REFERENCES

[1] P. Debye, *Polar Molecules*, Chemical Catalogue Co., New York, 1929.
[2] For an excellent account of this topic, see B. K. P. Scaife, *Complex Permittivity*. London: English Universities Press, 1971.
[3] K. S. Cole and R. H. Cole, "Dispersion and absorption in dielectrics, I. Alternating current characteristics," *J. Chem. Phys.*, vol. 9, pp. 341–351, 1941.
[4] G. W. Chantry and H. A. Gebbie, "Submillimetre wave spectra of polar liquids," *Nature*, vol. 208, p. 378, 1965.
[5] R. A. Sack, "Relaxation processes and inertial effects" (Pts. I and II), *Proc. Phys. Soc.*, vol. B70, pp. 402–426, 1957.
[6] Y. Rocard, "Analyse des orientations moléculaires de molecules en moment permanent dans un champ alternatif, application a la dispersion de la constant dielectric et l'effet Kerr," *J. Phys. Radium*, vol. 4, pp. 247–250, May 1933.
[7] E. P. Gross, "Inertial effects and dielectric relaxation," *J. Chem. Phys.*, vol. 23, pp. 1415–1423, 1955.
[8] B. Lassier and C. Brot, "Inertial effects in discrete sites model of rotational freedom. Autocorrelation function and dipolar absorption," *Chem. Phys. Lett.*, vol. 1, pp. 581–584, 1968.
[9] (a) G. J. Evans and M. W. Evans, "Use of the memory function to simulate the Debye and Poley absorptions in liquids," *J. Chem. Soc. Faraday Trans. II*, vol. 72, pp. 1169–1184, 1976.
(b) G. J. Davies and M. W. Evans, "Use of the generalised Langevin theory to describe far infrared absorptions in non-dipolar liquids," *ibid.*, pp. 1194–1205.
(c) M. W. Evans and G. J. Davies, "Effect of pressure and temperature on the intermolecular mean square torque in liquid CS_2 and CCl_4," *ibid.*, pp. 1206–1213.
[10] R. Kubo, "Statistical-mechanical theory of irreversible processes, I. General theory and simple applications to magnetic and conduction problems," *J. Phys. Soc. Japan*, vol. 12, pp. 570–586, 1957.
[11] H. Mori, "Transport, collective motion and Brownian motion," *Prog. Theor. Phys.*, vol. 33, pp. 423–455, 1965.
[12] J. S. Rowlinson and M. W. Evans, "The motion of simple molecules in liquids," Chemical Society, Annu. Rep. A, pp. 5–30, 1975.
[13] M. N. Afsar, J. Chamberlain, G. W. Chantry, R. Finsy, and R. Van Loon, "An assessment of random and systematic errors in high frequency dielectric measurements," *Proc. IEE*, to be published.
[14] J. Chamberlain, "Submillimetre-wave techniques," in *High Frequency Dielectric Measurement*. J. Chamberlain and G. W. Chantry, Ed., London: Guildford IPC Press, pp. 104–116, 1972.
[15] J. W. Fleming, P. A. Turner, and G. W. Chantry, "Far infrared absorption spectra of the monohalo-benzenes in the liquid and polycrystalline phases," *Molec. Phys.*, vol. 19, pp. 853–864, 1970.

Application of Submillimeter Spectroscopy to Magnetic Excitations

REINHART GEICK

Abstract—**Magnetic excitations are the collective excitations of the magnetic moments in ferro- and antiferromagnets. The frequencies are mostly in the far-infrared spectral range. Their study is of current interest with respect to the properties of phase transitions, since in ordinary 3-dimensional crystals the dominating exchange interactions can be 3-dimensional (MnF_2, NiO) or may be restricted to 2 dimensions (K_2MnF_4, $CoCl_2$) or even to 1 dimension ($CsNiF_3$, $CoCl_2 \cdot 2H_2O$). In this paper, an introduction and a review is given of the results on $q = 0$ magnon modes (ferro- or antiferromagnetic resonance) which can be studied rather directly by submillimeter-wave spectroscopy. Some results about 2 magnon bands are also mentioned. Experimentally, grating monochromators, Fourier-transform interferometers, FIR laser, and microwave techniques have been employed. In the past, not only pure materials have been studied but also doped crystals where localized magnon modes can occur ($MnF_2:Co^{2+}$, $CoF_2:MnF_2$, $NiO:Co^{2+}$).**

I. INTRODUCTION

MAGNETIC EXCITATIONS are the collective modes of a system of spins or magnetic moments which are usually observed in the ordered ferromagnetic or antiferromagnetic state of the system. The frequencies of these excitations fall in the microwave range and in the far-infrared or submillimeter spectral region, up to 1000 cm^{-1}.

The study of magnetic excitations is of current interest since the dominating exchange interaction between the magnetic ions may be 3 dimensional or may be restricted to 2 or 1 dimensions even though the crystal in an ordinary 3-dimensional one, but with an anisotropic structure. The properties of such systems, i.e., susceptibility, excitations, specific heat, etc., are of particular interest with respect to the theory of phase transitions and critical phenomena [14], [15]. Some materials are compiled as examples in Table I. Among the great number of existing materials of each kind, those have been selected which were actually

TABLE I
EXAMPLES OF 1-, 2-, AND 3-DIMENSIONAL MAGNETIC MATERIALS

Dominating exchange interaction		
1-dimensional	2-dimensional	3-dimensional
← pure materials →		
$CsNiF_3$ /35/	K_2MnF_4 /20,29/	MnF_2 /1,4/
$CoCl_2 \cdot 2H_2O$ /9,25/	K_2NiF_4 /13,16/	NiF_2 /6,23,28/
	Rb_2MnF_4 /20/	CoF_2 /5,23,32/
	$CoCl_2$ /7,24/	$KMnF_3$ /27/
	$FeCl_2$ /7,21,34/	MnO /3,22/
	$CoCl_2 \cdot 6H_2O$ /37/	NiO /3/
		CoO /11,12/
← doped materials, mixed crystals →		
	$K_2MnF_4:Ni^{2+}$ /19,29,38/	$MnF_2:Fe^{2+}$ /8,10/
		$MnF_2:Zn^{2+}$ /15,17/
		$MnF_2:Co^{2+}$ /10,31/
		$CoF_2:Mn^{2+}$ /18,30/
		CoO/NiO /33,36/

Manuscript received November 22, 1976.
The author is with the Physikalisches Institut, D-8700 Würzburg, Germany.

studied by means of submillimeter spectroscopy, and the references refer mostly to these investigations.

Materials with rather isotropic structures (cubic rock salt, cubic perovskite, and rutile structure) are generally 3-dimensional ferro- or antiferromagnets. In materials with perovskite-type layer structures, such as K_2NiF_4, the interlayer exchange interaction is partly cancelled and is much weaker as compared to the intralayer interaction. And in hexagonal $CsNiF_3$ and monoclinic $CoCl_2 \cdot 2H_2O$, for example, the spins are predominantly coupled along linear chains. Thus these magnetic materials represent very realistic model systems in 1, 2, or 3 dimensions. This was shown by neutron-diffraction studies. In addition to the lattice dimensionality discussed so far, we have to consider the so-called spin dimensionality. The exchange interaction is written as follows:

$$\mathcal{H}_{ex} = \sum_{ij} (\mathcal{J}_{ij}^{xx} S_i^x S_j^x + \mathcal{J}_{ij}^{yy} S_i^y S_j^y + \mathcal{J}_{ij}^{zz} S_i^z S_j^z). \quad (1)$$

If $\mathcal{J}_{ij}^{xx} = \mathcal{J}_{ij}^{yy} = \mathcal{J}_{ij}^{zz} = \mathcal{J}_{ij}$, we have the isotropic Heisenberg model and the spin dimensionality is 3. For the planar or X-Y model ($\mathcal{J}_{ij}^{xx} = \mathcal{J}_{ij}^{yy}$, $\mathcal{J}_{ij}^{zz} = 0$) and for the Ising model ($\mathcal{J}_{ij}^{xx} = \mathcal{J}_{ij}^{yy} = 0$, $\mathcal{J}_{ij}^{zz} \neq 0$), the spin dimensionality is 2 and 1, respectively. For materials with Mn^{2+} ions (ground state ^6S), usually the Heisenberg model is adequate to describe their properties. In systems with Co ions (ground state ^4F), with orbital contributions to the magnetic moment, however, the Ising model or an X-Y model may be more appropriate to account for the magnetic properties.

II. Experimental Technique

Magnetic excitations can be studied by means of inelastic neutron scattering, by Raman scattering, and by submillimeter spectroscopy. Due to wavenumber conservation, the two optical methods allow only the determination of the $q = 0$ modes of the spin-wave spectrum, apart from broad 2-magnon bands, while there is no such restriction for the neutron-scattering technique. The present paper is to review the role that submillimeter spectroscopy played in studying magnetic systems, and the other two methods and their results will not be further mentioned in detail here. Indeed, submillimeter spectroscopy is a rather direct method to study the $q = 0$ spin-wave excitations or the antiferromagnetic and ferromagnetic resonance in antiferromagnets and ferromagnets, respectively. For such investigations, various techniques have been employed: 1) conventional grating monochromator; 2) Fourier-transform spectrometer; 3) FIR-laser spectroscopy; and 4) microwave techniques.

In the frequency range 15–100 cm^{-1}, grating spectrometers have been widely used for the investigation of magnetic excitations, especially for the early work on 3-dimensional antiferromagnetics [1], [3], [9]. As a broad-band source, the mercury high-pressure arc is usually employed. Low-temperature carbon, silicon, or germanium bolometers improved as detectors the signal-to-noise ratio considerably. In the last decade, an increasing number of investigations was performed with the method of Fourier-transform spectroscopy [5], [6], [8], [10], [13], [15], [17], [18], [29], [33], [35], [36]. For the range above 15 cm^{-1}, the Michelson interferometer and a bolometer at 4.2 K may be used. Below 15 cm^{-1}, however, it is necessary to increase the interferometer efficiency by using a lamellar grating beam divider and to increase the signal-to-noise ratio by means of a ^{3}He-cooled detector [8], [10], [21], [29], [35].

In most cases, the frequency of the $q = 0$ magnon (antiferromagnetic resonance) is not only determined in zero magnetic field, but also as a function of an external static magnetic field. And with grating or Fourier-transform spectrometers, the transmission of the sample is usually measured as a function of wavelength or frequency at fixed magnetic field. In the microwave region, on the other hand, it is the usual magnetic-resonance technique to measure the transmission of the sample as a function of applied magnet field at a fixed frequency which is provided by a microwave source (klystron, carcinotron, etc.). This technique is of advantage at rather low frequencies and has been used there frequently [1], [16], [20], [22]–[24], [28], [30], [32], [37]. The frequencies range from 20 to 600 GHz. For higher frequencies, no microwave sources are available. But there are a number of molecular-laser sources in the submillimeter range which have been used for submillimeter spectroscopy, e.g., the HCN (29.7; 32.2 cm^{-1}), the DCN (51.4; 52.7 cm^{-1}), the H_2O (127.5 cm^{-1}), and the D_2O (118.7 cm^{-1}) lasers [25], [31], [34]. And it seems that lasers will be used increasingly in the future, since a great number of frequencies are available from a variety of molecular lasers which can conveniently be pumped by powerful CO_2 lasers.

III. Experimental Results

In this section, the results of studying magnetic excitations will be reviewed and discussed with respect to their contribution to the understanding of the properties of magnetic materials. Mostly, the antiferromagnetic resonance (AFMR) has been studied by means of submillimeter-wave spectroscopy and not so much absorption by 2-magnon excitations. Since the exchange field H_E is known from other experiments, very often the determination of the AFMR frequency means essentially a determination of the anisotropy field H_A.

A. Three-dimensional Pure Materials

For a simple 3-dimensional easy-axis antiferromagnet like MnF_2, the AFMR frequency is

$$\omega_{AFMR} = \gamma[\sqrt{H_A(2H_E + H_A)} \pm H_0] \quad (2)$$

(gyromagnetic ratio $\gamma = g\mu_B/\hbar$, isotropic exchange interaction $H_E = 2zS\mathcal{J}/\gamma$ with $z = 8$ and $S = 5/2$). In the case of MnF_2, the anisotropy field ($H_A = 0.75$ cm^{-1}) arises mainly from magnetic dipole–dipole interactions [1]. In an external magnetic field H_0 parallel to the easy axis, the doubly degenerate mode splits and varies linearly with H_0. In CoF_2, on the other hand, the exchange interaction is expected to be anisotropic and a large single-ion anisotropy

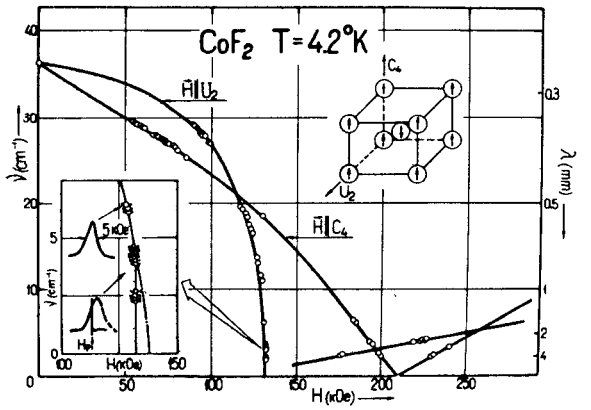

Fig. 1 AFMR frequency versus magnetic field for CoF_2, $H \parallel U_2$ and $H \parallel C_4$ (after [23]).

arises from orbital contributions. Therefore, the dependence of ω_{AFMR} on an external field H_0 is much more complicated [23], [32] (cf. Fig. 1). For $H_0 \parallel c$, ω_{AFMR} is no longer a linear function of H_0. At 210 kOe, ω_{AFMR} softens and the spin flop transition occurs. For $H_0 \parallel a$, ω_{AFMR} also approaches zero at about 135 kOe. Such a phase transition is expected in MnF_2 at much higher fields $H_0 \approx 2H_E$ (antiferromagnetic → paramagnetic). In a crude and more qualitative way, this behavior can be understood by means of a simple spin-wave calculation, including the (transverse) Dzyaloshinski interaction [23] (parameter H_D)

$$\omega_{AFMR}^2 = \gamma^2(2H_EH_A + H_A^2 - H_D^2) \cdot \left[1 - \frac{(H_A^2 + H_D^2)H_0^2}{(2H_EH_A + H_A^2 - H_D^2)^2}\right], \quad H_0 \parallel a \tag{3}$$

$$\omega_{AFMR}^2 = \gamma^2[(\sqrt{H_A(2H_E + H_A)} \pm H_0)^2 - H_D^2], \quad H_0 \parallel c.$$

Physically, the Dzyaloshinski interaction means additional terms of single-ion anisotropy or anisotropic exchange. For quantitative agreement with the experimental data and to describe finer details, such as $\partial\omega/\partial H_0 =$ finite for $H_0 \leq$ 210 kOe, a more elaborate theory is needed [32], [39].

Let us return to the simpler case of MnF_2 and consider the variation of ω_{AFMR} with temperature (cf. Fig. 2). ω_{AFMR} is closely related to the sublattice magnetization M. The temperature dependence of ω_{AFMR} and M cannot be understood only in terms of (4). A special temperature dependence of H_A has to be considered, and the AFMR studies in the submillimeter range provide information about the temperature dependence of H_A [1], [4]. In Fig. 2, the Brillouin function follows $\omega_{AFMR}(T)$ closely, but not $M(T)$. For comparison, approximate solutions of a 3-dimensional Ising and a Heisenberg model [14] are also shown in Fig. 2. With reasonable accuracy for temperatures not too close to T_N, the sublattice magnetization can be calculated by means of a renormalized, temperature-

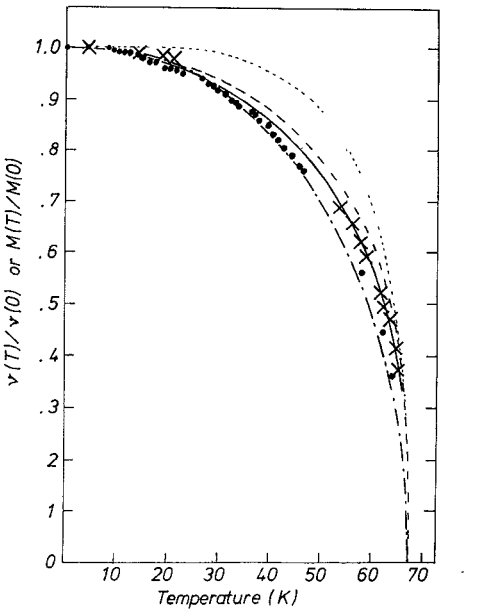

Fig. 2. Reduced AFMR frequency $\nu(T)/\nu(0)$ of MnF_2 (•, after [1]) and reduced sublattice magnetization $M(T)/M(0)$ of MnF_2 versus temperature, experimental data (×), and calculated by means of spin-wave theory (———) (after [4]). For comparison are given approximate results for $M(T)/M(0)$ of a Heisenberg model (— — —) for a FCC-lattice with $s = \frac{1}{2}$ and of an Ising model (. . . .) for BCC-lattice with $s = \frac{1}{2}$ (after [14]) as well as the Brillouin curve for $s = 5/2$ (—·—).

dependent spin-wave theory (Oguchi [2]) which yields for $H_0 = 0$

$$\omega_{AFMR} = \gamma\left\{\sqrt{H_A(2H_E + H_A)} - \frac{H_Eg_0}{2SN} \cdot \sum_k [(g_k - 1) + 2g_kn_k]\right\} \tag{4}$$

$$M_{subl} = \frac{Ng\mu_B}{V}\left\{S - \frac{1}{2N}\sum_k [(f_k - 1) + 2f_kn_k]\right\}$$

with

$$g_k = [H_E(1 - \gamma_k^2) + H_A] \cdot [(H_E + H_A)^2 - H_E^2\gamma_k^2]^{-1/2}$$

$$f_k = [H_E + H_A] \cdot [(H_E + H_A)^2 - H_E^2\gamma_k^2]^{-1/2}$$

$$\gamma_k = \frac{1}{Z}\sum_\delta \exp(ikr_\delta)$$

$$n_k = [\exp(\hbar\omega_k/k_BT) - 1]^{-1}.$$

We learn from (4) that there is a temperature independent and a temperature dependent "Oguchi-correction" in lowest order for both ω_{AFMR} and M.

B. Two-dimensional Pure Materials

In the 2-dimensional material K_2MnF_4, each magnetic ion is coupled to its four nearest in-plane neighbors by exchange. The interplanar exchange is negligible. And there should be no transition to an ordered magnetic state for $T_N > 0$ according to theory. However, the small anisotropy

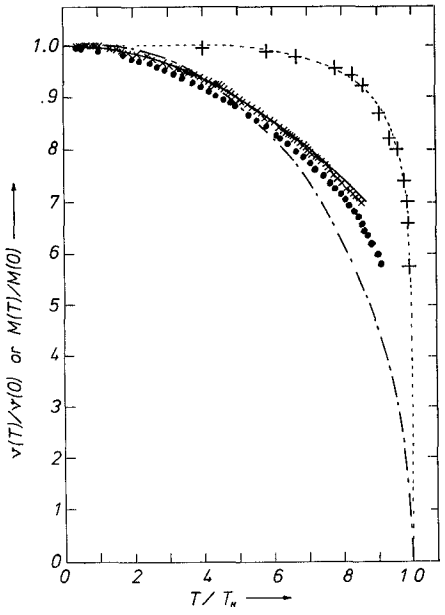

Fig. 3. Reduced AFMR frequency $\nu(T)/\nu(0)$ of K_2MnF_4 (•, after [20]) and reduced sublattice magnetization $M(T)/M(0)$ of K_2MnF_4 versus T/T_N, experimental data (×), and calculated by means of spin-wave theory (———) (after [20]). For comparison are given $M(T)/M(0)$ of Rb_2CoF_4 (+) and of a simple quadratic lattice Ising model (·····) with $s = \frac{1}{2}$ (after [14]) as well as the Brillouin curve for $s = 5/2$ (—·—).

field (dipole interactions!) causes a transition to an ordered antiferromagnetic state at $T_N = 42.1$ K (K_2MnF_4). But the spin waves are essentially those of 2-dimensional layers with practically no interlayer coupling. Due to the modified density of states in 2 dimensions, there is a rather large zero-point spin deviation of nearly 20 percent in these materials (2 percent in MnF_2) [13], [16], [20]. At $T = 0$, therefore, the correction terms [cf. (4)] $\sum_k (g_k - 1)$ or $\sum_k (f_k - 1)$ are more important for 2-dimensional than for 3-dimensional materials in calculating ω_{AFMR} and M by spin-wave theory. The lattice dimensionality is also reflected in the temperature dependence of ω_{AFMR} and M (cf. Fig. 3). Here again, the AFMR frequency measured independently from M provides information about the temperature dependence of H_A which is needed for the spin-wave calculations ($H_E = 58.5$ cm^{-1} and $H_A = 0.23$ cm^{-1} at $T = 0$ in K_2MnF_4 [20], [29], [38]). As in many other cases, the deviations of the data from simple mean field theory (Brillouin curve) are more significant in the 2-dimensional case (cf. Fig. 3), especially at temperatures close to T_N. In contrast to K_2MnF_4, the sublattice magnetization of Rb_2CoF_4 follows closely the predictions of a 2-dimensional Ising model which can be calculated rigorously [14].

C. One-dimensional Pure Materials

For the hexagonal compound $CsNiF_4$, it has been found by neutron-scattering experiments that the dominant exchange interaction is along linear chains. Above the 3-dimensional antiferromagnetic ordering temperature ($T_N = 2.61$ K), there exists a 1-dimensional short-range order along the chains, and ferromagnetic spin waves were observed up to 20 K. The antiferromagnetic resonance frequency is for a 1-dimensional easy plane ferromagnet [35]

$$\omega_{AFMR} = \gamma\sqrt{H_0(H_A + H_0)} \tag{5}$$

where H_0 is the external field applied perpendicular to $M(H_0 \parallel c)$ and $H_A = 3.3$ cm^{-1} is the anisotropy field, respectively. In Fig. 4, the FMR is shown as a function of temperature at fixed external field $H_0 = 2.675T$. The solid line in Fig. 4 has been calculated by means of a spin-wave renormalization. The agreement between experimental and calculated data is quite good. $CoCl_2 \cdot 2H_2O$ is also a 1-dimensional magnetic material. Its peculiar property is that the excitations in this material derived by submillimeter spectroscopy can well be approximated by a 1-dimensional Ising model [9], [25].

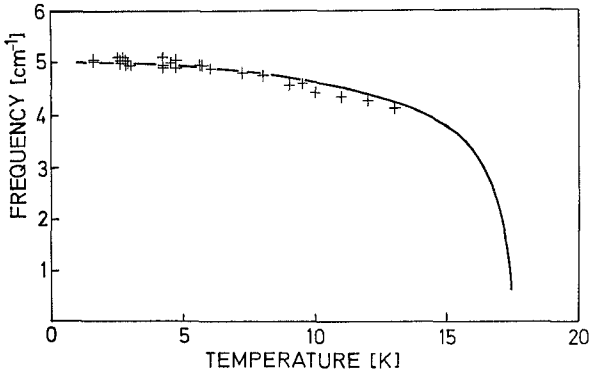

Fig. 4. FMR frequency of the 1-dimensional system $CsNiF_3$ versus temperature (+). The solid curve has been calculated by means of spin-wave theory (after [35]).

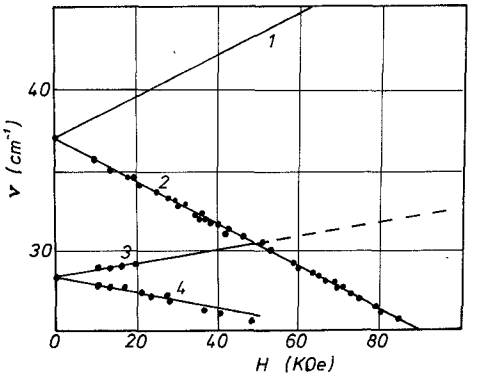

Fig. 5. AFMR frequencies (1,2) and impurity mode frequencies (3,4) of Mn^{2+} doped CoF_2 versus magnetic field.

D. Doped Materials and Mixed Crystals

In the last section, let us consider the properties of 3-dimensional materials doped with impurities. If an isolated impurity is subject to an effective field $H_{eff} = H_E' + H_A'$ (exchange and anisotropy field) and if the frequency $\omega = \gamma H_{eff}$ is above the spin-wave band, a localized spin-wave mode will occur. This happens for MnF_2: Fe^{2+} ($\nu_{Local} = 94.8$ cm^{-1}) and for MnF_2:Co^{2+} ($\nu_{Local} = 123.5$ cm^{-1}) [8], [10], [31]. If, on the other hand, $\omega = \gamma H_{eff}$ is smaller than ω_{AFMR}, a local mode will occur below the spin-wave band. This is the case for CoF_2/Mn^{2+} (cf. Fig. 5) [18], [30]. At a magnetic field of $H_0 \approx 50$ kOe, the frequencies of one

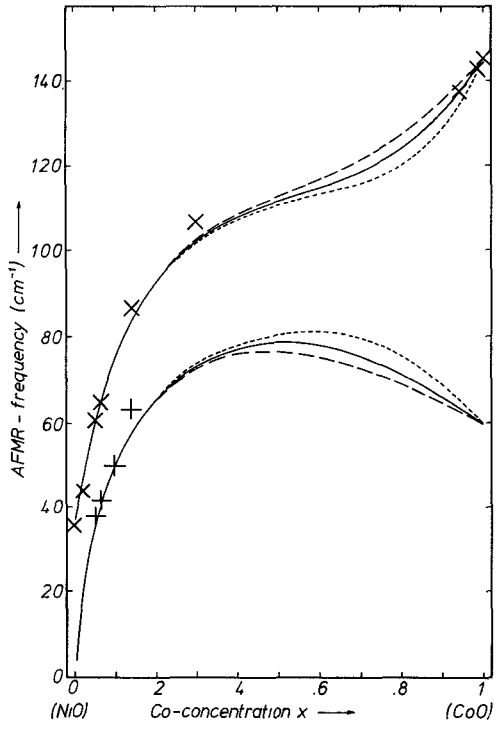

Fig. 6. Antiferromagnetic resonance of $Co_xNi_{1-x}O$ mixed crystals versus Co concentrations x, experimental data (upper mode ×, lower mode +) and results of calculations by means of model $E3$ (---), $E4$ (———), $E6$ (·····). The models are explained in the text.

AFMR-mode (2) and of one impurity mode (3) coincide. For $H_0 > 50$ kOe, the local mode is no longer observed because it is incorporated in the spin-wave band and is no longer localized. If MnF_2 is doped with the diamagnetic impurity Zn^{2+}, the exchange field is drastically reduced [15], [17].

NiO and CoO are antiferromagnets with the rock-salt structure [3], [11], [12]. The AFMR of CoO/NiO mixed crystals has been studied for various concentrations (cf. Fig. 6) [33], [36]. Here again the experimental data provide information about the anisotropy, especially of the Co^{2+} ions. The lower mode has been observed only for Co concentrations between 5 and 15 percent. The data can be interpreted by means of model considerations. In these, an average exchange field for the two kinds of ions is taken into account [33]. For the Co^{2+} ions, single-ion anisotropy terms are considered with cubic symmetry (parameter $K = 19.1\ cm^{-1}$ for models $E3$,$E4$,$E6$) and with trigonal symmetry (parameter $T = (10.9 + x^m \cdot 15.3)\ cm^{-1}$, with $m = 3$, 4, and 6 for models $E3$, $E4$, and $E6$, respectively). The model also allows for a rotation of the preferred spin direction, which is different in the two end members $\langle 11\bar{2}\rangle$ in NiO and $\approx\langle 33\bar{8}\rangle$ in CoO. The model considerations show that the drastic variation of ω_{AFMR} on the Ni-rich side is due to a drastic rotation of the preferred direction as a consequence of the much larger anisotropy of the Co^{2+} ions ($T = 0.25\ cm^{-1}$, $K = 0$ for NiO). The drastic variation on the Co-rich side is attributed to collective contributions of the Co ions to the anisotropy (~ third power of concentration!).

References

[1] F. M. Johnson and A. H. Nethercot, "Antiferromagnetic resonance in MnF_2," *Phys. Rev.*, vol. 114, p. 705, 1959.
[2] T. Oguchi, "Theory of spin wave interactions in ferro- and antiferromagnetism," *Phys. Rev.*, vol. 117, p. 117, 1960.
[3] A. J. Sievers and M. Tinkham, "Far infrared antiferromagnetic resonance in MnO and NiO," *Phys. Rev.*, vol. 129, p. 1566, 1963.
[4] G. G. Low, "Application of spin wave theory to three magnetic salts," *Proc. Phys. Soc.*, vol. 82, p. 992, 1963.
[5] P. L. Richards, "Antiferromagnetic resonance in CoF_2, NiF_2 and $MnCO_3$," *J. Appl. Phys.*, vol. 35, p. 850, 1964.
[6] ——, "Far infrared magnetic resonance in NiF_2," *Phys. Rev.*, vol. 138, p. A 1769, 1965.
[7] L. S. Jacobs, S. Roberts, and P. E. Lawrence, "Antiferromagnetic resonance in $CoCl_2$ and $FeCl_2$," *J. Appl. Phys.*, vol. 36, p. 1197, 1965.
[8] R. Weber, "Localized magnetic mode in $MnF_2:Fe^{2+}$," *Phys. Rev. Lett.*, vol. 21, p. 1260, 1968.
[9] (a) J. B. Torrance and M. Tinkham, "Far infrared absorption in $CoCl_2 \cdot 2H_2O$," *J. Appl. Phys.*, vol. 39, p. 822, 1968.
(b) ——, "Magnon bound states in anisotropic linear chains," *Phys. Rev.*, vol. 187, p. 587, 1969.
[10] R. Weber, "Localized magnetic modes in $MnF_2:Fe^{2+}$ and $MnF_2:Co^{2+}$," *J. Appl. Phys.*, vol. 40, p. 995, 1969.
[11] M. R. Daniell and A. P. Cracknell, "Magnetic symmetry and antiferromagnetic resonance in CoO," *Phys. Rev.*, vol. 177, p. 932, 1969.
[12] I. S. Austin and E. S. Garbett, "Far infrared electronic excitations of the Co^{2+} ions in antiferromagnetic CoO," *J. Phys. C*, vol. 3, p. 1605, 1970.
[13] R. J. Birgeneau, F. de Rosa, and H. J. Guggenheim, "Antiferromagnetic resonance in K_2NiF_4," *Solid State Commun.*, vol. 8, p. 13, 1970.
[14] R. F. Wielinga, "Critical behaviour in magnetic crystals," in *Progress in Low Temperature Physics VI*, C. J. Gorter, Ed. Amsterdam: North-Holland, 1970, p. 333.
[15] H. Mitlehner *et al.*, "Far infrared and Raman investigation of Zn^{2+} doped MnF_2 in the two magnon region," *Solid State Commun.*, vol. 9, p. 2059, 1971.
[16] H. Yamazaki, K. Watanabe, and H. Abe, "High field antiferromagnetic resonance in K_2NiF_4," *J. Phys. Soc. Japan*, vol. 32, p. 862, 1972.
[17] M. Buchanan *et al.*, "Two magnon Raman scattering and infrared absorption in (Mn Zn)F_2," *J. Phys. C*, vol. 5, p. 2011, 1972.
[18] B. Enders, P. L. Richards, W. E. Tennant, and E. Catalano, "Antiferromagnetic resonance modes in $(Co,Mn)F_2$ and $(Fe,Mn)F_2$," presented at the 1972 Conf. Magnetism and Magnetic Materials, also *AIP Conf. Proc. No. 10*, Part 1, p. 179.
[19] W. Lehmann and R. Weber, "Two magnon light scattering in K_2MnF_4," *Phys. Lett.*, vol. 45 A, p. 33, 1973.
[20] (a) H. W. de Wijn, L. R. Walker, S. Geschwind, and H. J. Guggenheim, "Antiferromagnetic resonance in the quadratic layer antiferromagnets K_2NiF_4, K_2MnF_4 and Rb_2MnF_4," *Phys. Rev. B*, vol. 8, p. 299, 1973.
(b) H. W. de Wijn, L. R. Walker, and R. E. Walsted, "Spin wave analysis of the quadratic layer antiferromagnets K_2NiF_4, K_2MnF_4 and Rb_2MnF_4," *Phys. Rev. B*, vol. 8, p. 285, 1973.
[21] K. C. Johnson and A. J. Sievers, "Hydrostatic pressure study of the antiferromagnetic resonance in $FeCl_2$," *Phys. Rev. B*, vol. 7, p. 1081, 1973.
[22] V. S. Mandel, V. D. Voronkov, and D. E. Gromzin, "Antiferromagnetic resonance in MnO," *Sov. Phys. JETP*, vol. 36, p. 521, 1973.
[23] E. G. Rudashevski, A. S. Prokhorov, and L. V. Velikov, "Submillimeter spectroscopy of weak antiferromagnets in magnetic fields up to 300 kOe," *IEEE Trans. Microwave Theory Tech.*, vol. MTT-22, p. 1064, 1974.
[24] A. F. Lozenko and S. M. Ryabchenko, "Antiferromagnetic resonance in layered $CoCl_2$ and $NiCl_2$," *Sov. Phys. JETP*, vol. 38, p. 538, 1974.
[25] D. F. Nicoli and M. Tinkham, "Far infrared laser spectroscopy of the linear Ising system $CoCl_2 \cdot 2H_2O$," *Phys. Rev. B*, vol. 9, p. 3126, 1974.
[26] L. de Jongh and A. R. Miedema, "Experiments on simple magnetic model systems," *Advances in Phys.*, vol. 23, p. 1, 1974.
[27] K. Saiki, "Spin wave orientation and antiferromagnetic resonance in the low temperature phase of perovskite crystal $KMnF_3$," *J. Phys. Soc. Japan*, vol. 38, p. 373, 1975.
[28] L. V. Velikov, L. A. Prozorova, A. S. Prokhorov, E. G. Rudashevski, and A. I. Smirnov, "Investigation of the low frequency antiferromagnetic resonance branch in NiF_2," *Sov. Phys. JETP*, vol. 41, p. 567, 1975.
[29] W. Lehmann, F. Macco, and R. Weber, "Optical investigations of K_2MnF_4 and $K_2MnF_4:Ni^{2+}$," *Physica*, vol. 80 B, p. 27, 1975.

[30] A. S. Prokhorov and E. G. Rudashevski, "Exchange amplification and magnetic impurity oscillation quenching in antiferromagnets," *JETP Lett.*, vol. 22, p. 99, 1975.
[31] U. Dür and K. J. Button, "Temperature dependence of the localized magnon mode in $MnF_2:Co^{2+}$," *Solid State Commun.*, vol. 16, p. 695, 1975.
[32] Yu. M. Gufan, K. N. Kocharyan, A. S. Prokhorov, and E. G. Rudashevski, "Dependence of the resonant frequencies of antiferromagnets on the magnetic field and antiferromagnetic resonance in CoF_2," *Sov. Phys. JETP*, vol. 39, p. 565, 1975.
[33] C. R. Becker, Ph. Lau, R. Geick, and V. Wagner, "Antiferromagnetic resonance in $NiO:Co^{2+}$ and $NiO:Fe^{2+}$," *Phys. Status Solidi*, (b), vol. 67, p. 653, 1975.
[34] A. R. Fert *et al.*, "Ferromagnetic resonance in $FeCl_2$ and $FeBr_2$," *Solid State Commun.*, vol. 18, p. 327, 1976.
[35] R. J. Grill, U. Dürr, and R. Weber, "FMR investigations on the one-dimensional ferromagnet $CsNiF_3$," in *Proc. Int. Conf. Magnetism* (Amsterdam, 1976), to be published.
[36] G. Geis, R. Geick, C. R. Becker, and V. Wagner, "Antiferromagnetic resonance in CoO/NiO mixed crystals," in *Proc. Int. Conf. Magnetism* (Amsterdam 1976), to be published.
[37] W. Ghidalia, J. Tuchendler, and J. Magarino, "Antiferromagnetic, spin flop and paramagnetic resonances of hexahydrated cobalt chloride at very low temperatures," in *Proc. Int. Conf. Magnetism* (Amsterdam 1976), to be published.
[38] W. Lehmann and R. Weber, "Optical investigation of the magnon spectra of pure and Ni^{2+} doped K_2MnF_4," *J. Phys. C*, to be published.
[39] B. G. Kukharenko, "Antiferromagnetic resonance in transition-metal fluorides," *Sov. Phys. JETP*, vol. 42, p. 321, 1976.

Dispersive Fourier Transform Spectrometry with Variable-Thickness Variable-Temperature Liquid Cells

M. N. AFSAR, D. D. HONIJK, W. F. PASSCHIER, AND J. GOULON

Abstract—**Dispersive Fourier transform spectrometry (DFTS) of liquids with variable-thickness variable-temperature cells is described. Different evaluative and computational methods are discussed and comparisons with the free layer method are shown with the aid of experimental results. Data for germanium and liquid chlorobenzene are presented.**

INTRODUCTION

DISPERSIVE Fourier transform spectrometry (DFTS) of liquids [1] in the millimeter and submillimeter-wave region has been extended to include precise measurement of the complex refractive index $\hat{n}$ or the complex relative permittivity $\hat{\varepsilon}$ of medium loss as well as high-loss volatile liquids over a wide temperature range (−80 to 80 °C) by the use of a variable-thickness windowed cell in one active arm of the Michelson-type two-beam interferometer. In the past these measurements were restricted to liquids of relatively low vapor pressure because of the necessity to use a free layer of liquid. An excess of liquid vapor absorbs radiation and gives its own characteristic spectrum [2]. The free layer method and subtraction [3], [4] and double subtraction [5] procedures enabled investigation of liquids of absorption coefficient α up to 250 Np/cm. But as the absorption increases it becomes more and more difficult to produce a sufficiently thin plane parallel layer held freely under gravity. However, for very absorbing liquids, like water, reflection DFTS [5], [6] has been successfully used in which accurate determination of the phase shift and an extremely stable interferometric system are essential.

In order to overcome these difficulties, two liquid cells with windows have been constructed, one at the University of Leiden, The Netherlands, and the other at the University of Nancy, Nancy, France, in cooperation with the National Physical Laboratory (NPL), United Kingdom. These cells were used at the NPL with an improved Michelson-type interferometric system. Different evaluation methods [7]–[13] can be used with these cell techniques. Knowledge of the complex refractive index of the window $\hat{n}_w$ is required in all evaluation methods except the two thicknesses method. $\hat{n}_w$ is evaluated directly from the same set of measurements [7], [8], [14].

EXPERIMENTAL

The ray diagram of the interferometer and the cell arrangement is shown in Fig. 1. The fixed mirror arm is mounted vertically upwards. The mirror can be moved up and down above the window to produce different thicknesses. The interferometer can be readily interchanged to either the dielectric beam splitter mode or the polarization mode [5]. The interferometer in the polarization mode with free standing wire grid beam splitters covers the frequency range between 3 and 250 cm^{-1} while the dielectric mode has been normally used between 100 and 600 cm^{-1}. The scanning mirror arm is bent at 90° with the use of a half-cube. This half-cube accommodates the phase modulator assembly.

Manuscript received December 20, 1976.
M. N. Afsar is with the Division of Electrical Science, National Physical Laboratory, Teddington, Middlesex, United Kingdom.
D. D. Honijk and W. F. Passchier are with the Gorlaeus Laboratoria, afd. Fysische Chemie, Rijksuniversiteit, Leiden, The Netherlands.
J. Goulon is with the Laboratoire de Chimie Théorique, Université de Nancy, Nancy, France.