$$\frac{C_V}{3R}=\int_0^{\omega_{\max}} d\omega\left(\frac{\omega}{T}\right)^2 \frac{e^{\omega/T}}{(e^{\omega/T}-1)^2}\rho(\omega)\,, \qquad (2)$$

where R is the gas constant, $\omega_{\max}$ the maximum frequency of the crystal, and T the temperature measured in energy units, has been computed for all three metals. Tables I–III compare the calculated specific heat with measured values,[5] for the vibrational spectra of Be, Mg, and Zn, respectively. The agreement is quite good in all cases, although specific heat comparisons do not provide a good test.

TABLE III. C_V for zinc (cal/g).

T (°K)	Computed value	Measured value
72	0.0538	0.0573
173	0.0826	0.0814
300	0.0882	

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The authors would like to express their appreciation to D. Naliboff and D. Houston for their competent programming of the equations.

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[5] *Handbook of Chemistry and Physics* (Chemical Rubber Publishing Company, Cleveland, Ohio, 1963).

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Electron Spin Resonance Studies with Superconducting Magnets: The Spectrum of Dy^{3+} and Sm^{3+} in CaF_2

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An electron spin resonance spectrometer has been constructed using strong magnetic fields up to 46 000 G generated by a superconducting magnet. It is being used for the measurement of the magnetic properties of transition elements in ionic crystals such as (a) small g factors, (b) energy level separations up to 20 cm^{-1}, (c) isotropic and anisotropic exchange terms in spectra of pairs of paramagnetic ions, (d) spin-lattice relaxation times at high magnetic fields. The method is illustrated in the measurements of (1) the energy level separation of $\Gamma_8-\Gamma_7$ levels of Dy^{3+} in CaF_2 which is found to be $7.3_5\pm0.2$ cm^{-1}; (2) the g factors of the tetragonal spectrum of Sm^{3+} in CaF_2 which are found as $g_{\parallel}=0.907\pm0.01$, $g_{\perp}=0.544\pm0.015$.

INTRODUCTION

ELECTRON spin resonance methods have been widely used in determining the magnetic properties of transition elements in ionic and semiconducting crystals.[1] Most of these experiments have been performed with magnetic fields of less than 20 000 G.[2] The availability of superconducting magnets with fields of the order of 50 000 G permit a number of additional experiments of interest. These experiments are of the kind: (a) Measurements of energy level separations of the order of 3–20 cm^{-1}. (b) Measurement of small g factors, i.e., $g\ll1$. (c) Measurement of some isotropic or anisotropic exchange splittings of neighboring paramagnetic ions. (d) Spin-lattice relaxation phenomena in high magnetic fields.

Many iron group and rare-earth elements have an energy level scheme in which a few levels are closely bunched together. Examples of such ions are V^{3+}, Cr^{4+} (d^2) in trigonal fields which have a singlet as a ground state and a doublet at 7–10 cm^{-1} above the singlet. A similar case is Fe^{2+} (d^6) in noncubic fields. In some crystal hosts, transitions between the two levels of the non-Kramers doublet can be induced. However, transitions between the singlet and the doublet cannot be seen with conventional resonance spectrometers and magnetic fields. With very strong magnetic fields one of the doublet levels can be brought close enough to the singlet so that transitions between these levels can be effected. One usually can find a suitable magnetic-field orientation with respect to the crystal axis which will permit transitions of the type $\Delta S_z=\pm1$ of sufficient intensity. The appropriate spin Hamiltonian is

$$\mathcal{H}=g_{\parallel}\beta HS_z+g_{\perp}\beta(H_xS_x+H_yS_y)+D(S_z^2-\tfrac{1}{3}S(S+1))+E(S_x^2-S_y^2)\,, \qquad (1)$$

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[1] See, for example, W. Low, *Paramagnetic Resonance in Solids* (Academic Press Inc., New York, 1960).

[2] S. Foner and W. Low, Phys. Rev. **120**, 1585 (1960), have performed ESR experiments using pulsed magnetic fields of the order of 2 000 000 G. However, this method has the disadvantage of poor accuracy in the field measurements. Relaxation effects due to fast variation of the magnetic field as a function of time effect the intensity of the spectrum. It can be used, however, to some advantage in the measurement of relaxation times at high magnetic fields [L. Rimai (private communications)].

with $S=1$. When $E=0$ the initial separation of $|\pm 1\rangle$ levels from the $|0\rangle$ level can be determined. When $E\neq 0$ then the separation of one of the nearly degenerate levels from the $|0\rangle$ level can be measured.

Of greater interest are the rare-earth and uranium group elements. Here the various J levels are split into a number of Stark levels through the crystal field. In many cases, the total amount of the splitting of 5–10 Stark levels may be only of the order of a 100 cm^{-1}. There are levels separated by less than 20 cm^{-1}. The position of these levels can be estimated by diverse methods such as by measuring (1) the magnetic susceptibility or specific heat as a function of temperature, (2) the spin-lattice relaxation time as a function of the temperature and evaluation of the Orbach process,[3,4] (3) the fluorescence in the optical spectra, (4) the Faraday rotation, and (5) the intensity of the spin resonance of the excited state as a function of the temperature, provided this resonance can be observed in the temperature range where this level is still sufficiently populated. Most of these methods are not very accurate and permit the evaluation of the level only to an accuracy of about 1 cm^{-1}. Others do not work well in dilute salts which are used in spin resonance methods.

Since many of the g factors of rare-earth ions are large, one can bring levels, which in the absence of a magnetic field are far apart, close together and even cause them to cross.[5] Assuming a magnetic field of about 50 000 G and g factors of about 6 for the two levels, and operating K-band frequencies, one can determine energy levels separated by about 15 cm^{-1}.

The g factors in the rare-earth ions depend on the crystal-field parameters $A_n{}^m\langle r^n\rangle$. In general there are many more crystal-field parameters than the measured three or less g factors. Paramagnetic resonance measurements of these g factors on one single Kramers doublet does not permit the evaluation of these crystal-field parameters. These can be determined from the optical spectra which give the average value of the $A_n{}^m\langle r^n\rangle$ over all the optical levels. There are reasons to believe that the crystal-field parameters may depend to some extent on the various $J\Gamma$ levels because of the shielding and antishielding factors,[6,7] i.e., that $A_n{}^m\langle r^n\rangle_{\mathrm{true}}$ $(1-p_n{}^m(J,\Gamma))$, where $p_n{}^m$ is a shielding factor. It is, therefore, of interest to measure sufficient g factors and a separation of Stark levels of a given J level in order to determine the $A_n{}^m\langle r^n\rangle$ for this particular level and to compare it with the weighted average over all optical levels.

Separation of energy levels in the range of 1–20 cm^{-1} are also found in exchange coupled pairs of paramagnetic ions. For example the spectrum of exchange couplet Ir^{4+} in $\mathrm{K_2IrPtCl}^6$ can be explained by the interaction spin Hamiltonian[8]

$$\begin{aligned}\mathcal{H}_{ij}=J_1\mathbf{S}^i\cdot\mathbf{S}^j+D(2S_z{}^iS_z{}^j-S_x{}^iS_x{}^j-S_y{}^iS_y{}^j)&\\ +E(S_x{}^iS_x{}^j-S_y{}^iS_y{}^j)&,\\ \text{with } S^i=S^j=\tfrac{1}{2},\quad \text{and } J_1=8\ \mathrm{cm}^{-1}.&\quad(2)\end{aligned}$$

The isotropic exchange parameter can be determined by one or more of the methods described above. Strong magnetic fields would permit a more accurate determination of these parameters.

Some of the g factors in paramagnetic resonance are smaller than one. An example of this is Sm^{3+}. A magnetic field of about 50 000 G and at K_μ band frequency would permit the determination of g factors as small as 0.2.

Finally, it would be very interesting to determine the spin-lattice relaxation in high magnetic fields, in particular, the magnetic-field dependence of the direct process, the Orbach process, and the Raman process both for Kramers and non-Kramers doublets.

We report here the techniques of using superconducting magnets for spin resonance experiments. We illustrate this by two types of experiments (a) the determination of the $\Gamma_8-\Gamma_7$ separation of Dy^{3+} in $\mathrm{CaF_2}$ and (b) the determination of the small g factors of Sm^{3+} in $\mathrm{CaF_2}$. Experiments as outlined in (c) and (d) are in progress.

EXPERIMENTAL DETAILS

We briefly describe here the experimental setup. A fuller description of the apparatus will be given elsewhere.

The experiments were made with a stabilized K_μ spectrometer operating between 15 000–18 000 Mc/sec and at liquid-helium temperature. The cavity and the stainless-steel waveguide section were enclosed in a 1-in. i.d. thin stainless-steel tubing. This tubing was inserted into the bore of the superconducting magnet. The modulation coils were wound around the stainless-steel tubing concentric with the cylindrical cavity. Fifty to 100 turns of thin pure copper wire were sufficient for a modulation depth of about 80 G. The heat dissipation at such modualtion depth was not excessive. About 8 liters of liquid helium were required to cool the superconducting magnet and waveguide section to fill the Dewar for a 3–4-h experiment.

The superconducting magnet was about 4 in. long

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[3] R. Orbach, Proc. Roy. Soc. (London) **A264**, 458 (1961).

[4] C. B. P. Finn, R. Orbach, and W. P. Wolf, Proc. Phys. Soc. (London) **77**, 261 (1961).

[5] An interesting experiment is to measure the fluorescence or absorption of light when the energy levels cross. The polarization of the light or the angular distribution of the light would be expected to change. This experiment is very similar to the optical atomic level crossing experiments except that in the case of a crystal you have the advantage of the symmetry planes and axes. Such an experiment should permit the accurate determination of g factors and splittings of both of the ground state as well as optically excited states of transition group elements in crystals.

[6] R. E. Watson and A. J. Freeman, Phys. Rev. **133**, A1571 (1964).

[7] W. Low, Enrico Fermi Summer School, Varena, 1963 (to be published).

[8] J. H. E. Griffiths, J. Owen, J. G. Park, and M. F. Partridge, Proc. Roy. Soc. (London) **A250**, 84 (1959).

and i.d. slightly larger than 1 in.[9] The power supply was a standard stabilized supply. The magnetic field could be swept by putting a small dc error signal in the sensing elements of the power supply. The rate of sweep could be controlled by varying the magnitude of the error voltage. Sweeps of several minutes to several hours over the range of 46 000 G could be achieved without difficulty. A superconducting switch permitted the magnet to be operated in the persistent mode.

The measurement of the magnetic field presents a little difficulty. The inhomogeneity of this particular magnet over a sample volume of 0.02 cm^3 and a sample height of about 2 mm was of the order of 10–15 G at the center field of about 20 000 G. This inhomogeneity was estimated by putting small crystals with paramagnetic impurities of known linewidth and g factors. Calibrating the sweep, one could estimate the broadened linewidth in the superconducting magnet. The linewidth would probably be even larger for a proton resonance sample which has a larger volume and would not permit an accurate or easy determination of the magnetic field. (Since our spectrometer was inserted in the liquid-helium bath, a solid-state proton sample would have to be used. However, one could use also a liquid sample by using an inner Dewar so that the spectrometer and proton resonance could be operated at any temperature.) We have used a more primitive method. By placing various paramagnetic samples of known g factors in the magnetic field, we have made an experimental plot of the magnetic field H against the current I. It was found that the magnetic field was not quite linear with the current, particularly at high magnetic fields. There is also a noticeable hysteresis. At center band, near 20 000 G, and sweeping rapidly over the whole range back forth the hysteresis amounts to 100–150 G. In all measurements reported here were made with slow sweep rates and always in the same direction. The maximum error in the determination of the magnetic field is estimated to be about 0.2%.

Once a line was observed on the scope or by phase-sensitive detection the superconducting solenoid was switched to the persistent mode. In this case the line stayed at a constant magnetic field with only a very small drift.

Such a system, with a more homogenous magnet, could be used for magnet of frequency stabilization. It also permits the use of the continuous averaging technique[10] to greater advantage. In this technique the signal and the noise are fed into a multichannel analyzer. The signal is additive, i.e., proportional to the number n of sweeps across the line, whereas the noise is proportional to $n^{1/2}$, so that the signal to noise is proportional to $n^{1/2}$. This is also true for phase-sensitive detection. However, in practice it is found that low-frequency noise components are difficult to filter out, even with large time constants in the R.C. filter of lock-in detector. A system, such as a superconducting magnet, in which the magnetic field is constant and ripple is nearly absent, lends itself admirably to such a technique.

THE SPECTRUM OF Dy^{3+} IN THE CUBIC FIELD OF CaF$_2$

The cubic field of CaF$_2$ splits the $J=15/2$ of the $^6H_{15/2}$ level into three Γ_8, one Γ_7 and one Γ_6. The ground state is a $\Gamma_8^{(1)}$ and the g factors within the Γ_8 quartet have recently been determined by Bierig and Weber[11] as 2.63±0.05, 5.48±0.15, and 14±1. The next excited state Γ_7 has been measured by Low[12] as $g=7.47\pm0.03$ and by the above authors at 7.52±0.05. These authors estimate from the temperature dependence of the intensity of the Γ_7 level to be at 8.5±1.0 cm^{-1} above the Γ_8 level. All other levels are far removed. In addition Bierig and Weber observed many lines associated with tetragonal or trigonal symmetries and with g factors varying from 1.50 to 16.

This spectrum, therefore, has a wealth of lines which can be used for field calibration. We have confirmed many of the g factors determined by these authors (the high g factor is found to be 13.7±0.3). In addition we observe lines at near 29 000 and 34 000 G when $H\|$ to the 100 axis. These two lines are identified to belong to the cubic transition before and after crossover from the

$$\begin{aligned}\Gamma_8{:}\;\; & a_1|\pm15/2\rangle+a_2|\pm7/2\rangle \\ & \qquad +a_3|\mp1/2\rangle a_4|\mp9/2\rangle \text{to the} \\ \Gamma_7{:}\;\; & c_1|\pm13/2\rangle+c_2|\pm5/2\rangle \\ & \qquad +c_3|\mp3/2\rangle+d_4|\mp11/2\rangle \text{ levels.}\end{aligned}$$

From these measurements and the known g factors of the Γ_8 and Γ_7 levels we evaluate the $\Gamma_8-\Gamma_7$ separation as $7.3_5\pm0.2$ cm^{-1}. The main errors arise from the additive errors of the g factors and the field calibration.

These data permit the evaluation of the crystal-field parameters. Writing in the notation of Lea *et al.*,[13]

$$\frac{A_4\langle r^4\rangle}{A_6\langle r^6\rangle}=\frac{x}{1-|x|}\,\frac{F(6)}{F(4)},$$

where $A_m\langle r^n\rangle$ are the crystal-field parameter, $F(4)$ and $F(6)$ multiplication factors, and we find $x=0.59\pm0.01$. From this we find

$$A_4\langle r^4\rangle=-242\pm20\text{ cm}^{-1},$$
$$A_6\langle r^6\rangle=41\pm5\text{ cm}^{-1}.$$

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[9] Manufactured by Magnion, Inc., Cambridge, Massachusetts. The power supply is made by Kepko Model KS-36-30M.

[10] M. P. Klein and A. W. Barton, Jr., in *Proceedings of the First International Conference on Paramagnetic Resonance,* edited by W. Low (Academic Press Inc., New York. 1963), Vol. 2, p. 699.

[11] R. W. Bierig and M. J. Weber, Phys. Rev. **132**, 164 (1963).

[12] W. Low, Proc. Phys. Soc. (London) **76**, 307 (1960).

[13] K. R. Lea, M. J. Leask, and W. P. Wolf, Phys. Chem. Solids **23**, 1381 (1962).

In these calculations we have not taken into account the admixtures from the $J=13/2$ level at about 3500 cm^{-1}.

THE SPECTRUM OF Sm^{3+} IN THE TEGRAGONAL FIELD OF CaF_2

The Landé g factor of the ${}^6H_{5/2}$ level is small, only 2/7, and one would expect that the spectroscopic splitting factor of the Sm^{3+} in crystals would be small as well.

In the cubic field the $J=5/2$ levels is split into a Γ_8 and Γ_7. The Γ_8 level in the absence of admixture of higher excited states gives rise to transitions at $g=22/21$, 2/3, and 2/7 with relative intensity of 25/36, 2/3, and 9/8, respectively, when $H\|$ (100). With the magnetic field parallel to the (111) direction the calculated g factors are 16/21, 2/3, and 2/12 with relative intensities of 16/9, 4/9, 25/18. However, the $J=7/2$ is only at about 1000 cm^{-1} followed by $J=9/2$ near 2000 cm^{-1} and one expects that the various levels would be admixed considerably, reducing in general the g factors from the values given above. In the presence of an axial field the Γ_8 level splits into two doublets. Rabbiner[14] has observed the fluorescence spectrum of Sm^{3+} supposedly in an axial field and has analyzed the spectrum. The interpretation, however, should be treated with caution because of the complexity of this spectrum.

We have looked for the resonance spectrum of two CaF_2 with nominal concentration of 0.05 and 0.1%. One set of crystals was nearly colourless supposedly contained mainly trivalent Sm^{3+}, and the other set of deep green color and containing a mixture of Sm^{3+} and Sm^{2+}. The spectrum of the green crystal was very rich in lines whereas the other showed only a few lines. The lines common to both samples could be shown to have tetragonal point symmetry with

$$g_{\parallel}=0.907\pm0.01\,,$$
$$g_{\perp}=0.544\pm0.15\,.$$

[*Note added in proof.* M. J. Weber and R. W. Bierig have observed a similar spectrum with

$$g_{\parallel}=0.93\pm0.04$$
$$g_{\perp}=0.57\pm0.05$$

(private communication).]

In addition there were many other lines (apart of hyperfine structure from the Sm^{147} and Sm^{149}, both with spins $I=\frac{7}{2}$). These lines have not been yet interpreted, some of which no doubt are of cubic and trigonal symmetry. The presence of the rich hyperfine structure complicated the identification of the spectra. For example along the (111) direction, lines were found with $g=0.893$, 0.87, 0.70, 0.67 (tetragonal), 0.62 and 0.415. (It is likely that line at 0.415 belongs to the cubic set. Possibly the line at $g=0.89$ or 0.87 may also belong to the cubic set. However, this needs further confirmation.) It is of interest to note that there are so many more lines in the mixed $\text{Sm}^{2+}-\text{Sm}^{3+}$ crystal. Possibly some of the Sm^{2+} which presumably is in the cubic site oxidizes later to Sm^{3+}.

The above g factor can be interpreted to arise from a wave function of the $a|\pm5/2\rangle+b|\mp3/2\rangle$ with a $\sim$0.86. This is indicative of considerable tetragonal admixture and is consistent with similar results found for[15,16] Nd^{3+} and for Ce^{3+}.[17]

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[14] N. Rabbiner, Phys. Rev. **130**, 507 (1963).

[15] B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956).

[16] A. Vincow and W. Low, Phys. Rev. **133**, 1390 (1961).

[17] J. M. Baker, W. Hayes, and D. A. Jones, Proc. Phys. Soc. (London) **73**, 942 (1959).