

ENHANCED NUCLEAR MAGNETISM

B. BLEANEY

Clarendon Laboratory, Parks Road, Oxford, U.K. OX1 3PU

[Received March 1992]

ABSTRACT-Enhanced nuclear magnetism is of particular interest in Van Vleck paramagnets, in which the electronic ground state is a singlet or non-Kramers doublet. The enhancement of the nuclear moment arises through admixture of electronic magnetic moment by the hyperfine interaction. Magnetic resonance measurements on ions of the lanthanide group, using both electromagnetic and acoustic waves, are surveyed. In some compounds an ordered magnetic state is observed at milliKelvin temperatures.

1- PREFACE

The earliest direct measurements of atomic magnetic moments were based on the deflection of atoms by a magnetic field gradient [1, 2]. The results agreed with values from optical Zeeman spectroscopy, and with those calculated from the orbital and spin magnetic moments, interacting through the spin-orbit coupling. Values of nuclear magnetic moments were deduced indirectly from optical spectroscopic measurements of the hyperfine interaction. It soon became apparent that nuclear moments

were not easily predictable, nor simply related to the nuclear magneton, even for the proton with spin $1/2$. The neutron, though an uncharged particle, was also found to have spin $1/2$, and a magnetic moment.

In 1939 Rabi [3] took the bold step of making direct measurements of nuclear moments by magnetic resonance, detected through changes in the deflection of molecular beams by magnetic field gradients. Interrupted by the second world war, this method was overtaken by simpler radio-frequency techniques, but the use of atomic or molecular

beams continued to be developed for measurements of many kinds; a detailed account is given by Ramsey [4]. High precision can be obtained, and since 1963 [5] the unit of time has been defined as the interval containing exactly 9 192 631 770 cycles of the hyperfine frequency in zero magnetic field of the stable isotope (mass 133) of the caesium atom.

In 1944-6, two forms of magnetic resonance in condensed matter were developed independently. The first electron

paramagnetic resonance (EPR) experiments were carried out in the U.S.S.R. by Zavoisky [6] on manganese ions in solution and in solids. The electronic magnetic moment is much greater than any nuclear moment, and the frequencies used by Zavoisky were of order 500 MHz. These measurements were made at room temperature, where spin-lattice relaxation rates are sufficiently fast to allow the electron spins to reach thermal equilibrium, even in a solid.

n	Configuration	Atom	Divalent ion	Trivalent ion	ξ_J
2	3H_4	-	-	Pr^{3+}	0.805
4	5I_4	Nd	Nd^{2+}	Pm^{3+}	0.603
6	7F_0	Sm	Sm^{2+}	Eu^{3+}	
8	7F_6	-	-	Tb^{3+}	1.492
10	5I_8	Dy	Dy^{2+}	Ho^{3+}	1.242
12	3H_6	Er	-	Tm^{3+}	1.164

Table 1. Ground configuration for some non-Kramers atoms and ions of the 4f group, with n electrons in the 4f shell. Note that the atoms, not the ions, also have two electrons filling the 6s shell. Values of ξ_J are rounded to the third decimal place.

In condensed matter, nuclear magnetic resonance (NMR) was observed in the U.S.A. at frequencies of order 10 to 50 MHz [7, 8]. The nuclei were protons in water, the advantage of a liquid with low viscosity being that the resonance

lines have an exceedingly small width because of motional narrowing. A further important point is that spin-lattice relaxation rates are not prohibitively slow, as would be expected in a solid. Early efforts by Gorter [9] to observe

NMR at low temperatures in solids were defeated by excessively long times to achieve thermal equilibrium. The first successful experiments below room temperature were in Oxford [10] and extended to protons in liquid hydrogen at 20 K [11].

The effects considered in this review involve both nuclear and electronic moments, coupled together through the large magnetic field exerted on the nucleus by the surrounding atomic electrons - the hyperfine interaction. Such effects occur quite generally, but this article is concerned mainly with the rare earth group, with magnetic electrons in the 4f shell. For the trivalent ions the

electronic configurations are listed in Table 1.

Most ions of the lanthanide group have stable isotopes of odd mass. Nuclei with an odd number of protons have a single stable isotope with a large nuclear magnetic moment; the exceptions are La, Eu & Yb, that each have two stable isotopes. Nearly all the nuclei with an even number of protons have a range of isotopes, mostly of even mass and nuclear spin $I = 0$, but with some isotopes of odd mass; these have nuclear spins and relatively small nuclear moments. Table 2 lists their mass, spin, unenhanced magnetic resonance frequency and hyperfine interaction constant.

Ion	Isotope	I	$\gamma_I/2\pi$ MHzT ⁻¹	A_J/h MHz
Pr	141	5/2	+12.93	+1093
Sm	147	7/2	-1.76	-240
	149	7/2	-1.45	-193
Eu	151	5/2	+10.49	-
	153	5/2	+4.63	-
Tb	159	3/2	+10.13	+530
Ho	165	7/2	+8.99	+812
Tm	169	1/2	-3.49	-394

Table 2. Nuclear data for the trivalent lanthanide ions mentioned in the text. Values of the isotopic mass, the nuclear spin I, the unenhanced nuclear resonance frequency $\gamma_I/2\pi$ in a field of 1 tesla, and the hyperfine interaction A_J/h .

2. THEORY

Most free atoms possess electronic magnetic moments, while many nuclei have moments, smaller by a factor of order 10^{-3} . In chemical compounds, a few gases (O_2 , NO, NO_2) are paramagnetic, but permanent magnetic moments are generally restricted to transition group ions with partly filled 3d, 4d, 5d, 4f or 5f electron shells.

For electrons, both orbit and spin contribute to the permanent magnetic moment; the Zeeman Hamiltonian is

$$\mathcal{H} = \mu_B(\mathbf{L} + g_S\mathbf{S}) \cdot \mathbf{B} = \mu_B g_J(\mathbf{J} \cdot \mathbf{B}) \quad (1)$$

μ_B is the Bohr magneton, and g_S is very close to 2. Diagonal terms give a first order Zeeman effect; in second order, quadratic terms produce an induced moment [12], often known as "Van Vleck paramagnetism". In an applied field with component B_x , the quadratic energy shift may be written as

$$W = - (a_x/2) (g_J \mu_B B_x)^2 \quad (2)$$

with similar terms for the y, z axes. In many compounds the effects are anisotropic, and the x, y, z axes are then the principal axes of a tensor. The parameter a_x gives the "paramagnetic shift", a sum of terms ($2\alpha_x^2/X$), where α_x is a matrix element of (1) between two levels separated by energy X. From (2), the

induced electronic moment is

$$m_x = -dW/dB_x = a_x (g_J \mu_B)^2 B_x \quad (3)$$

The second form in (1) applies where L, S are coupled to a resultant J by spin-orbit interaction, as in the lanthanide group, for which the theory below was derived [13]. If the nucleus has spin I, the Hamiltonian in an applied field B becomes

$$\mathcal{H} = g_J \mu_B(\mathbf{B} \cdot \mathbf{J}) + A_J(\mathbf{J} \cdot \mathbf{I}) - \gamma_N \hbar(\mathbf{B} \cdot \mathbf{I}) \quad (4)$$

here the second term is the magnetic hyperfine interaction, and the third is the true nuclear Zeeman interaction. For a free ion, a further rather complex term is required for the nuclear electric quadrupole interaction; only a simpler form is needed in the following discussion.

The quadratic energy (2) now has the form

$$W = - (a_x/2) (g_J \mu_B B_x + A_J I_x)^2 \quad (5)$$

which contains a cross-term in $B_x I_x$ with magnitude

$$a_x (g_J \mu_B A_J) = \hbar(\gamma_x - \gamma_I). \quad (6)$$

This constitutes the enhanced nuclear Zeeman interaction; $\gamma_x/2\pi$ is the resonant frequency in unit magnetic field along the x-axis, and there are similar

terms for the y, z axes. In the absence of cubic symmetry, anisotropy arises when the coefficients a_x , a_y , a_z are not all equal. Measurements of the NMR frequency may be used to derive indirect values for the Van Vleck moment, since

$$m_x/B_x = (g_J \mu_B / A_J) \hbar (\gamma_x - \gamma_I). \quad (7)$$

This has the advantage that individual contributions from inequivalent ions can be determined, whereas the bulk susceptibility gives only a net value. Quadratic effects of the magnetic hyperfine interaction give rise to a quadrupole-like term

$$P_x I_x^2 + P_y I_y^2 + P_z I_z^2, \quad (8)$$

where

$$P_x = -(a_x/2) A_J^2 = -(A_J/2 g_J \mu_B) \hbar (\gamma_x - \gamma_I). \quad (9)$$

In cubic symmetry the x, y, z components are equal, and their sum becomes a constant that may be ignored. With axial symmetry (8) reduces to

$$P_2 [I_x^2 - I(I+1)/3] \quad (10)$$

with

$$P_2 = (A_J/2 g_J \mu_B) \hbar (\gamma_{\perp} - \gamma_{\parallel}), \quad (11)$$

where the last two subscripts refer to directions perpendicular and parallel to the axis of symmetry. In addition terms

P_1, P_3 arise from true quadrupole interactions [14] with field gradients of the 4f electrons on the parent ion and the remainder of the lattice respectively.

3. LANTHANIDE IONS

In condensed matter, a magnetic ion is subjected to an electric field set up by the surrounding ions, the "crystal field". This is represented by an electrostatic potential of complex form that depends on the crystal lattice, and its symmetry. If the symmetry is cubic, the levels may be singlets, doublets, triplets or quartets. In lower symmetry, ions with an even number of electrons may have a singlet ground state, but for other ions the levels must retain at least double degeneracy, by Kramers' theorem. In the 4f group, the $2J \pm 1$ electronic levels of a manifold J' are split by amounts ranging up to several hundred wave numbers; at low temperatures, only a few levels have appreciable thermal population. The hyperfine parameter in eq. (4) has form

$$A_J = 2 \mu_B \gamma_N \hbar \langle r^{-3} \rangle \langle J \parallel N \parallel J \rangle \quad (12)$$

for the lanthanide group; the parameter $\langle J \parallel N \parallel J \rangle$ is positive, and so is g_J . Thus the matrix elements that contribute to the cross term of eq. (6) are positive provided that they are within a manifold

of given J . Other terms involving the neighbouring manifolds $J \pm 1$ are of opposite sign, but are generally much smaller because the energy denominators in perturbation theory are much larger. Typically, the energies of manifolds $J+1$ lie at several thousand wavenumbers, while excited states of the same J may be separated only by ten to a few hundred wave numbers. Effects involving the latter are therefore generally dominant, but two exceptions are mentioned below.

For magnetic ions not at a site of cubic symmetry, the effective nuclear Zeeman interaction becomes anisotropic, and for nuclei with $I > 1$, there may be an appreciable nuclear quadrupolar interaction from quadratic effects of the magnetic hyperfine interaction [14]. Such effects occur also for 3d ions, but are more important for lanthanide ions, where the crystal field splittings tend to be smaller, and the hyperfine interaction larger.

In electron spin resonance (ESR) using a large magnetic field, electronic transitions are strongest in which the nuclear magnetic quantum number m_x does not change. The frequency is displaced by the hyperfine interaction, but does not directly involve the nuclear Zeeman interaction. At lower frequencies comparable with those of hyperfine interaction, transitions in which m_z changes are allowed, and the resonant frequen-

cies are then displaced by amounts proportional to the nuclear Zeeman energy, including the "enhanced nuclear Zeeman effect". However, the latter is determined more directly and much more accurately by means of ENDOR. A simple illustration is given by the detailed measurements [15] on the stable samarium isotopes of mass 147, 149 in (La, Sm) Cl_3 . The crystal symmetry is hexagonal, and the trivalent samarium ion (configuration $4f^5$, ^6H) has a number of levels relatively low in energy. The electronic ground state is a Kramers doublet, and the enhancement of the effective nuclear magnetic moment is anisotropic. In fact it is positive for magnetic fields normal to the symmetry axis, but negative for fields along this axis, because effects from excited states of J are then dominant. The second order contribution to the nuclear electric quadrupole interaction was also determined.

Similar terms arise also for an electronic singlet, and were first derived [16] for the trivalent europium ion, $4f^6$, for which the ground state is $J = 0$. Matrix elements to the first excited state $J = +1$ give a negative contribution that nearly cancels the true nuclear Zeeman effect for the singlet. For other ions the enhancement is generally positive, and greatest when there are matrix elements to a low lying crystal field level; the anisotropy may be large. An enhanced

NMR signal can sometimes be followed up to temperatures at which excited levels are populated, if there is rapid relaxation between the electronic levels; the measured parameters are then thermal averages. Results for a range of insulating compounds with axial or cubic symmetry are summarised in section 5.

4. MEASUREMENTS ON CONDUCTING COMPOUNDS

Following the suggestion of Al'tshuler [17] of magnetic cooling by substances with singlet electronic ground states, several investigations began on inter-metallic compounds [18] with conduction electrons, for which thermal contact should be much better than with insulators. Compounds of the ions ^{141}Pr or ^{169}Tm were chosen to minimize exchange interaction, assumed to vary as $(g_J - 1)[J(J+1)]^{1/2}$. Nevertheless, many were found [18] to order at liquid helium temperatures. In general, thulium compounds showed larger enhancement [19], but the nuclear moment is small (Table 2) and $I=1/2$; for Pr, with a larger nuclear moment and $I = 5/2$, it is much easier to remove a large fraction of the nuclear entropy in fields of a few tesla.

Two examples are PrCu_5 , which is hexagonal but shows ferromagnetism below ~ 50 mK [20], and PrTi_3 [21]. The latter

is cubic, and could be cooled to 1.6 mK; extrapolation suggested that ferromagnetic ordering would set in at about 1 mK. Conventional magnetic measurements were used; other early results are surveyed by Teplov [22].

Some conductors with the cubic NaCl structure [23] were investigated by NMR. In compounds without cubic symmetry, the enhancement is often highly anisotropic, and single crystals are needed. The nuclear resonant frequencies have been measured for the hexagonal compound PrNi_5 . The enhancement factors at 1.2 K [24] are 6.56 and 13.13, parallel and perpendicular to the symmetry axis. The corresponding resonance frequencies are 82 and 164 MHzT^{-1} , calculated from $\gamma_I/2\pi = 12.5 \text{ MHzT}^{-1}$. [Enhancement factors have often been quoted without specifying the unenhanced value; for praseodymium, the most recent value is 12.93 MHzT^{-1}]. In this compound the quadrupole splitting parameter P/h is not more than 0.6 MHz, considerably less than $P_2/h \approx +4$ MHz, calculated from eq. (11). Since P_1/h is estimated to be -0.66 MHz, the lattice contribution P_3/h must also be negative.

The small value of P/h is an advantage for magnetic cooling. After adiabatic demagnetisation [25] from a field of 6 T at temperatures between 10 & 29 mK, 0.2 mK was reached, though ferromagnetic order sets in at 0.40(2) mK. The

enhancement factor measured for the randomly oriented sample is 12.2(5); this corresponds to a resonance frequency of 159 MHzT^{-1} , rather higher than the mean value of 137 MHzT^{-1} , derived from the resonance values for the single crystal. The discrepancy may arise because the sample was not completely random in orientation, or from small induced moments on the nickel ions, that contribute to the bulk susceptibility but do not affect the nuclear resonance frequencies.

The classic compound for magnetic cooling was cerium magnesium nitrate, $\text{Ce}_2\text{Mg}_3(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$, for which the lowest temperature reached after demagnetisation is about 3 mK. The electronic entropy is $R \ln 2$, but the nuclear entropy of PrNi_5 is $R \ln 6$; this makes it a useful substance for magnetic cooling into the sub-millikelvin range. With it as a first stage, and metallic copper as a second stage, a temperature of 0.027 mK has been reached after adiabatic demagnetisation [26].

5. MEASUREMENTS ON INSULATING COMPOUNDS

The first investigations on insulating compounds began [27] at Kazan in 1967 with hydrated praseodymium sulphate, followed by other single crystals grown from aqueous solution. A wide range of

results has been reviewed recently by Aminov and Teplov [28]. The discussion below is mainly limited to measurements in Oxford on tetragonal crystals with the zircon structure, together with the elpasolites (cubic at room temperature). In most cases the presence of singlet ground states was revealed by optical Zeeman spectroscopy; the data in Table 3 were then obtained by nuclear magnetic resonance.

In many cases the resonant frequencies are highly anisotropic, particularly when large matrix elements to a low lying level exist for one direction of the magnetic field. The NMR signal can be followed up to temperatures at which some excited levels are populated if the hyperfine field is motionally averaged by rapid relaxation between the electronic levels. The measured parameters are then thermal averages; an example is PrVO_4 , where the results [29] were fitted from 1 to 20 K by including parameters for the first and second excited states.

Holmium vanadate, HoVO_4 has been studied in considerable detail. The crystal field splittings, measured by high-resolution optical spectroscopy [30], showed that the singlet ground state and doublet at 21 cm^{-1} , are nearly pure states: $|J_z\rangle = |0\rangle$ and $| \pm 1 \rangle$ respectively. Application of a magnetic field confirmed that the former has almost no magnetic moment along the c-axis, but a

Compound	$\gamma_{ }/2\pi$	$\gamma_{\perp}/2\pi$	P/h
PrVO ₄	24.5	77.62	(+)3.35(3)
HoVO ₄	15(5)	1526(3)	+25.9(3)
LiTmF ₄	7.94(1)	245(1)	-
TmPO ₄	11.3	276	-
TmVO ₄	3450(10)*	24 & 94	
TmAsO ₄	706.5*	360 & 60	

Table 3. Enhanced NMR data for insulating compounds with tetragonal symmetry. Values of $(\gamma/2\pi)$ in MHzT⁻¹, and P/h in MHz.

The ground states of TmVO₄ and TmAsO₄ are doublets, split by Jahn-Teller distortions below 2.156 K and 6.1 K respectively. These lower the symmetry and there are domains; the constants marked * are estimated values, extrapolated to T= 0 K.

large moment normal to it because of matrix elements between the singlet and the doublet.

The single stable isotope is ¹⁶⁵Ho, with I = 7/2, and (unenhanced) 9.0(1) MHzT⁻¹. Novel circuits for NMR experiments at 500 MHz were used [14] to determine the principal resonance parameters (see Table 3); values for a crystal of YVO₄ containing 2% Ho are almost identical. At 1.3 K the anisotropy in the induced magnetic moment is over 200:1, but is considerably less at 20 K. The contributions to the nuclear electric quadrupole interaction are estimated to be P₁/h = -35(2) MHz, P₂/h = +35.3 MHz; since these almost cancel, the measured value P/h = (+)25.6(3) MHz implies a lattice

contribution P₃/h ≈ +25 MHz. The NMR signals are strong, because the enhancement applies also to the r.f. field, provided this is in the (001) plane, and normal to the steady field. Essentially the r.f. field causes the induced moment to oscillate in direction, producing a greatly enhanced r.f. field at the nucleus through the hyperfine interaction. A further study [31] has provided more detail and a better fit between optical spectroscopy and NMR results.

TmPO₄ [32] also shows considerable anisotropy (see Table 3). Changes above 4 K were fitted to crystal field levels determined by optical and Raman spectroscopy. The anisotropic paramagnetic shifts in the NMR spectrum of ³¹P (I =

1/2) were found to be proportional to the electronic susceptibilities.

For TmVO_4 and TmAsO_4 the tetragonal field leaves non-Kramers doublets as ground states, but these are split by Jahn-Teller distortions at temperatures below 2.156(5) K [33] and 6.13(3) K respectively [34]. At lower temperatures the enhanced NMR frequency is unusually large along the c-axis, particularly so for the former, since the doublet splitting is rather small, with a maximum value of $2.97(4) \text{ cm}^{-1}$ for $T = 0 \text{ K}$ [35]. Zeeman effects in some excited electronic states have been observed in fields up to 7 T [36].

Elpasolite compounds with the formula $\text{Cs}_2\text{NaLnCl}_6$ are cubic at room temperature, but many undergo structural transitions at lower temperatures. Three compounds with the non-Kramers trivalent ions $\text{Ln} = \text{Pr, Tb and Tm}$ have singlet states; for these, investigations by enhanced NMR [37] have revealed small tetragonal distortions, but $\text{Cs}_2\text{NaHoCl}_6$ was shown to remain cubic [38]. It differs in that the ground state of the trivalent holmium ion is a non-Kramers doublet, split in second order by the Zeeman effect; this produces a temperature-dependent anisotropy consistent with the cubic symmetry. Below 4 K it was studied by enhanced NMR of the ^{165}Ho ions, together with the NMR paramagnetic shifts of the diamagnetic Na and Cs

ions. Electron spin resonance of the impurity ions Gd^{3+} , Dy^{3+} , Er^{3+} and Yb^{3+} , and of the holmium ion [39] has also been observed. The latter was shown to be consistent with theory [40]; an improved theory of the nuclear interactions was given later [41].

6- ENHANCED ACOUSTIC RESONANCE

Longitudinal acoustic waves were used for enhanced nuclear resonance in a single crystal of PrF_3 [42] at 20-40 MHz; much higher frequencies (0.8 GHz) were used later for HoVO_4 [43]. The acoustic strains produce an effect in third order, involving both the applied magnetic field and the hyperfine interaction. Essentially the fluctuating acoustic strain modulates the direction of the electronic moment induced by the applied field; at the nucleus, through the magnetic hyperfine interaction, this produces an oscillating magnetic field, giving rise to resonance transitions within the nuclear spin system. Matrix elements from electric quadrupole interactions also cause transitions, but the intensity is smaller at a given frequency [44].

For HoVO_4 , measurements were made with a magnetic field in the (001) plane; acoustic waves, propagated in this plane, were generated by a transducer of

zinc oxide, grown directly onto a single crystal by sputtered epitaxial deposition. Pulses of order 100 ns duration were applied, the transducer being switched alternately from transmit to receive. Signals are observed from two sets of transitions in which the nuclear magnetic quantum number changes either by ± 1 , or by ± 2 ; the former are much stronger, and have maxima and minima at different orientations of the magnetic field. Also, the intensities are larger by a factor 100 for acoustic waves propagated along a [100] axis than for similar waves along a [110] axis. The non-resonant magneto-acoustic absorption has also been studied and analysed [45].

As in magnetic resonance with electromagnetic waves, the signal intensity is proportional to the energy quantum and the difference in population of the two levels involved; it has contributions involving both second and fourth powers of the frequency. The process of absorption of energy from an acoustic wave is identical with the "direct process" by which thermal phonons induce transitions in the spin system, maintaining it in thermal equilibrium with the lattice. Rates calculated from the acoustic absorption measurements are in marked contrast to the overall relaxation rate, determined by observing recovery of the signal after saturation [46]. Between 0.08 and 1.33 K, the latter is faster by a factor 10^{13} to 10^{15} at a

field of 5 millitesla. Though transverse waves may give faster rates of relaxation, this enormous discrepancy must be ascribed primarily to paramagnetic impurities. The mechanism has been identified by novel experiments [47] on the enhanced holmium spin system in holmium vanadate, magnetized at a temperature of 50 mK in a field of 2 T, and then demagnetized to about 5 mK in a field of 50 mT. The results suggest that energy is transferred by spin-spin interaction to impurity ions with electronic moments. For example, the electronic resonance frequency of dysprosium would be 7 GHz, with a width 1.5 GHz resulting from interactions with the enhanced holmium moments. These impurity spins "talk" to a wide band of phonons that transmit energy rapidly to the dilute liquid Helium 3 bath at 100 mK, the last barrier being the Kapitza resistance at the surface. Such a mechanism may well account for the much faster relaxation rates observed directly.

7- THE ORDERED STATE

Most electronic paramagnetic compounds enter an ordered state at milliKelvin or much higher temperatures; nuclear moments order only at much lower temperatures (58 nanoKelvin in copper metal). Obviously, enhanced

nuclear magnets form an intermediate group. Holmium vanadate enters an antiferromagnetic state at about 4.5 mK, close to the predicted value [48]; this has been studied by nuclear orientation [49], [50] of radioactive isotope $^{166\text{m}}\text{Ho}$ ($I = 7$), as well as by nuclear quadrupole resonance of ^{51}V [51]. A neutron diffraction study [52] has also produced a structure consistent with the proposed model.

In TmVO_4 , enhanced nuclear cooling produced no signs of ordering [53] at suggested temperature [33] of 0.2 mK.

For TmPO_4 a different approach was used - first dynamical nuclear polarisation (60%) of the enhanced thulium moments by "pumping" on an impurity ion, Yb^{3+} , followed by "adiabatic demagnetisation in the rotating frame" [54], [55]. The existence of the ordered state was monitored through the NMR signal of the nucleus ^{31}P .

The elpasolite $\text{Cs}_2\text{NaHoCl}_6$ is of particular interest because its electronic ground state is a non-Kramers doublet (see above). It orders at 4.8 mK, and measurements of magnetic susceptibility and heat capacity have been made [56], [57]. In a neutron diffraction study [58], no antiferromagnetic diffraction peaks were observed, but enhanced antiferromagnetic resonance has been detected [59]. A theoretical study of electronic and nuclear order suggests that a transition at about 600 mK [61] arises

from electronic quadrupole-quadrupole interactions.

REFERENCES

- [1] Stern, O., *Zeits.f. Physik Z.*, 418 (1921).
- [2] Gerlach, W. and Stern, O., *Ann.Physik*, **74**, 673 (1924); *Ann.Physik*, **76**, 163 (1925).
- [3] Rabi, I. I., Millman, S., Kusch, P. and Zacharias, J. R., *Phys.Rev.*, **55**, 526, (1939).
- [4] Ramsey, N. F., "Molecular Beams", Clarendon Press, Oxford (1956).
- [5] Essen, L., *Vistas Astron.*, **2**, 45 (1969).
- [6] Zavoisk, E., *Fiz. Zh.* **9**, 211 (1945).
- [7] Purcell, E. M., Torrey, H. C. and Pound, R.V., *Phys. Rev.* **70**, 474 (1946).
- [8] Bloch, F., Hansen, W. W., and Packard, M., *Phys. Rev.* **70**, 474 (1946).
- [9] Gorter, C. J., *Paramagnetic Relaxation* (Elsevier), 126 (1947).
- [10] Rollin, B. V., *Nature* **158**, 669 (1946).
- [11] Rollin, B. V. and Hatton, J., *Nature* **159**, 201 (1947).
- [12] Van Vleck, J. H., *Phys. Rev.*, **31**, 587 (1928).
- [13] Baker, J. M. and Bleaney, B., *Proc. R. Soc. Lond.* **A245**, 156 (1958).
- [14] Bleaney, B., Robinson, F. N. H., and Wells, M. R., *Proc. R. Soc.Lond.* **A362**, 170 (1978).
- [15] Chan, I. Y. and Hutchison, C.A. Jr., *Phys.*

- Rev. **B5**, 3387 (1972).
- [16] Elliott, R. J., Proc. Phys. Soc. **B70**, 119 (1957).
- [17] Al'tshuler, S. A., JETP lett. **3**, 112 (1966).
- [18] Andres, K., Cryogenics 473-478 (1978).
- [19] Andres, K. and Bucher, E., J. App. Phys. **42**, 1522 (1971).
- [20] Andres, K., Bucher, E., Schmidt, P. H., Maita, J. P. and Darack, S., Phys. Rev. **B11**, 4364 (1975).
- [21] Andres, K. and Darack, S., Phys. Rev. **B10**, 1967 (1974).
- [22] Teplov, M. A., in Crystal Field Effects in Metals and Alloys, (ed. A. Furrer, Plenum Press, N. Y.), 318 (1977).
- [23] Jones, E. D., Phys. Rev. Lett. **19**, 432 (1967); Phys. Rev. **180**, 455, (1969).
- [24] Kaplan, N., Williams, D. LL. and Grayevsky, A., Phys. Rev. **821**, 899 (1980).
- [25] Kubota, M., Folle, H. R., Buchal, Ch., Mueller, R. M. and Pobell, F. Phys. Rev. Lett. **45**, 1812 (1980).
- [26] Ishimoto, H. N., Nishida, T., Furubayashi, M., Shinohara, Y., Takano, Y., Miura, Y. and Ono, K., J. Low Temp. Phys. **55**, 17 (1984).
- [27] Al'tshuler, S. A., and Teplov, M. A., JETP Lett. **5**, 167 (1967).
- [28] Aminov, L. K. and Teplov, M. A., Sov. Sci. Rev. A Phys., **14**, 1(1990).
- [29] Bleaney, B., Harley, R. T., Ryan, J. F., Wells, M. R. and Wiltshire, M. C. K., J. Phys.C. **11**, 3059 (1978).
- [30] Battison, J. E., Kasten, A., Leask, M.J. M. and Lowry, J. B., Phys. Lett. **55A**, 173 (1975).
- [31] Bleaney, B., Gregg, J. F., Hansen, P., Huan, C.H.A., Lazzouni, M., Leask, M. J. M., Morris, I. and Wells, M. R., Proc. R. Soc. Lond. **A416**, 63 (1980).
- [32] Bleaney, B., Pasman, J. H. T. and Wells, M. R., Proc. R. Soc. Lond. **A387**, 75-90 (1983).
- [33] Bleaney, B. and Wells, M. R., Proc. R. Soc. Lond., **A370**, 131-153 (1980).
- [34] Bleaney, B., Gregg, J. F., Leask, M. J. M. and Wells, M. R., Proc. R. Soc. Lond. **A394**, 69-85 (1984).
- [35] Becker, P. J., Leask, M. J. M. and Tyte, R. N., J. Phys. C. **5**, 2027-2036 (1972)
- [36] de Wolf, I., Janssen, P. amd Bleaney, B., Phys. Lett. **108A**, 221 (1985).
- [37] Bleaney, B., Stephen, A. G., Walker, P. J. and Wells, M. R., Proc. R. Soc. Lond. **A381**, 1 (1982).
- [38] Bleaney, B., Stephen, A. G., Walker, P. J. and Wells, M. R., Proc. R. Soc. Lond. **A376**, 235 (1982).
- [39] Bleaney, B., Stephen, A. G., Sung Ho Choh and Wells, M. R., Proc. R. Soc. Lond. **A376**, 253 (1982).
- [40] Bleaney, B., Proc. R. Soc. Lond. **A376**, 217 (1982).
- [41] Abragam, A. and Bleaney, B., Proc. R. Soc. Lond. **A382**, 61 (1982).

- [42] Al'Tshuler, S. A., Duglav, A. Kh., Kasanov, I. G. and Teplov, M.A., JETP Lett. **29**, 625 (1979).
- [43] Bleaney, B., Briggs, G. A. D., Gregg, J. F., Huan, C. H. A., Morris, I. D. and Wells, M. R. Proc. R. Soc. Lond. **A416**, 93 (1988).
- [44] Bleaney, B. and Gregg, J. F., Proc. R. Soc. Lond. **A413**, 313 (1987).
- [45] Bleaney, B., Gregg, J. F., Huan, C. H. A., Morris, I. D. and Wells, M. R., Proc. R. Soc. Lond. **A416**, 75 and 83 (1988).
- [46] Suzuki, H., (private communication) (1986).
- [47] Jacquinet, J-F., Gregg, J. F. Roinel, Y., Fermon, C. and Bouffard, V., J. Low Temp. Phys. **64**, 115 (1986).
- [48] Bleaney, B., Proc. R. Soc. Lond., **A370**, 313 (1980).
- [49] Allsop, A. L., Bleaney, B., Bowden, G. J., Nambudripad, N., Stone, N. J. and Suzuki, H. Proc. R. Soc. Lond., **A372**, 19 (1980).
- [50] Clark, R. G., Allsop, A. L., Stone, N. J. and Bowden, G. J., J. Phys. C. **20**, 797 (1987).
- [51] Bleaney, B., Clark, R. G., Gregg, J. F. Roinel, Y., and Stone, N. J., J. Phys. C **20**, 3175 (1987).
- [52] Suzuki, H., Ohtsuka, T., Kawarazaki, S., Kunitoni, N., Moon, R. M. and Nicklow, R. M., Solid State Comm. **49**, 1157 (1984).
- [53] Suzuki, H., Inoue, T., Higashino, Y. and Ohtsuka, T., Physics Letters **77A**, 185 (1980).
- [54] Abragam, A., Bouffard, V., Fermon, C., Fournier, G., Gregg, J. F., Jacquinet, J-F. and Roinel, Y., Comptes Rendus, **99**, 509 (1984).
- [55] Fermon, C., Gregg, J. F., Jaquinot, J-F., Roinel, Y., Bouffard, V., Fournier, G. & Abragam, A., J. Phys. (Paris), **47**, 1053 (1986).
- [56] Suzuki, H., Miyamoto, M., Masuda, Y. and Ohtsuka, T., J. Low. Temp. Phys., **48**, 297 (1982).
- [57] Suzuki, H., Masuda, Y, Miyamoto, M., Dakatsume, S., Walker, P. J. and Ohtsuka, T., J. Mag. Magn. Mat., **31**, 741 (1983).
- [58] Masuda, Y., Suzuki, H., Ohtsuka, T. and Tamaki, A., Jap. J. Applied Physics, **26**, Supplement 26-3, 433 (1987).
- [59] Suzuki, H., Masuda, Y. and Arthur, J., Jap. J. Appl. Phys, **26**, Supplement 26-3, 437 (1987).
- [60] Bowden, G. J., Elliott, R. J. and Oitmaa, J., Proc. R. Soc. Lond., **A399**, 73 (1985).
- [61] Bongers, E., Brom, H. B., Veenendal, E. J., Huiskamp, W. J. and Amberger, H. D., Physica **115B**, 72 (1983).