Strain-ion coupling effects on elastic constants of $FeCl_2$ †

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Measurements of the elastic constants c_{33}, c_{44}, and c_{66} in $FeCl_2$ are reported. The temperature dependence of c_{44} and c_{66} in the paramagnetic region is explained by the strain–single-ion coupling mechanism. Similar effects were previously observed for rare-earth ions but not for transition metal ions. The effect of this coupling for c_{33} is expected to be small and was not observed experimentally. A critical behavior of c_{33} is observed near the Néel temperature.

I. INTRODUCTION

Ultrasonic studies of magnetic materials reveal interesting aspects of various coupling mechanisms, e.g., magnon-phonon interactions,[1] soft modes,[2] critical phenomena (mode-mode coupling) at second-order magnetic phase transitions, etc.[3,4] Recently, effects due to coupling between strain and single-ion energy levels of rare earths in the paramagnetic region have been observed and studied.[5,6] We report here what we believe is the first observation of such effects due to interaction with a transition-metal ion. This work is part of a study of ultrasonic-sound propagation in $FeCl_2$ and we will focus here mainly on the paramagnetic region (above $T_N = 23.5$ °K) at zero magnetic field. There has recently been a great interest in this material because of its metamagnetic properties[7] and its tricritical point.[8,9]

$FeCl_2$ is a trigonal crystal belonging to space group D_{3d}^5 and can be seen as built by layers of Fe^{++} ions separated by double layers of Cl^- ions. There is a ferromagnetic exchange between ions in the same layer (perpendicular to the trigonal axis) and an antiferromagnetic exchange between planes that is about twenty times weaker than the in-plane exchange. A relatively strong anisotropy aligns the magnetic moments along the trigonal axis. The free-ion $3d^6\,{}^5D$ level of the Fe^{++} ion is split by the cubic part of the crystal field into an upper orbital doublet and a lower triplet with an effective angular momentum $L = 1$. The Hamiltonian for this triplet, including spin-orbit coupling and axial component of the crystal field, can be written in the usual way[10] as

$$H_{\text{ion}} = \lambda \vec{\mathbf{L}} \cdot \vec{\mathbf{S}} + \delta(L_z^2 - \tfrac{2}{3}) \quad (S = 2). \tag{1}$$

Here $\vec{\mathbf{L}}$ is the effective angular momentum of the triplet and L_z its component along the trigonal axis, λ is the effective spin-orbit coupling and the second term is the axial component of the crystal field. For λ and δ we used the values of Alben[11] $\lambda = 67$ cm^{-1}, $\delta = -88$ cm^{-1} that were determined as best fit to susceptibility, resonance, and magnetization data. These values have been also used recently by Birgeneau *et al.*[12] to fit the results of their neutron study of the magnon spectra. The 15-fold degenerate state is split into three groups of states corresponding roughly to $J = 3, 2, 1$. For more details we refer to Ref. 12.

II. THEORY

The theory of the coupling between the single ion and the ultrasonic strain can be summarized as follows: The strain modulates the crystal field and the corresponding strain-ion Hamiltonian per ion in a hexagonal symmetry can be written[13]

$$\begin{aligned} H_{si} = {} & (b_a \epsilon_a + b_b \epsilon_b)[L_z^2 - \tfrac{1}{3}L(L+1)] \\ & + b_{xy}[\tfrac{1}{2}(\epsilon_1 - \epsilon_2)(L_x^2 - L_y^2) + \epsilon_6(L_x L_y + L_y L_x)] \\ & + b_{yz}[\epsilon_4(L_y L_z + L_z L_y) + \epsilon_5(L_x L_z + L_z L_x)]. \end{aligned} \tag{2}$$

$$\epsilon_a = \epsilon_1 + \epsilon_2 + \epsilon_3, \quad \epsilon_b = \epsilon_3 - \tfrac{1}{3}\epsilon_a.$$

Here the b's are coupling constants and the ϵ's are the strains with the usual notation $1 \longleftrightarrow xx$, $4 \longleftrightarrow yz$. H_{si} is therefore a sum of products of Stevens operators acting on the ion and "symmetry mode" strains having the same symmetry properties as the corresponding Stevens operators. In the trigonal symmetry of $FeCl_2$ there are two extra terms

$$\begin{aligned} & b_c[\tfrac{1}{2}(\epsilon_1 - \epsilon_2)(L_y L_z + L_z L_y) + \epsilon_6(L_x L_z + L_z L_x)] \\ & + b_d[\epsilon_4(L_x^2 - L_y^2) + \epsilon_5(L_x L_y + L_y L_x)]. \end{aligned}$$

We will use in our analysis an hexagonal approxi-

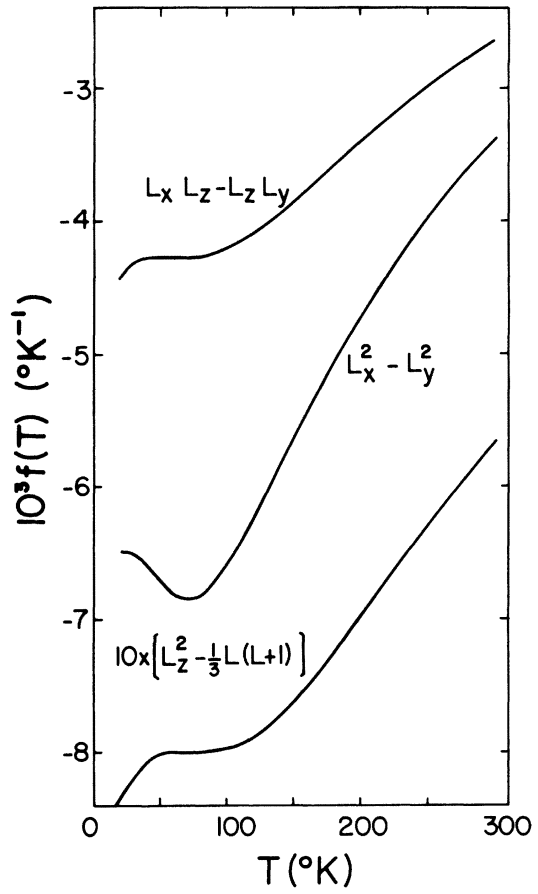

FIG. 1. Calculated values of $f(T)$ [Eq. (6)] vs temperature for the three Stevens operators. Note that for $L_z^2 - \frac{1}{3}L(L+1)$ the scale has been increased tenfold. The dimension of $f(T)$ is (energy)$^{-1}$ and is given in (°K)$^{-1}$.

mation assuming these two terms to be small. The elastic free energy density for one of the symmetry mode strains ϵ can be written

$$F = \tfrac{1}{2}c_0\epsilon^2 + NkT\ln Z. \tag{3}$$

Here c_0 is the background elastic constant, N is the number of ions per unit volume ($N = 1.55 \times 10^{22}$ cm^{-3}), and Z is the single-ion partition function

$$Z = \sum e^{-\beta E_j(\epsilon)}, \tag{4}$$

where $\beta = 1/kT$ and the summation is over the energy levels $E_j(\epsilon)$ of the Hamiltonian $H = H_{\text{ion}} + H_{si}$ of Eqs. (1) and (2). The elastic constant c is then given by

$$c = \frac{\partial^2 F}{\partial \epsilon^2} = c_0 + NkT\,\frac{\partial^2 \ln Z}{\partial \epsilon^2}. \tag{5}$$

It is convenient to define $B = Nb$, $\eta = b\epsilon$. The expression for c becomes

$$c = c_0 + (B^2/N) f(T), \tag{6}$$

with

$$f(T) = kT\,\frac{\partial^2 \ln Z}{\partial \eta^2} = \left\langle \frac{\partial^2 E}{\partial \eta^2} \right\rangle - \beta \left\langle \left(\frac{\partial E}{\partial \eta} \right)^2 \right\rangle + \beta \left\langle \frac{\partial E}{\partial \eta} \right\rangle^2 .$$

Here $\langle\ \rangle$ indicates thermal average. The calculated values of $f(T)$ are plotted in Fig. 1 for all three Stevens operators $L_z^2 - \frac{1}{3}L(L+1)$, $L_x^2 - L_y^2$ (or $L_x L_y + L_y L_x$), and $L_x L_z + L_z L_x$ (or $L_y L_z + L_z L_y$). The calculations were performed by computer diagonalization of the matrix of $H = H_{\text{ion}} + H_{si}$ and numerical computation of the derivatives of the energy eigenvalues. As always, $f(T)$ is negative and is an increasing function of temperature almost everywhere, thus causing a trend opposite to that of the normal elastic constant c_0.

III. RESULTS AND DISCUSSION

Single crystals of $FeCl_2$ were grown by Bridgman technique.[12] Samples were cleaved perpendicular to the trigonal axis and prepared with flat and parallel end faces. Velocity measurements were carried out at 30 MHz using a phase comparison set up similar to the one described in Ref. 14. The resolution was 3 ppm for velocity changes and the absolute velocity was determined with an accuracy of 2%.

The measured values of c_{44} as function of temperature obtained from the sound velocity of a shear wave propagating along the z axis are shown in Fig. 2. We used the x-ray density value $\rho = 3.25$

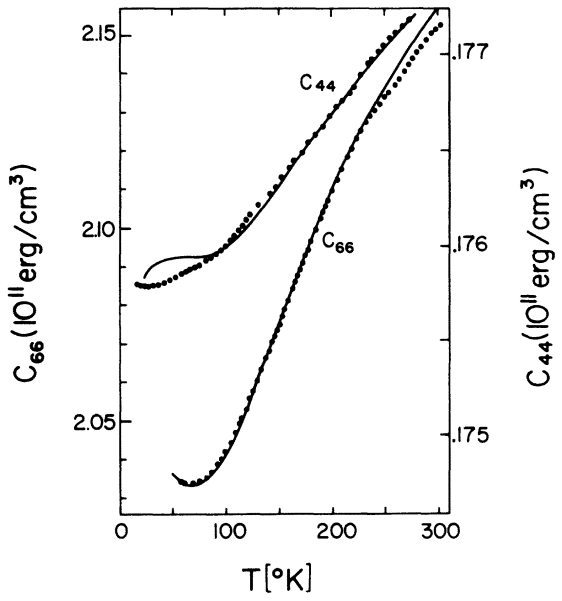

FIG. 2. Measured values of c_{44} and c_{66}. The solid lines are the theoretical fit.

g/cm^3. The data show no critical effect at $T = T_N$ as is often the case with shear waves.[4,15-17] The solid curve is a fit to the theory from the corresponding $f(T)$ (operator $L_x L_z + L_z L_x$), and using $c_0 = 0.1795 \times 10^{11}$ erg/cm^3 and $|B_{xz}| = 4.25 \times 10^8$ erg/cm^3. The fitting is satisfactory in view of the approximation in the theory, and cannot be improved by introducing a temperature dependence of c_0. It can only be stated that the main temperature dependence of c_{44} comes from the strain-ion interaction. The theory of interaction with single ion is not valid in the ordered state because it neglects the effects of exchange on the ions' energy levels. Therefore, the fit shown is limited to the paramagnetic region.

Also shown in Fig. 2 is the elastic constant derived from measurements of shear waves propagating along the x axis (perpendicular to the vertical mirror plane) and excited along the y direction. This is c_{66} in the hexagonal approximation where the sound velocity is independent of the direction of propagation in the xy plane. Cursory measurements of waves propagating along the y direction (that gives c_{66} in the trigonal symmetry of $FeCl_2$) showed similar temperature dependence and a difference of 4% in the absolute value of the sound velocity. Again the solid curve is the fit to the theory from the corresponding $f(T)$ (operator $L_x^2 - L_y^2$) and with $c_0 = 2.279 \times 10^{11}$ erg /cm^3 and $|B_{xy}| = 2.77 \times 10^9$ erg/cm^3. Here the fit is better than for c_{44}, in particular the positions of the experimental and calculated minima coincide well. The deviation at high temperature is probably due to our neglect of the temperature dependence of c_0.

Let us turn to the modes that couple to the ions' energy via the operator $L_z^2 - \frac{1}{3}L(L+1)$. There are two such strains denoted as ϵ_a and ϵ_b in Eq. (2). The elastic free energy owing to these deformations can be shown from symmetry arguments to be of the form[13]

$$F(\epsilon_a, \epsilon_b) = \tfrac{1}{2} c_{aa} \epsilon_a^2 + c_{ab} \epsilon_a \epsilon_b + \tfrac{1}{2} c_{bb} \epsilon_b^2 , \qquad (7)$$

with no cross terms with the other symmetry modes. The c's in Eq. (7) can be expressed as combination of the Cartesian-coordinate elastic coefficients c_{33}, c_{11}, c_{12}, c_{13}. The three expressions are given in Ref. 13. From these expressions it can be shown by straightforward algebra that c_{33} and $c_{11} - c_{66} = \frac{1}{2}(c_{11} + c_{12})$ are a combination of c_{aa}, c_{ab}, and c_{bb} only and therefore are affected by the strain-ion interaction only via the operator $L_z^2 - \frac{1}{3}L(L+1)$. The experimental results for c_{33} obtained from measurements of the velocity of a longitudinal wave propagating along the z axis are presented in Fig. 3. Here we have a normal behavior of increasing velocity with decreasing temperature, characteristic of the background elastic constant c_0, but for a small dip at $T = T_N$. It appears therefore that there is no noticeable effect of the strain-ion coupling on this mode. This result is not surprising as the corresponding $f(T)$ is about one order of magnitude smaller than for the shear modes (see Fig. 1). The dip at T_N is characteristic of critical effects of mode-mode coupling at the second-order transition. The analysis of the critical behavior will be published elsewhere.

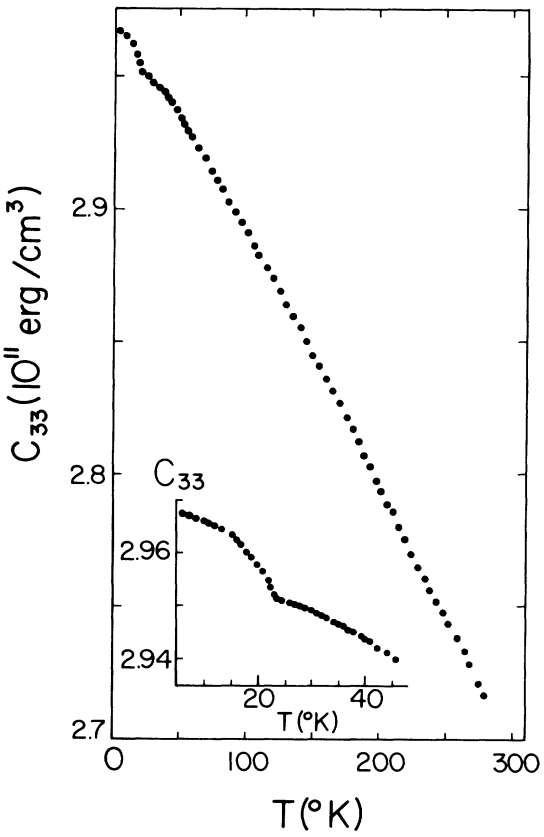

FIG. 3. Measured values of c_{33}. The insert is an expanded plot of the critical region.

As we mentioned, this appears to be the first time that effects of strain-ion coupling for transition-metal ions have been observed in ultrasonic measurements. In many cases, the large crystal-field splitting in transition-metal ions leaves a ground singlet or Kramers doublet that is the only populated state and therefore in these cases the $f(T)$ are constant and no temperature dependence of the sound velocity is expected. In $FeCl_2$ there are low-lying excited levels and the strain-ion coupling mechanism can be detected via the temperature dependence of the sound velocity. The values of the coupling coefficient B_{xy} and B_{xz} are of the same order of magnitude as the

ones found in rare-earth ions.[6] The elastic constant c_{44} is one order of magnitude smaller than c_{66} and therefore the effect of the trigonal terms that we neglected in H_{si} may be relatively more important for c_{44} than for c_{66}.

The dip of c_{33} near T_N seems to be somewhat broad as compared to the critical effects observed in other magnetic insulators, e.g., MnF_2,[15] and $RbMnF_3$.[17] An almost two-dimensional ferromagnet should have a broad transition. This could be the case in $FeCl_2$ as the in-plane exchange is much stronger than the between-planes exchange. Birgeneau *et al.*[12] have found that the magnon spectrum of $FeCl_2$ collapses suddenly at T_N leaving a broad background. They concluded that $FeCl_2$ does not behave like a two-dimensional Heisenberg system, and suggested that because of the anisotropy it behaves like a spin 1 Ising system. Heat-capacity data can also be explained with a sharp singularity at T_N.[18] However, measurement of antiferromagnetic resonance shows no sharp transition.[19] The broadness of the dip in c_{33} at T_N is also consistent with a partial two-dimensional behavior. Preliminary data on $c_{11} - c_{66}$ also show a broad dip at T_N and no apparent effects of the strain-ion coupling.

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