6, 7]; the ground state is a Kramers doublet with $g_c = 19.5(4)$, $g_{a,b} = 0.51(3)$.

For this compound, spin-flip (or technically spin-flop, since the value of g normal to the c axis is not quite zero) occurs at 0.57 T. $HoPO_4$ also has the zircon structure; the ground state of the trivalent holmium ion, $4f^{10}$, $^5I_8$,

Table 1. Values of the Néel temperature T_N, the exchange field B_{ex}, the dipolar field B_{dip} and the spin-flop or spin-flip field B_{sf} in the fully ordered state of three compounds with the tetragonal zircon structure, space group ($I4_1$/amd).

Crystal	T_N/K	B_{ex}/T	B_{dip}/T	B_{sf}/T
$GdVO_4$	2.496	1.275	0.147	1.08
$DyPO_4$	3.39	0.616	0.236	0.57
$HoPO_4$	1.39	0.202	0.200	0.18

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split by the crystal field, is a non-Kramers doublet, with $g = 16.7$ along the c axis. It orders at 1.39 K with the moments aligned ferromagnetically along this axis [8]. Spin-flip occurs in a field of 0.18 T along this axis. Table 1 lists several compounds with the same structure that order at 0.1–1 K.

3. Electron paramagnetic resonance of impurity ions in an antiferromagnet

In the antiferromagnetic state, if the external field B is at an angle θ to the c axis, the resonant frequency for an impurity ion is given by

$$(h\nu)^2 = \mu_B^2 g_z^2[(B\cos\theta \pm B_i)^2 + (g_x B \sin\theta)^2]. \qquad (1)$$

Thus for $\theta = 90°$,

$$h\nu = \mu_B[(g_z B_i)^2 + (g_x B)^2]^{1/2}. \qquad (2)$$

Here B_i is the internal field along the c axis, and from equation (2) it follows that no electron spin resonance can be observed normal to the c axis unless the frequency is greater than the value for this field.

The possibility of making electron spin resonance measurements on impurities in the antiferromagnetic phase of gadolinium vanadate was discussed by Bleaney [9].

In the antiferromagnetic state, the internal fields contain both exchange and dipolar interactions. The exchange field is found by subtracting the dipolar contribution, which can be calculated. Such measurements have been made on two impurities in dysprosium phosphate, $DyPO_4$ [10]. An external magnetic field parallel to the c axis adds to or subtracts from the internal field; the fields acting on the impurity ions are each of the order of 1 T or less. This produces two electron magnetic resonance spectra, from which the internal field acting on the impurity ion can be deduced.

The two impurity ions, also from the 4f group, were identified as trivalent erbium ($4f^{11}$), for which the internal field is 0.426 T, and ytterbium ($4f^{13}$), with field 1.277 T. Subtraction of the dipolar field of 0.236 T gives the exchange fields, but neither of them agrees with the values suggested by a simple theory in which the exchange field is expected to scale with the expectation value of the electron spin.

The hyperfine structure was not resolved but the splittings should be close to those deduced from measurements in the diluted compounds, which could be determined by NMRON.

Perpendicular to the c axis, there should be considerable enhancement of the radiofrequency field, which makes the resonance more intense. The nuclear moments of the stable isotopes are known quite accurately, and those of the radioactive isotopes could be determined from the ratios of the hyperfine structures.

4. Further measurements

The lanthanide group contains a range of radioactive isotopes for which the nuclear spin, magnetic and electric quadrupole moments have not been determined or are known only to low accuracy. Incorporation of these at a low concentration in one of the antiferromagnetic substances listed in table 1 would make possible NMRON measurements at millikelvin temperatures.

In a field sufficient to pass through spin-flop in $GdVO_4$ the nuclei should cool to the ambient temperature of a dilution refrigerator. In both dysprosium phosphate and holmium phosphate, reversal of the hyperfine field in one of the antiferromagnetic sublattices at spin-flip should produce a similar effect. However, the majority of the radioactive isotopes to be investigated have short half-lives, of the order of a few days, so that the choice might be restricted to those isotopes which can be produced by neutron irradiation of existing single crystals.

Details of the ground states of trivalent lanthanide ions in lanthanum magnesium nitrate have been measured by paramagnetic resonance. In Abragam and Bleaney [11], table 5.12 includes the trivalent ions of Ce, Pr, Nd, Sm, Dy and Er, with hyperfine data for all the stable odd isotopes. In an experiment using cerium magnesium nitrate, the radioactive isotope ^{142}Pr ($I = 2$, half-life 19.2 h) was cooled to 3 mK [12].

An alternative is to grow single crystals from aqueous solution at room temperature of other compounds similar to the lanthanide double nitrates, in which both ions of the 3d and 4f groups can be incorporated. These analogues of lanthanum magnesium nitrate have axial symmetry at both 4f and 3d sites.

Pr^{3+} is a trivalent non-Kramers ion with $g = 1.55$ along the c axis; the neighbouring trivalent ions Ce and Nd have values of $g = 1.84$ and 2.72, respectively, along this axis, but larger values normal to it. For samarium the values of g are both small: 0.76 (parallel) and 0.40 (perpendicular).

Crystals with trivalent lanthanum or bismuth containing small amounts of manganese, cobalt and copper have been investigated [13, 14]. Undiluted crystals of lanthanum double nitrates have been grown [15] in which the divalent ions are members of the 3d group. Lanthanum nickel nitrate orders as a ferromagnet at 393 mK, while the compounds with manganese, cobalt and copper become antiferromagnetic at temperatures of 230, 189 and 89 mK, respectively. Crystals of similar compounds containing lanthanum manganese nitrate can be grown with small amounts of radioactive lanthanide ions, and experiments by NMRON would determine their nuclear spins and moments.

Since the lighter members of the 4f series can replace lanthanum in the magnesium compounds, they presumably would do so also in compounds with 3d ions.

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