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High Field Magnetic Resonance Experiments

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This paper summarizes recent magnetic resonance experiments with high magnetic fields and millimeter wave radiation in antiferromagnetic, paramagnetic and ferromagnetic single crystals. The magnetic field is applied along an appropriate direction in order to "tune" the zero-field resonance to relatively low values. The angular dependence of the resonance frequency and resonance field is discussed in order to indicate some limitations of these experiments. Results of antiferromagnetic resonance experiments in $(Cr_2O_3)_{1-x}\cdot(Al_2O_3)_x$ crystals are discussed in more detail. The crystalline field contribution to the anisotropy changes sign at $x\simeq 0.08$, and is approximately a linear function of x. The critical field at 4.2°K increases from 59 kgauss for $x=0$, to about 80 kgauss for $x\geq 0.1$.

The experiments summarized here are an extension of those discussed at the Grenoble Conference[1] of 1958. A large magnetic field is employed to "tune" magnetic systems to the relatively low resonance frequencies of 35 or 70 kMcps. The method requires converging energy levels for paramagnetic ions with large zero-field splittings, and analogous conditions are necessary for concentrated spin systems. Since pulsed fields of 750 kgauss can be produced in the laboratory, the method permits surveys to be made over a large effective frequency range. This is illustrated in Fig. 1 for uniaxial magnetic systems when H is applied parallel to the principal axis.

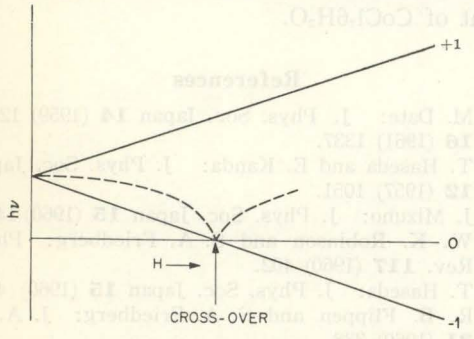

Fig. 1. Energy versus magnetic field for uniaxial spin systems where the magnetic field is applied along the axial direction.

The paramagnetic case for $S=1$ and $D>0$ is given by the straight lines for $M_s=-1$, 0, and $+1$. The distance between the $M_s=\pm 1$ and 0 lines at $H=0$ corresponds to the zero-field splitting. The same lines indicate the behavior of antiferromagnetic resonance (AFMR) in a system with positive anisotropy for H less than the critical (cross-over) value $(2\lambda K)^{1/2}=H_c$. Above H_c, a "spin-flop" resonance can be observed which follows approximately the dashed curve. Finally, the case for a ferro- or ferrimagnetic material with a large positive anisotropy energy is shown by the dashed curves (adapted from Weiss and Anderson[2]).

In practice, H must be carefully oriented with respect to the principal axis of the magnetic system. Numerical calculations

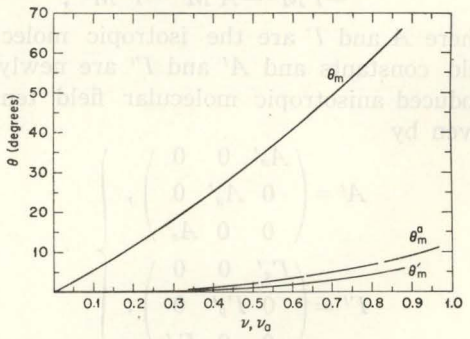

Fig. 2. Maximum angle θ between H and the axial direction at which resonance can be observed for uniaxial systems versus $\nu=\omega/\gamma/(2\lambda K)^{1/2}$ for antiferromagnetic resonance, and $\nu_a=\omega/\gamma/H_A$ for ferri- or ferromagnetic resonance. The respective maximum angles are θ_m for AFMR below $H=(2\lambda K)^{1/2}$, θ_m', for AFMR above $H=(2\lambda K)^{1/2}$, and $\theta_m{}^a$ for anisotropic ferri- or ferromagnetic materials (for AFMR we assumed $\chi_{\|}=0$).

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which show the dependence of the resonance frequency, ω, on both H and the angle, θ, between H and the principal axis are summarized in Fig. 2. The maximum angles for AFMR are indicated by θ_m for resonance below H_c and θ'_m for the spin-flop resonance. Here the parallel susceptibility, $\chi_\parallel$, is assumed equal to zero and ν is the ratio of applied frequency to that required for resonance at $H=0$. The maximum angle, $\theta_m{}^a$ for ferro- or ferrimagnetic resonance (FMR) is close to that of θ'_m. In particular if θ is 2 degrees, then for 70 kMcps radiation, a value of $(2\lambda K)^{1/2}$ of as much as 700 kgauss can be measured for $H<H_c$. The conditions for spin-flop resonance and FMR are much more stringent for the same frequency and angle limitations. The useful field range is then reduced to about 70 kgauss or less. On the other hand, with the same limitations, zero-field splittings of up to 700 kgauss can be measured in paramagnetics.

In some cases high fields are necessary in order to scan very broad resonance lines. Apparent line widths of 10 to 20 kgauss or more have been observed in paramagnets and in antiferromagnets. Such apparent line widths can result from very short spin-lattice relaxation times, or from transitions which take place between two energy levels for which the difference in energy is almost constant. Broad lines are observed at constant frequency in AFMR when $\theta \simeq \theta_m$ or θ'_m.

Results of AFMR with several mixed crystals are presented here and some of the other experiments are briefly mentioned. Details of each of these investigations will be published elsewhere.

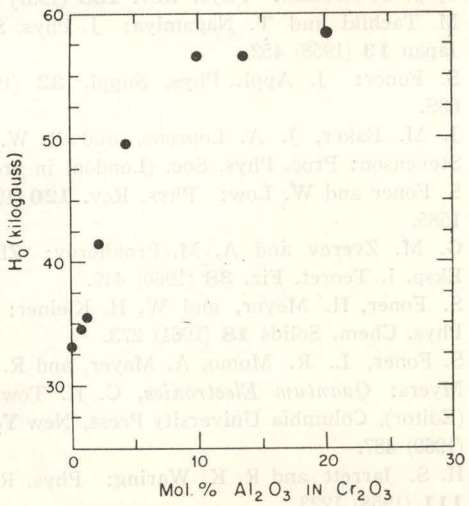

Fig. 3. Resonance field, H_0, for AFMR at 70kMcps and 4.2°K versus mol. percent Al_2O_3.

Earlier AFMR experiments[1] in Cr_2O_3 showed that the total anisotropy energy was less than the dipolar anisotropy, K_d, calculated by Tachiki and Nagamiya[3]. The difference was attributed to a small negative crystalline field contribution, K_c. Because K_c for Cr^{3+} in Al_2O_3 (ruby) was large and positive, AFMR experiments in the $(Cr_2O_3)_{1-x}\cdot(Al_2O_3)_x$ system were performed[4] in order to examine the variation of K_c with x. The resonance field, H_0, at 4.2°K and 70 kMcps is plotted in Fig. 3 for several compositions. The rapid rise of H_0 reflects the rapid increase in K_c with increasing x, and also indicates the utility of the pulsed field technique. Inclusion of a small correction for $\chi_\parallel$ obtained from static susceptibility measurements, shows that H_c rises to about 80 kgauss for $x=0.1$ and then is almost constant. However, K_c increases almost linearly so that K_c is zero at $x\simeq 0.08$. Linear extrapolation of K_c from the data for low x leads to $K_c=5.1\pm 0.5\times 10^5$ erg/gm for $x=1.0$ which compares favorably with K_c for ruby. The dependence of $(2\lambda K)^{1/2}$ versus temperature is compared for $x=0.0$ and 0.2 in Fig. 4. The dashed lines, normalized Brillouin functions for $S=3/2$, are below the experimental data as is also observed for several other antiferromagnets. The Néel temperature decreases almost linearly with x, similar to results obtained with NMR experiments on F^{19} in $(MnF_2)_{1-x}\cdot(ZnF_2)_x$ by Baker, Lourens

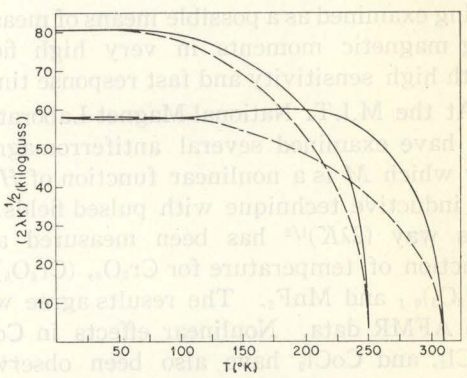

Fig. 4. $(2\lambda K)^{1/2}$, versus temperature, T, for Cr_2O_3 ($T_N=308$°K) and for $(Cr_2O_3)_{0.8}\cdot(Al_2O_3)_{0.2}$. The dashed curves are associated Brillouin functions for $S=3/2$.

and Stevenson[5].

A number of EPR experiments have been carried out at high fields. A zero-field splitting for V^{3+} in Al_2O_3 of $7.85 \pm 0.4\,cm^{-1}$ was measured[6] with the pulsed field technique and has recently been confirmed[7]. EPR experiments on O_2 molecules trapped in single crystal β-quinol clathrates have also been performed[8]. Here a fine structure of three lines was resolved, and the structure was attributed to van der Waals interactions between the O_2 and neighboring trapped N_2 molecules. Finally, the pulsed fields have been used in conjunction with a ruby maser to generate millimeter wavelength radiation[9].

Preliminary FMR experiments with $NiMnO_3$, a ferrimagnet[10] with $H_A > 50$ kgauss, have also been made for a wide range of angles and will be discussed elsewhere.

The above examples illustrate the utility of high magnetic fields for tuning magnetic resonance experiments over a very wide effective frequency range. In this way some technical problems of generating very high frequencies can be circumvented, although higher frequency sources would often be helpful. In principle some of the parameters, i.e., zero-field splittings, relaxation times, critical fields[11], and field limits for various stable spin-configuration can be studied with only magnetic moment measurements in high magnetic fields under special circumstances. Such measurements would be particularly useful when the field range is far above any reasonable resonance frequency. With this objective, the Faraday rotation of optically transparent magnetic crystals is currently being examined as a possible means of measuring magnetic moments in very high fields with high sensitivity and fast response times.

At the M.I.T. National Magnet Laboratory we have examined several antiferromagnets for which M is a nonlinear function of H by an inductive technique with pulsed fields. In this way $(2\lambda K)^{1/2}$ has been measured as a function of temperature for Cr_2O_3, $(Cr_2O_3)_{0.9}\cdot(Al_2O_3)_{0.1}$ and MnF_2. The results agree with the AFMR data. Nonlinear effects in CoF_2, $FeCl_2$, and $CoCl_2$ have also been observed. The temperature dependence of EPR and AFMR in $CoCl_2$ has also been studied, AFMR experiments have been extended in α-Fe_2O_3 and $FeTiO_3$ and experiments in $(MnF_2)_{1-x}\cdot(ZnF_2)_x$ are also in progress. Preliminary results on the latter system show the expected decrease in $(2\lambda K)^{1/2}$ as x is increased.

In summary, the use of high magnetic fields for magnetic resonance studies is limited mainly by the spin system, and secondarily by the availability of high frequency sources. Pulsed fields permit a wide variety of magnetic systems to be investigated over an extremely wide range of effective frequencies. This short paper attempts to briefly summarize a few of these experiments. There is no question that applications to many new areas of magnetism will be made in the future.

The author is grateful to Messrs. L. R. Momo and B. Feldman for valuable assistance with the experiments and tabulation of data, to Mr. E. P. Warekois for obtaining many of the materials[12] needed for these experiments and for X-ray orientation data, and to Dr. E. B. Owens for quantitative chemical analyses. The author is also grateful to many of his associates at Lincoln Laboratory for assistance throughout the course of this work, and to S. L. Hou and J. B. Comly for assistance at the M. I. T. National Magnet Laboratory.

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DISCUSSION

T. NAGAMIYA: It appears to me that the crystalline field anisotropy energy of Cr^{3+} depends sensitively on lattice parameters. This might be due to the fact that these ions are situated at positions which are very asymmetrical with respect to neighboring oxygen ions. Tachiki suspects also that the variation of the crystalline field anisotropy constant with temperature of Cr_2O_3 might be due to the change of the position of Cr^{3+} as a result of its anharmonic thermal oscillation. He expects the same for α-Fe_2O_3, where there is a crossing of the crystalline field anisotropy and dipolar anisotropy at $-13°C$, since these two should vary in the same way at low temperatures according to spin wave theory if the crystalline field were fixed.

S. FONER: It may well be that the crystalline field depends on the lattice parameter. In this regard, Greenwald *et al.* of the Naval Ordnance Laboratory reported on the variation of the lattice parameters of Cr_2O_3 over a wide range of temperature. *X*-ray data shows a fairly uniform variation of lattice parameter with concentration on the mixed $(Cr_2O_3)_x \cdot (Al_2O_3)_{1-x}$ system. In order to see if the crystalline field is strongly sensitive to lattice dimensions we are currently attempting AFMR experiments applied axial stresses. [Note added in proof: Pressure effects have been observed and being analyzed.]