ANOMALOUS ACOUSTIC RELAXATION ABSORPTION AND ACOUSTIC PARAMAGNETIC RESONANCE IN KMgF₃ CONTAINING Fe²⁺*

PETER JOHN KING,** JOHN MONK,** Nottingham

We have studied the acoustic relaxation absorption due to Fe^{2+} ions in $KMgF_3$ as a function of temperature at the frequency of 580 MHz and 1 GHz. We find an excited state at 96 cm^{-1} in agreement with Kim and Lange rather than with earlier authors. The ratio of the magnetoelastic coupling constants G_{11} and G_{44} disagrees with estimates from acoustic paramagnetic resonance and it is shown that static strains in the lattice may be responsible for this apparent discrepancy.

АНОМАЛЬНОЕ РЕЛАКСАЦИОННОЕ ПОГЛОЩЕНИЕ УЛЬТРАЗВУКА И АКУСТИЧЕСКИЙ ПАРАМАГНИТНЫЙ РЕЗОНАНС В KMgF₃, СОДЕРЖАЩЕМ ИОНЫ Fe²⁺

В статье изучается температурная зависимость релаксационного поглощения ультразвука при частотах 580 Мгц и 1 Ггц, которое обусловлено ионами Fe^{2+} в $KMgF_3$. Обнаружено возбужденное состояние с волновым числом 96 cm^{-1}, которое находится в соответствии с работой Кима и Ланге, но не с работами более ранних авторов. Отношение магнитоупругих констант связи G_{11} и G_{44} не согласуется с оценкой, следующей из акустического парамагнитного резонанса. Показано, что причиной этого явного расхождения могут быть относительные статические деформации в решетке.

I. INTRODUCTION

The low lying energy levels of a magnetic ion situated in a dielectric host lattice can often be investigated acoustically either by the technique of acoustic paramagnetic resonance (APR) or by studying the non-resonant relaxation absorption. The information obtainable from studies includes energy level separations, the strength of the lattice-ion coupling and the spin lattice relaxation times.

Iron substitutes for magnesium when introduced into the $KMgF_3$ lattice producing Fe^{2+} ions expected to be on sites of octahedral symmetry, the iron being

surrounded by six fluorine atoms. $3d^6$, Fe^{2+} ions when placed in a cubic crystal field have a ground state triplet lying below a set of closely spaced levels consisting of a triplet and a doublet. The effect of covalency and the dynamic Jahn—Teller effect are expected to merely alter the scale of the energy level spacings. The ground state triplet is split both by the magnetic field and by strain so that both APR and relaxation absorption may be observed. APR measurements have been made by Wigmore, Rosenberg and Garrod [1] who found strain broadened resonances and obtained $|G_{11}| = 1340 \pm 100$ cm^{-1} and $|G_{44}| = 1000 \pm 100$ cm^{-1} for the magnetoelastic coupling constants. Combaz [2] has also studied this system and finds $|G_{11}| \cong |G_{44}|$. More recently Kim and Lange [3] and the present authors have studied Fe^{2+} in $KMgF_3$ using relaxation techniques. Kim and Lange find that relaxation absorption modes purely associated with C_{11}, G_{11}. An analysis of their results assuming cubic sites appears to give $|G_{44}| \gg |G_{11}|$ in disagreement with the APR data. Kim and Lange also report excited states at 94 cm^{-1} an estimate larger than those of previous authors [4], [5] (in far infrared). It is the intention in the present paper to give some experimental results which confirm the findings of Kim and Lange and to suggest an explanation for the disagreement between the APR and the relaxation data.

II. EXPERIMENTAL RESULTS

The attenuation of ultrasound has been measured in samples of $KMgF_3$ containing a nominal 500 ppm of iron (by weight) and on a sample containing iron as a trace impurity in addition to the main dopants Ni (2%) and V (2%). Measurements have been made at 580 MHz and 1 GHz between 1.5 K and 300 K using a pulse echo technique. Samples cut along the crystallographic (100) axis into the form of a rod were optically polished and given a thin aluminium coating. Cadmium sulphide thin film piezoelectric transducers were then deposited in such a way that either compressional or transverse modes could be observed. The attenuation was obtained by comparing the echo heights at each temperature with those in the limit of low temperatures. In an extensive set of measurements on the 500 ppm iron doped samples only thermal phonon attenuation was found for the compressional mode but for the transverse mode a relaxation peak was present in addition. The form of the peak is shown in Fig. 1, the thermal phonon background having been removed.

The peak was analysed using the expression for the relaxation attenuation

$$\alpha = \frac{4.34 G^2 N(T)}{2kT\varrho v^3} \cdot \frac{\omega^2 \Gamma(T)}{(1 + \omega^2 \Gamma^2(T))} \qquad (1)$$

together with an expression for the relaxation time containing a direct process and a single Orbach term (see for example [6]):

$$\frac{1}{\Gamma} = AT + \frac{B}{(e^{\Delta/kT} - 1)}. \qquad (2)$$

In these expressions $N(T)$ is the number of relaxing ions, ϱ is the density, v is the velocity of sound appropriate to the mode and $\Gamma(T)$ is the relaxation time, Δ is the separation of the group of excited states from the ground state. We obtained a good fit to our data with those expressions if a good agreement between our data and
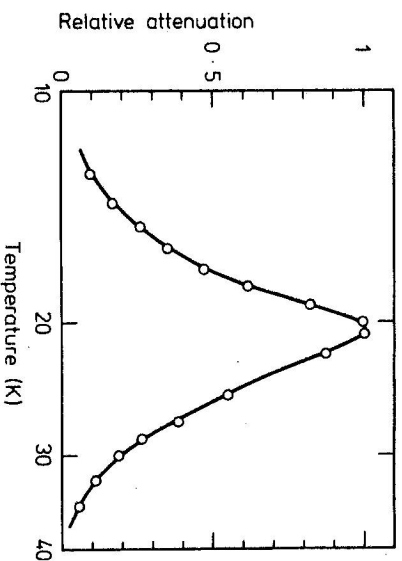
Relative attenuation

1

0·5

0

10   20   30   40

Temperature (K)

Fig. 1. The form of the relaxation peak as a function of temperature at 580 MHz

those expressions with $A = 0$, $B = 2.1 \times 10^{12}$ Hz, $\Delta = 96$ cm^{-1}. This value of Δ confirms that of Kim and Lange rather than those previously obtained. It is also possible from expression (1) to obtain and estimate of the limits on $|G_{11}|/|G_{44}|$ from the ratio of the transverse mode attenuation (α_S) to estimates of the upper limit on the compressional mode attenuation (α_L). Noting that

$$\frac{\alpha_L}{\alpha_S} = \frac{G_{11}^2}{G_{44}^2} \frac{v_S^3}{v_L^3} \frac{2}{3}$$

we find $|G_{11}|^2 \leq 0.3 |G_{44}|^2$. It is to be noted that the ratio v_L/v_S is particularly large for $KMgF_3$.

III. THE EFFECT OF STATIC STRAINS

In the analysis of acoustic relaxation loss caused by Fe^{2+} ions in MgO it has been noted that random static strains present in the lattice can considerably influence the magnitude of the relaxation absorption [6][1]. The sensitivity of the energy levels and

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[1] It is to be noted that the vertical scales of Figure 3 in paper [6] are uncorrectly labelled — see the present Figure 2.

thus the populations to the acoustic dynamic strains are reduced by varying amounts by static strains known to exist both in MgO and KMgF$_3$ from APR data.

We have calculated the reduction in G_{11} and G_{44} caused by this effect using the data of Wigmore, Rosenberg and Garrod [1]. Two static strain vectors ε_L (ε_{xx}, ε_{yy}, ε_{zz}) and ε_S (ε_{xy}, ε_{xz}, ε_{yz}) are defined. In the most simple case these are taken to be random in direction. Using computer diagonalisation of the appropriate Hamiltonian, reduction factors $|G_{11}|_{eff}/|G_{11}|^2$ and $|G_{44}|_{eff}/|G_{44}|^2$ can be computed.
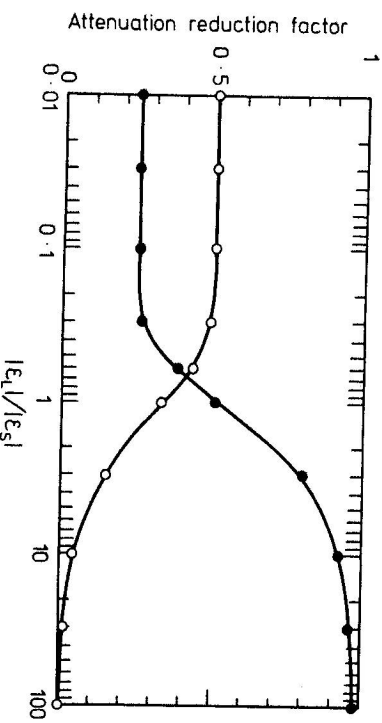

Fig. 2. The attenuation reduction factors $|G_{11}|_{eff}/|G_{11}|^2$ (●) and $|G_{44}|_{eff}/|G_{44}|^2$ (○) as a function of $|\varepsilon_L|/|\varepsilon_S|$.

Readers are referred to [6] for details of this calculation. The results are given as a function of $|\varepsilon_L|/|\varepsilon_S|$ in Fig. 2. (ε_L, ε_S are both assumed to be larger than the acoustic dynamic strain). We note that the region $|\varepsilon_L/\varepsilon_S| > 1$ has been used to explain the absence of a relaxation peak in the $\langle 100 \rangle$ transverse mode in MgO.

If the condition $|\varepsilon_L/\varepsilon_S| < 1$ is appropriate for KMgF$_3$, although the reduction in $|G_{11}|_{eff}^2/|G_{44}|_{eff}^2$ of about by two is as it stands barely sufficient to explain the data, preliminary calculations performed with non-isotropic shear strain distributions give slightly different reduction factors but until more is known about the actual environment of the Fe^{2+} ion, it is difficult to say which distribution is more appropriate.

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