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Antiferromagnetic resonance in the $(K_{1-x}Na_x)MnF_3$ and $(K_{1-x}Li_x)MnF_3$ systems

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Abstract. The X-band antiferromagnetic resonance (AFMR) spectrum of $KMnF_3$ with Li^+ and Na^+ impurities was studied at temperatures from 40 K to T_N. From comparison of the AFMR measurements with results of x-ray studies for the same good-quality crystals it was found that complete coincidence between the magnetic and structural phase transitions does not occur. It was also ascertained that, for $T < T_N$, low-temperature magnetic phase transitions are highly sensitive to the presence of even small quantities of impurities. Consequently, these transitions depend markedly on the quality of the samples analysed.

1. Introduction

Recently, results have been reported of precise x-ray diffraction measurements of the lattice parameters as a function of temperature for $KMnF_3$ [1] and for the mixed systems $(K_{1-x}Na_x)MnF_3$ and $(K_{1-x}Li_x)MnF_3$ [2]. From the splitting of the cubic (004) Bragg reflection the temperatures of the structural phase transitions which occur in these systems have been determined. Studies on the structural phase transitions in $KMnF_3$ have been carried out over many years and for equally long the controversy concerning the evolution of the crystal structure has persisted [3]. Recent studies by Gibaud *et al* [1] and Ratuszna [2] appear to clarify a number of problems. It has been ascertained that the introduction of a small amount of impurities (less than 5%) into $KMnF_3$ in place of Mn^{2+} [1] or K^+ [2] has a considerable influence on the structural transitions of this compound. The explanation of this given by Gibaud *et al* and by Ratuszna conforms with the concept that tilting of MnF_6 octahedra is facilitated owing to their loose packing and to the occurrence of internal stresses caused by the introduction of additional point defects in the form of small amounts of impurities. It is clear that much of the earlier controversy concerning the description of the $KMnF_3$ structure may have resulted from using samples of different origins and qualities. The $KMnF_3$ crystal becomes antiferromagnetic below the Néel temperature $T_N = 88.3$ K and further transforms to a canted antiferromagnet at the critical temperature $T_1 = 81.5$ K. The magnetic structure is G type in the uniaxial antiferromagnetic region ($T_1 < T < T_N$) with the sublattice magnetization parallel to the z axis and is pseudo-G type in the weak-ferromagnetic region ($T < T_1$) with the sublattice magnetization nearly parallel to the x (or y) axis and slightly canted towards the y (or x) axis. The temperatures T_N and T_1 coincide with the temperatures T_{2c} and T_{3c} observed by Gibaud *et al* [1] for the structural phase transitions. Maartense and Searle [4] also studied the question of the anomalies in magnetic susceptibility near T_N and T_1 for $KMnF_3$. They noticed that, in samples with decreasing particle size, the width and the thermal hysteresis of the canting transition T_1 increase and the canted state can persist up to T_N. The temperature dependence of anisotropy fields of

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the canted antiferromagnet $KMnF_3$ in the low-temperature phase has been investigated by Saiki and Yoshioka [5]. The results show that there exists a magnetic transition associated with spin reorientation at $T_2 \simeq 50$ K, in the absence of any external applied field.

It therefore seems worthwhile to investigate the influence of these impurities on the magnetic properties of $KMnF_3$. The $KMnF_3$ crystal is characterized by a strong exchange interaction and small anisotropy and thus represents an attractive material for the study of antiferromagnetic resonance (AFMR). In this paper the results of AFMR studies on the mixed systems $(K_{1-x}Na_x)MnF_3$ and $(K_{1-x}Li_x)MnF_3$ are presented. The measurements were made on single crystals obtained by the same technological procedure as those analysed by Ratuszna [2]. The AFMR spectra of $(K_{1-x}Na_x)MnF_3$ and $(K_{1-x}Li_x)MnF_3$ crystals were recorded on an X-band spectrometer (about 9.3 GHz), over the range of temperatures from 40 K to T_N using a helium gas-flow cryostat (Oxford Instruments).

2. Experimental results and discussion

2.1. Magnetic phase transitions

In the range from 88 to 300 K the EPR spectrum obtained for samples of $(K_{0.995}Li_{0.005})MnF_3$, $(K_{0.99}Na_{0.01})MnF_3$ and $(K_{0.98}Na_{0.02})MnF_3$ is represented by a single symmetric resonance line, Lorentzian in shape. The g-value is 2.002 and the linewidth ΔB_{pp} is 6 mT, and these values remain constant throughout the entire temperature range. The resonance spectrum shifts towards lower fields when the temperature is reduced below $T = 88$ K. Simultaneously the spectrum was found to be anisotropic and temperature dependent. The temperature $T = 88$ K is the Néel temperature T_N for all samples measured. Hence it is clear that magnetic properties such as the exchange interaction and the Néel temperature are unaffected by the low concentrations of Li^+ and Na^+ and have the same values as in pure $KMnF_3$.

The spectra observed in the AFMR are the superimposed resonance lines corresponding to the various types of domain in the distorted crystals. The theoretical formula of the AFMR includes terms expressing the internal effective fields, which are also temperature dependent. Those dependences usually have a monotonic character. Thus any discontinuities observed in the resonance field versus temperature dependence, shown as new resonance lines, would suggest the presence of phase transitions. The temperature dependences of the resonance field $B_0(T)$ for the samples examined are shown in figures 1–6; the external magnetic field was applied along the ⟨100⟩ and ⟨110⟩ pseudo-cubic directions.

2.1.1. $(K_{0.995}Li_{0.005})MnF_3$ crystal. Figures 1 and 2 show the temperature dependences of the resonance field for this sample. Below $T_N = 88$ K an AFMR spectrum appears which is a superposition of two resonance lines of different amplitudes; this clearly demonstrates that the domain distribution is not homogeneous. These lines move towards low-field values, with a simultaneous decrease in amplitudes. At a temperature T_1 of about 84 K a new group of resonance lines appear at the higher field. Thus, at temperatures slightly below T_1, two kinds of resonance line coexist and the AFMR spectrum becomes very complex. At about $T_2 = 69$ K a new group of lines of small amplitude appear, shifting towards lower fields with decreasing temperature. At the same time a resonance line appears at a field higher than the paramagnetic resonance field. It is assumed that this corresponds to the spin-flop mode.

From data presented in figures 1 and 2, it follows that with a decrease in the sample temperature, the AFMR spectrum undergoes changes. The discontinuities observable at the temperatures T_N, T_1 and T_2 suggest that certain phase transitions occur at these temperatures.

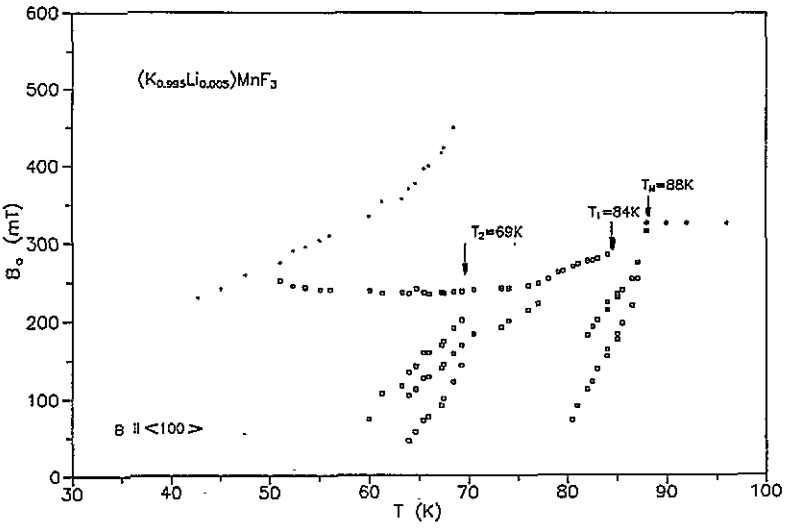

Figure 1. Temperature dependence of the resonance fields for $(K_{0.995}Li_{0.005})MnF_3$ for $B\|\langle 100\rangle$: *, EPR mode; □, AFMR modes; •, spin-flop mode.

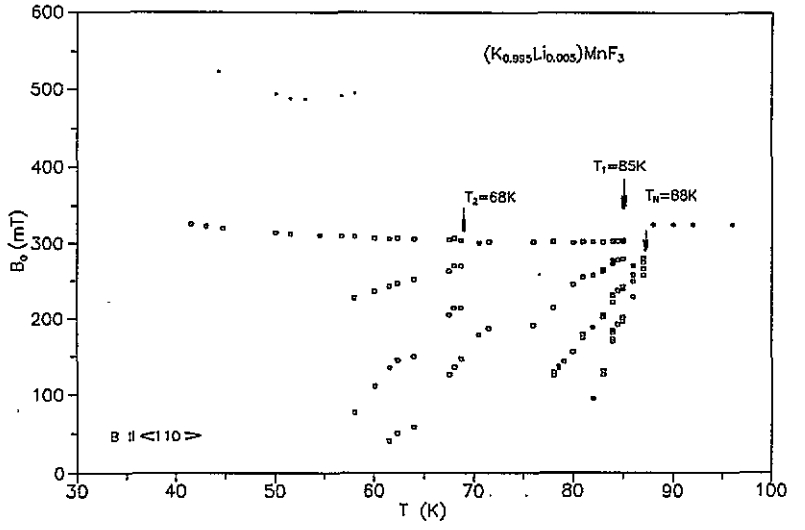

Figure 2. Temperature dependence of the resonance fields for $(K_{0.995}Li_{0.005})MnF_3$ for $B\|\langle 110\rangle$: *, EPR mode; □, AFMR modes; •, spin-flop mode.

2.1.2. $(K_{0.99}Na_{0.01})MnF_3$ crystal. The temperature dependences of the resonance field $B_0(T)$ for $(K_{0.99}Na_{0.01})MnF_3$ are shown in figures 3 and 4. Below $T_N = 88$ K the AFMR resonance lines appear at the fields close to $B_0 = 300$ mT, from which it may be concluded that here the magnetic phase transition temperatures T_N and T_1 coincide. With further decrease in temperature, certain new groups of lines appear in the temperature interval from 70 to 77 K. The temperature $T = T_2$ is recognized as the onset of the discontinuity.

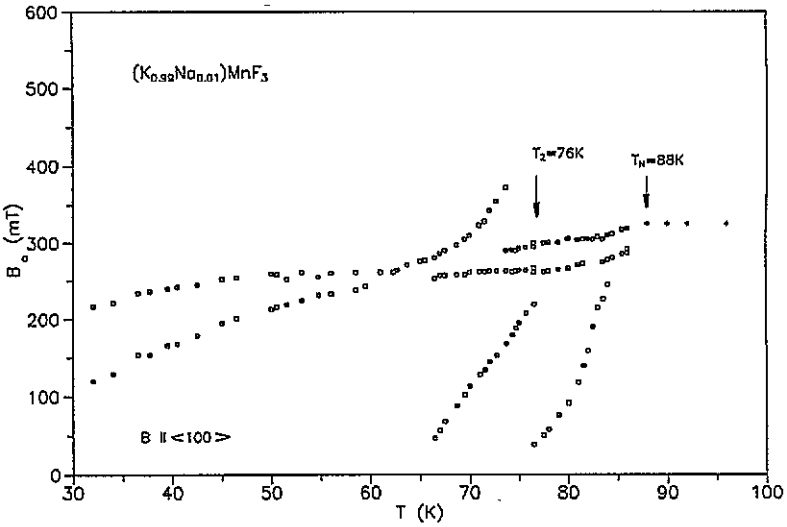

Figure 3. Temperature dependence of the resonance fields for $(K_{0.99}Na_{0.01})MnF_3$ for $B\|\langle 100\rangle$: * EPR mode; □, AFMR modes.

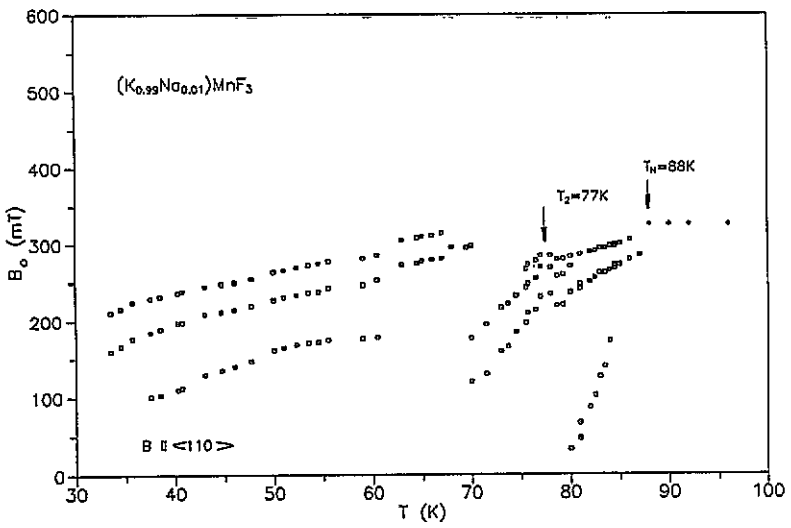

Figure 4. Temperature dependence of the resonance fields for $(K_{0.99}Na_{0.01})MnF_3$ for $B\|\langle 110\rangle$: *, EPR mode; □, AFMR modes.

2.1.3. $(K_{0.98}Na_{0.02})MnF_3$ crystal. The temperature dependences of the AFMR resonance fields for $(K_{0.98}Na_{0.02})MnF_3$ are shown in figures 5 and 6. Two AFMR modes appear below $T_N = 88$ K. On decrease in the temperature these modes shift towards low-field values and simultaneously their amplitudes are reduced. For this sample, at $T_1 = 84$ K a new small-amplitude resonance line appears, which also markedly decreases with decrease in temperature. The temperature T_2 is difficult to determine owing to the 'broadening' effect in the transition region. We have estimated this temperature to be about 70 K. For the sample

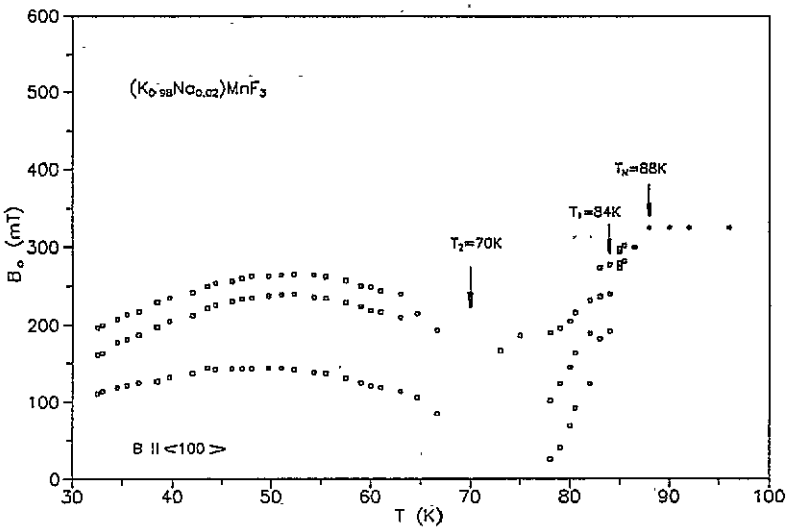

Figure 5. Temperature dependence of the resonance fields for $(K_{0.98}Na_{0.02})MnF_3$ for $B\|(100)$: *, EPR mode; □, AFMR modes.

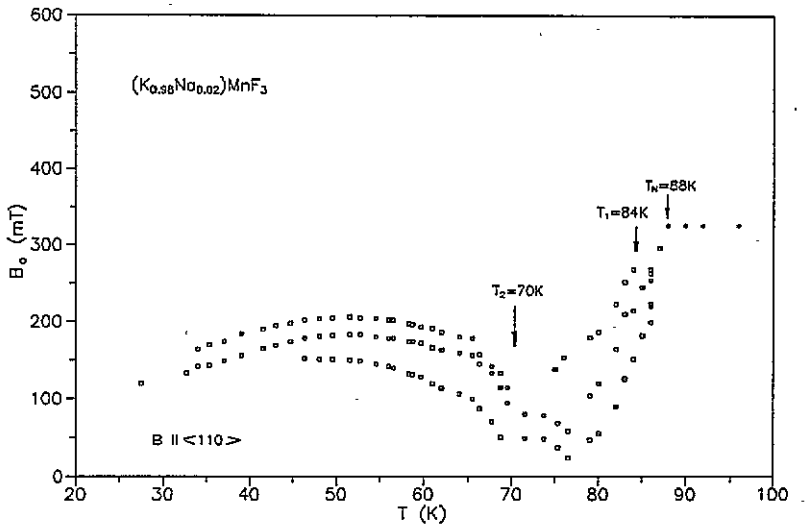

Figure 6. Temperature dependence of the resonance fields for $(K_{0.98}Na_{0.02})MnF_3$ for $B\|(110)$: * EPR mode; □ AFMR modes.

analysed, the spin-flop mode was not observed throughout the whole range of temperatures.

We believe that the magnetic phase transitions observed in the samples studied correspond to phase transitions characteristic of 'pure' $KMnF_3$. Thus, $T = T_N$ corresponds to the transition to the antiferromagnetic phase, $T = T_1$ to the transition to the weak-ferromagnetic phase and $T = T_2$ is a magnetic phase transition associated with a spin reorientation inside the domain.

The temperature values T_N, T_1, T_2 for the particular compounds are presented in table 1.

Table 1. Comparison of structural and magnetic properties.

	Structural phase transitions (temperatures (K))			Magnetic phase transition (temperatures (K))		
Compound	T_{1c}	T_{2c}	T_{3c}	T_N	T_1	T_2
$KMnF_3$	186	88	82	88.3	81.5	50
$(K_{0.995}Li_{0.005})MnF_3$	190	98	93	88	84	69
$(K_{0.99}Na_{0.01})MnF_3$	201	122	92	88	88	76
$(K_{0.98}Na_{0.02})MnF_3$	206	—	84	88	84	70

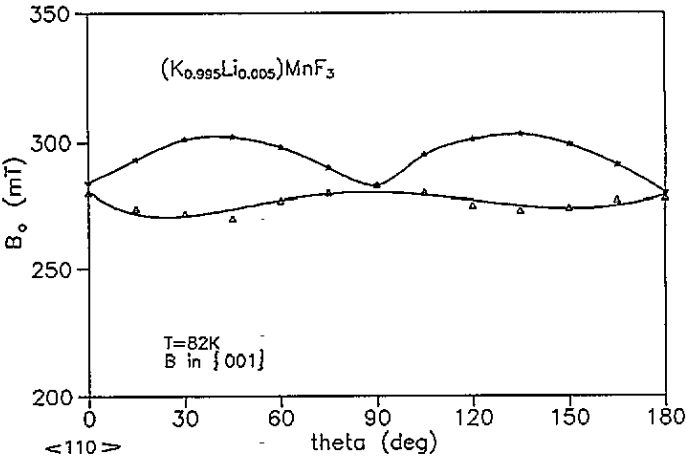

Figure 7. Angular dependence of the resonance fields for $(K_{0.995}Li_{0.005})MnF_3$ (angle in a {100} plane; $T = 82$ K).

The angular dependence of the resonance field for several cases is shown in figures 7 and 8. Over the range of temperatures $T_1 < T < T_N$, measurement of anisotropy was not feasible owing to the appearance of a new phase and the extremely marked temperature dependence of the AFMR spectrum. The anisotropy was therefore measured at $T_A = 82$ K and $T_B = 40$ K, i.e. for $T_A < T_1$ and $T_B < T_2$. In both cases the external magnetic field was applied in the {001} plane. In figure 8 the anisotropy can also be seen for the spin-flop mode. A fourfold type of angular dependence in T_A and T_B may be observed.

2.2. *Resonance analysis*

In [2] the structural evolution of $(K_{0.995}Li_{0.005})MnF_3$, $(K_{0.99}Na_{0.01})MnF_3$ and $(K_{0.98}Na_{0.02})MnF_3$ crystals as a function of temperature was established. Table 1 presents the temperatures of structural phase transitions for several compounds. The temperature T_{1c} is attributed to the appearance of the tetragonal phase (the space group of which evolves from $Pm3m$ for $T > T_{1c}$ to $I4/mcm$ for $T < T_{1c}$). The real tetragonal unit cell has dimensions $2a_p \times 2a_p \times 2c_p$ where the subscript p refers to relative pseudo-cubic parameters. The next deformation of the cubic perovskite unit cell to orthorhombic symmetry took place at temperature T_{2c} (space group, $Bmmb$). The dimensions of the real orthorhombic cell are $2a_p \times 2b_p \times 2c_p$. The next deformation of the pseudo-cubic unit cell below T_{3c} leads to the monoclinic phase. The values of the lattice parameters enable us to make a transformation from the monoclinic cell to the orthorhombic cell with dimensions

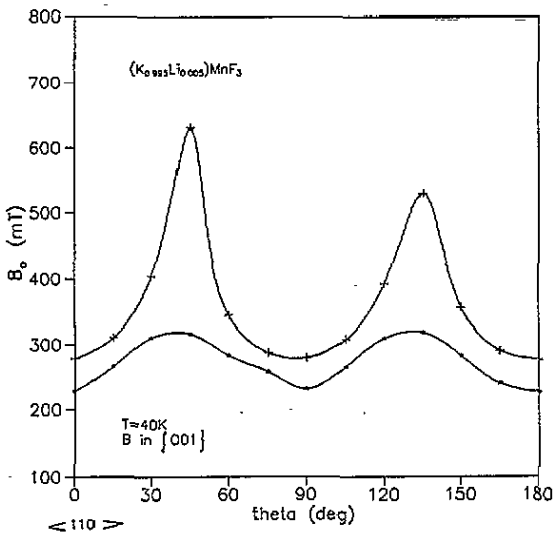

Figure 8. Angular dependence of the resonance fields for $(K_{0.995}Li_{0.005})MnF_3$ (angle in a {001} plane: $T = 40$ K).

$2a_p \cos(\beta/2) \times 2b_p \times 2a_p \sin(\beta/2)$, where β is the angle of the monoclinic unit cell (for $T < T_{3c}$ the space group is $Pnma$).

In further considerations of the AFMR properties it is assumed that the form of the free energy is based on the symmetry of the structure. For the low-temperature phase, the free energy for the studied compounds is represented as

$$F = JM_1 \cdot M_2 - D \cdot (M_1 \times M_2) - H \cdot (M_1 + M_2) + \sum_{i/1}^{2} \left[-\frac{K}{2M_0^2} M_{iz}^2 - \frac{K'}{2M_0^2} M_{ix}^2 + \frac{K_4}{2M_0^4} \left(M_{iz}^4 + \frac{(M_{ix} + M_{iy})^4}{4} + \frac{(M_{ix} - M_{iy})^4}{4} \right) \right] \tag{1}$$

where the X, Y and Z axes are taken in the directions of the a, b and c axes of the orthorhombic cell, respectively, M_1 and M_2 are the sublattice magnetizations, J is the exchange interaction constant, K and K' are the orthorhombic anisotropy constants, K_4 is the cubic anisotropy constant, and D is the Dzyaloshinsky–Moriya vector. We introduce a cubic anisotropy parameter since x-ray measurements of the samples show that deviation from the cubic symmetry at low temperatures is small [2]. This is confirmed by the angular dependence of the resonance field (see figures 7 and 8). As the sequence of structural phase transitions of the samples under investigation is the same as in pure $KMnF_3$, we suggest that the resonance behaviour of these samples can be explained using the assumptions of Saiki and Yoshioka [5] for $KMnF_3$, i.e. the canting of the sublattice magnetizations is due to the antisymmetric exchange interactions with the Dzyaloshinsky–Moriya vector D. We conjecture that an additional AFMR mode appearing at low temperatures and high applied fields (see figures 1–3) as a spin-flop mode. For this case the frequency of the resonance mode excited by a RF field perpendicular to the applied field is given by [5]†

† We did not include demagnetization effects in the resonance expressions for the AFMR modes as the shift in AFMR frequency produced by demagnetization effects is only of significance for antiferromagnets with small exchange fields.

$$(\omega/\gamma)^2 = H^2 + H_D H - 2H_E H_K + 2H_E H_{K'} - 2H_E H_4 + 2H_E H_N \qquad (2a)$$

for H along [001] and

$$(\omega/\gamma)^2 = H^2 + H_D H + 2H_E H_K - 2H_E H_{K'} - 4H_E H_4 + 2H_E H_N \qquad (2b)$$

for H along [110], where we define the effective fields by $H_E = -JM_0$ is the exchange field, $H_D = DM_0$ is the Dzyaloshinsky–Moriya field, $H_K = K/M_0$, $H_{K'} = K'/M_0$ and $H_4 = K_4/M_0$ are the anisotropic fields and H_N is the effective nuclear field due to the hyperfine interaction of an antiferromagnetic system with the Mn^{55} nuclear moments.

The values of the effective fields were calculated from the experimental data (2); for $(K_{0.995}Li_{0.005})MnF_3$ they are $(H_E H_4)^{1/2} = 3.6$ kOe and $[H_E(H_K - H_{K'})]^{1/2} = 4.8$ kOe for $T = 40$ K, $H_D = 1.9$ kOe [5] and $H_E H_N = 0$ (the nuclear field is inversely proportional to the temperature and we can take $H_N = 0$ for our temperature region).

Despite the very small amount of Li^+ ions present in $KMnF_3$, the values of anisotropic fields are much higher than those for 'pure' $KMnF_3$ [5]. This means that all structural defects (in our case, controlled introduction of defects via an impurity) will markedly affect the anisotropic field in these crystals and hence also their magnetic properties.

2.3. *AFMR linewidth*

The analysis of the linewidth in our studies is hindered by the domain structure, by the appearance of the phase transitions and also by the magnetization movement in the magnetic field. At temperatures below the Néel temperature T_N the spectra observed in the AFMR of $(K_{1-x}Li_x)MnF_3$ and $(K_{1-x}Na_x)MnF_3$ are composed of the resonance lines corresponding to different types of antiferromagnetic domains. These lines differ considerably in intensity and are situated at varying distances from one another, depending on the impurity concentration. Figure 9 presents the function ΔB_{pp} versus temperature for $(K_{0.995}Li_{0.005})MnF_3$. Over the range of temperatures $T_1 < T < T_N$ the spectrum resolution is poor and determination of the resonance linewidth is not feasible. For $T_2 < T < T_1$, the AFMR line shows a very weak temperature dependence. A marked increase in ΔB_{pp} is related to the fluctuation occurring within the phase transition region T_2. For $T < T_2$, outside the critical region variations in resonance linewidths with temperature can be observed conforming to the relation $\Delta B_{pp} \sim T^2$. According to Rezende and White [6], the temperature dependence of the linewidth of the AFMR is a result of multimagnon processes. The comparison between our experimental data and the theory of Rezende and White suggests that the relaxation rate of the $k = 0$ magnon mode above $1/4T_N$ is dominated by the four-magnon process with a T^2 dependence of the linewidth.

3. Conclusions

It is noteworthy that, in our studies, the magnetic properties were evaluated for the same good-quality crystals as those used in [2]. In this way, by analysis of the mutual correlation between structural properties and magnetic properties of such compounds we were able to elucidate some of the controversial points arising in detailed studies on $KMnF_3$. Small amounts of impurities introduced into the $KMnF_3$ host can produce point defects, leading to internal stresses and thus affect the properties of the crystals. The EPR and AFMR measurements showed that values of the Néel temperatures T_N are determined by the exchange interactions which do not undergo any changes while small admixtures of Na^+

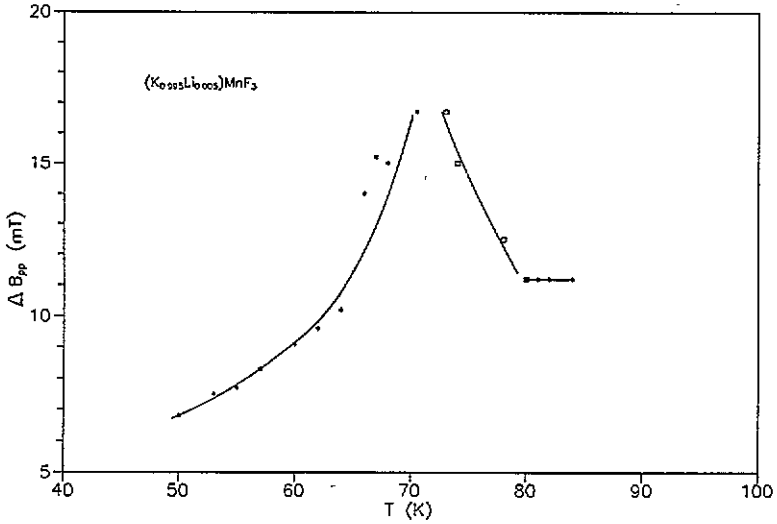

Figure 9. Temperature dependence of the resonance linewidth for $(K_{0.995}Li_{0.005})MnF_3$.

and Li^+ ions are in $KMnF_3$. Any qualitative alterations in the character of the AFMR spectrum, such as the appearance of new resonance lines, or any discontinuities in the temperature dependence of a resonance field, we have considered as evidence of phase transition phenomena. On this basis, as well as the T_N temperature describing the transition to the antiferromagnetically ordered phase, we have determined the presence of two further magnetic phase transitions at T_1 and T_2 for the compounds studied. These phase transitions are very sensitive to the presence of certain other ions in the $KMnF_3$ host. On comparison of the temperature values for structural phase transitions and magnetic phase transitions (see table 1), it may be concluded that the temperature T_1 at which the new resonance lines appear can be taken as the temperature of transition to a weak-ferromagnetic phase, which is in turn associated with monoclinic distortion of the pseudo-cubic lattice.

The magnetic phase transition designated as occurring at the T_2-value is very 'smeared' in its temperature scale. The relevant AFMR spectrum is composed of many resonance lines originating from many different domains. From the experimental results reported by Saiki and Yoshioka [5] it follows that for the $KMnF_3$ crystal a second-order phase transition occurs as a result of the onset of a gradual rotation of the antiferromagnetic axis.

This paper, containing only experimental data at frequency $\nu \simeq 9.3$ GHz, must be regarded as merely an introduction to the problem; can even small non-magnetic admixtures exert a significant influence on the magnetic properties of weak-ferromagnetic perovskites? A full analysis of AFMR properties would require experiments made at several different frequencies.

Acknowledgment

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