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LETTER TO THE EDITOR

Determination of the phase diagram of 2% Zn-doped $CuGeO_3$ by means of ultrasound measurements in high magnetic fields

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Abstract. Measurements of the elastic constant C_{33} of the 2% Zn-doped $CuGeO_3$ spin–Peierls system under high magnetic fields up to 20 T are reported. The successive magnetic ordering and the spin–Peierls transition are confirmed. The magnetic phase diagram has been determined. A transition line between the magnetic ordered phase and the uniform phase is observed at very high magnetic fields above 15 T.

The quasi-one-dimensional (quasi-1D) Cu^{2+} ($S = \frac{1}{2}$) antiferromagnet $CuGeO_3$ has been recently intensively studied. This compound is the first inorganic material to exhibit a spin–Peierls (SP) transition, which has so far been only found among 1D magnetic organic systems [1]. The SP transition at $T_{SP} = 14$ K in $CuGeO_3$ is driven by the interaction between 1D antiferromagnetic chains and the 3D phonon field [1]. This transition opens a finite energy gap in the spin excitations by linear dimerization of the lattice [1–4]. $CuGeO_3$ exhibits three structurally different phases [1–7] : uniform (U), dimerized (D) and incommensurable (I) phases in the temperature–magnetic field space. The interesting feature of doped $CuGeO_3$ is the coexistence at low temperature of SP and antiferromagnetic states which was observed for Zn doping [3–5] and Si doping [6]. The successive transitions taking place upon lowering the temperature into the SP phase followed by an antiferromagnetically ordered phase have been studied by magnetic and neutron measurements [3–5]. The SP transition temperature decreases from 14 to 10 K for a Zn concentration of 2% [4, 5].

In the present investigation we report measurements of the longitudinal elastic constant C_{33} along the orthorhombic c axis, which were carried out on a 2% Zn-doped $CuGeO_3$ single crystal in a magnetic field up to 20 T. C_{33} exhibits anomalies at the transition lines, the study of which allows the determination of a phase diagram.

The $Cu_{1-x}Zn_xGeO_3$ single crystals used in this study were cut from a large crystal several centimetres long grown from the melt by a floating zone method associated with an image furnace [8]. The standard pulse echo technique was used with $LiNbO_3$ transducers and the longitudinal constant C_{33} along the crystallographic c axis was measured at 15 MHz by phase coherent detection. The elastic constant C_{33} is related to the sound velocity V by the

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relation $C_{33} = \rho V^2$ where ρ is the mass density, equal to 5.1 g cm^{-3}. $C_{33} = 31 \times 10^{11}$ N m^{-2} corresponding to a sound velocity of 7900 m s^{-1} at room temperature and zero applied field. The determination of the anomalies in the three longitudinal elastic constants in pure $CuGeO_3$ has already been reported in [9].

The high-magnetic-field measurements were performed at the High-Magnetic-Field Laboratory in Grenoble. The magnetic field H was aligned along the c axis and H was swept continuously from 0 to 20 T at a rate of 100 mT s^{-1}. Temperature was controlled by a capacitance sensor.

The isofield variations of C_{33} as a function of temperature are shown in figure 1. Softening of C_{33} is observed at the SP temperature $T_{SP} = 10$ K. However, the decrease of C_{33} around $T_{SP} = 14.3$ K in pure $CuGeO_3$ was sharper [9, 10] and this may reflect same inhomogeneity in the Zn doping. A second softening of C_{33} is observed at the Néel temperature $T_N \approx 3$ K [10]. The thermodynamic analysis of a second-order phase transition relates the discontinuity of the longitudinal elastic constant to the specific heat anomaly at the transition temperatures T_{SP} and T_N [12, 13]. The decrease of C_{33} observed at T_N in this 2% Zn-doped $CuGeO_3$ is comparable with that observed in other antiferromagnetic systems [13]. The values of T_{SP} and T_N found in the present experiment are in agreement with those determined for the same 2% Zn concentration from susceptibility and neutron experiments [3–5]. In figure 1 and subsequent figures, the values of T_{SP} and T_N have been taken at the end of the softening of C_{33}.

For field values below $\sim$10 T, T_{SP} is reduced with respect to the value at zero field. It appears also that T_N is slightly reduced with increasing H as seen in figure 1(a). The minimum of C_{33} is not reached at 2.2 K for $H = 5$ and 10 T, indicating a lower value for T_N. For higher fields it can be seen in figure 1(b) that C_{33} exhibits a broad maximum around 10 K and drops sharply at 4 K independently of the value of H between 15 and 19 T. The isothermal variation of C_{33} as a function of H is shown in figures 2–4. In figure 2 are reported the data taken in the lowest temperature range (2–3 K), and in figure 4 those taken in the highest temperature range (6–8 K) which show the decrease of T_{SP} with increasing H. The field dependence in the intermediate temperature range 3–5 K is quite complicated, as emphasized in figure 3. A drastic change is clearly observed in figures 2 and 3 at several constant temperatures below and above 3.2 K. At the lowest temperature, 2.2 K, a symmetric and broad minimum of C_{33} is found around 10 T. Asymmetry in the field behaviour increases with increasing temperature (figure 2). It can also be seen that the value of the magnetic field at the minimum of C_{33} increases with increasing temperature in figure 2; above 3.5 K, two distinct minima are observed at the two critical fields H_{c1} and H_{c2}. The value of $H_{c1} \sim 9.5$ T remains constant whereas H_{c2} increases rapidly up to 20 T (as shown in figure 3) when temperature increases up to 4.5 K.

Collecting all the data from the isotherm and isofield variations one can draw the phase diagram for the 2% Zn-doped sample as shown in figure 5.

Five different phases can be identified: the corresponding U, D and I phases as in pure $CuGeO_3$; the AF phase, which occurs below 3 K and a new magnetic phase observed below 4 K for $H > 10$ T that we call I′ by analogy with the incommensurate phase I observed at intermediate temperatures around 4 K for $H > 10$ T. The existence of the I phase has been proved by recent x-ray experiment performed on a 1.5% Zn-doped crystal [7], but to our knowledge such an I′ phase has not been demonstrated so far by x-ray or neutron experiments. The present results point out clearly the existence of this I′ phase. The different transition lines are clearly identified: the U–I′ transition line for $H \geqslant 15$ T (figure 1(b)); the U–I and I–I′ lines deduced from the temperature variation of C_{33} with applied field $H = 12.5$ T (figure 1(a)); the D–I and I–I′ lines deduced from the field variation around

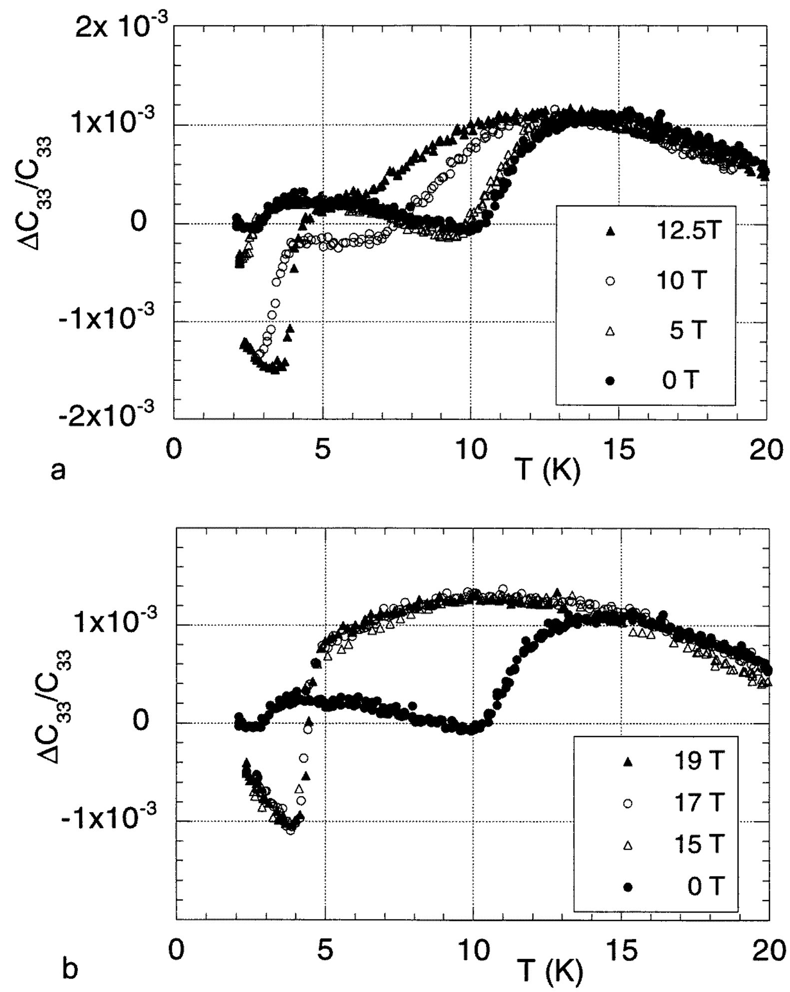

Figure 1. Relative variation versus temperature of C_{33} of $Cu_{0.98}Zn_{0.02}GeO_3$ at different constant magnetic fields $H \parallel c$: $H \leqslant 12.5$ T (a) and $H \geqslant 12.5$ T (b).

4 K in figure 3, the critical fields H_{c1} and H_{c2} corresponding to the transition lines D–I and I–I′ respectively; around 2 K the minimum of C_{33} found around 10 T is related to the AF–I′ transition line; however further measurements are needed to define with accuracy the AF–I′ below 2 K. Thus the D–AF and AF–I′ transition lines are indicated by dotted lines in figure 5. Nevertheles it appears that several transition lines converge to the multicritical point defined by $H_0 = 10$ T and $T_0 \approx 2$ K.

A hysteresis of about 0.5 T at the D–I transition line is observed around 4 K. A similar hysteresis of 0.5 T is observed for magnetic field values around 10 T at the lowest temperatures ≈ 2 K. It emerges that the AF–I′ and D–I transition lines are of first order. The other lines, U–D and I–U, are second-order transition lines as in the pure $CuGeO_3$ [1]. The D–I transition line is also first order in pure $CuGeO_3$ [1]. The phase diagram of the 2% Zn-doped crystal, given in figure 5, is in agreement with that reported recently in [13] on a 1.5% Zn-doped crystal in the same temperature range but at lower magnetic fields.

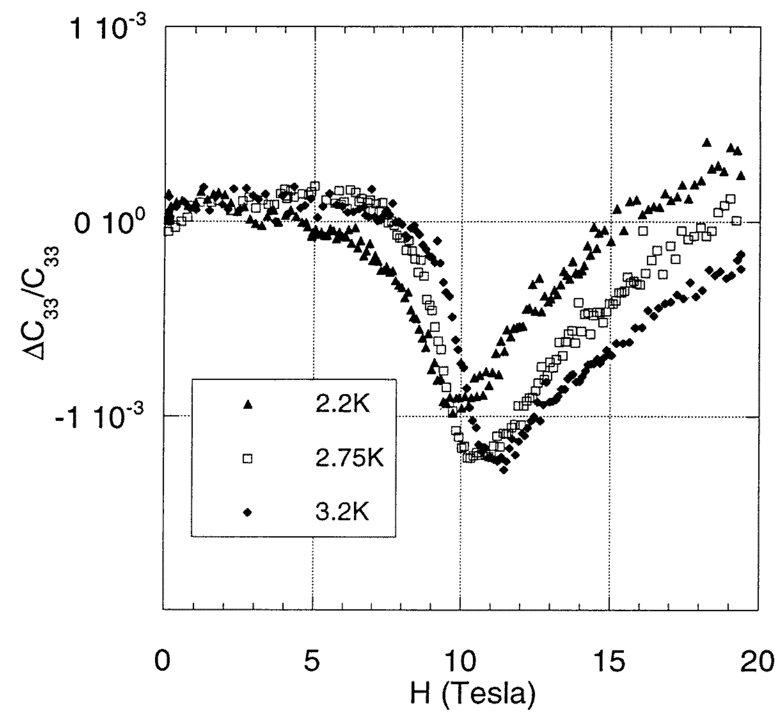

Figure 2. The magnetic field dependence of C_{33} of $Cu_{0.98}Zn_{0.02}GeO_3$ at different temperatures ($H \parallel c$).

However the U–I′ transition line was not observed in [13].

The changes in the elastic constant C_{33} at the various transition lines are reported in table 1.

Table 1. Softening of the elastic constant C_{33} of a $Cu_{0.98}Zn_{0.02}GeO_3$ single crystal at the various transition lines.

U–D transition ($H < 10$ T)	$C_{33}(\mathrm{D}) - C_{33}(\mathrm{U})/C_{33}(\mathrm{U}) = -1 \times 10^{-3}$
D–AF transition ($H < 10$ T)	$C_{33}(\mathrm{AF}) - C_{33}(\mathrm{D})/C_{33}(\mathrm{D}) = -5 \times 10^{-4}$
U–I transition ($H > 10$ T)	$C_{33}(\mathrm{I}) - C_{33}(\mathrm{U})/C_{33}(\mathrm{U}) = -1 \times 10^{-3}$
I–I′ transition ($H > 10$ T)	$C_{33}(\mathrm{I}') - C_{33}(\mathrm{I})/C_{33}(\mathrm{I}) = -1.5 \times 10^{-3}$
U–I′ transition ($H > 15$ T)	$C_{33}(\mathrm{I}') - C_{33}(\mathrm{U})/C_{33}(\mathrm{U}) = -1.8 \times 10^{-3}$

The elastic anomalies at the second-order phase transitions can be accounted for by a simple Landau theory [14]. The total free energy is the sum of three components:

(i) the interaction energy F_c between strain e_{33} and the order parameter Q related to the lattice modulation which takes place in the dimerized phase or the antiferromagnetic order which occurs below T_N

$$F_c = \lambda e_{33} Q^2$$

where λ is the coupling constant;

(ii) the elastic energy

$$F_e = \tfrac{1}{2} C_{33} e_{33}^2$$

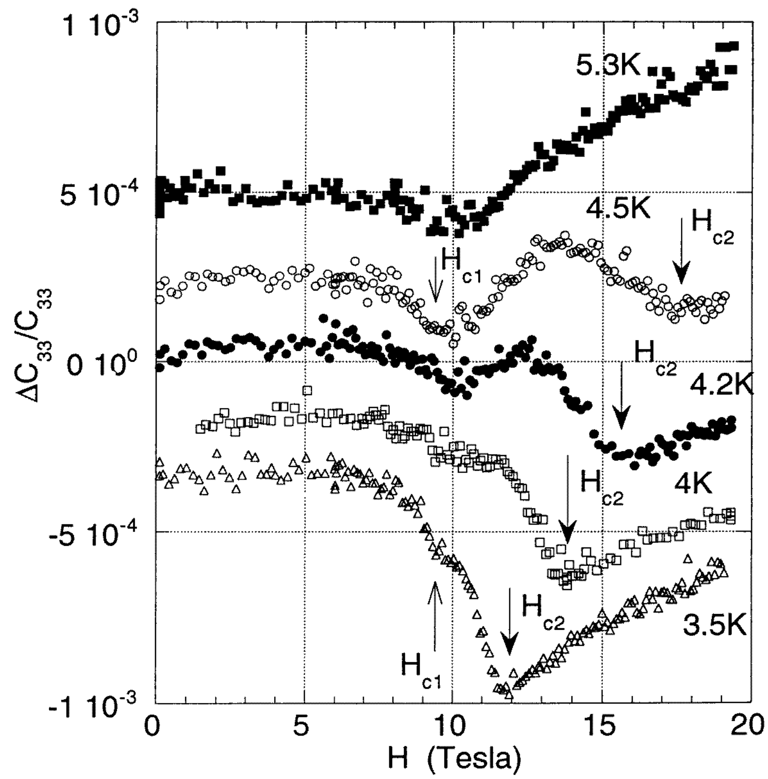

Figure 3. The magnetic field dependence of C_{33} of $Cu_{0.98}Zn_{0.02}GeO_3$ at different temperatures between 3.5 and 5.3 K, with $H \parallel c$. For clarity, the curves have been shifted. The critical magnetic fields H_{c1} and H_{c2} related to the D–I and I–I′ transitions are indicated.

and

(iii) the Landau energy

$$F_0 = \tfrac{1}{2}aQ^2 + \tfrac{1}{4}bQ^4.$$

The elastic constant of the ordered phase is obtained by minimizing the free energy with respect to e_{33}:

$$C_{33}^{OR} = C_{33}^{HT} - \lambda^2/2b \tag{1}$$

where C_{33}^{OR} and C_{33}^{HT} are the elastic constants in the ordered and high-temperature phases, respectively.

Relation (1) explains the decrease of C_{33} at the second-order transition lines crossed on decreasing temperature in a constant applied field (figure 1 and table 1).

The field behaviour of C_{33}, at fixed temperatures, showing an increase (figure 2) with increasing H at the D–U and I–U transition lines, is similar to that observed on the undoped $CuGeO_3$ crystal [9]. Such a behaviour is in agreement with relation (1) but a broad variation is observed in the 2% Zn-doped crystal at the critical field, in contrast with the sharp increase observed in the pure $CuGeO_3$ crystal [9]. Such a behaviour must be related either to fluctuations and a broad field behaviour of the order parameter or inhomogeneities in the Zn-doped crystal. In the same manner around 4 K the transition D–I line is characterized by an increase of C_{33} at the critical field H_{c1} with a slope which is half that observed in the

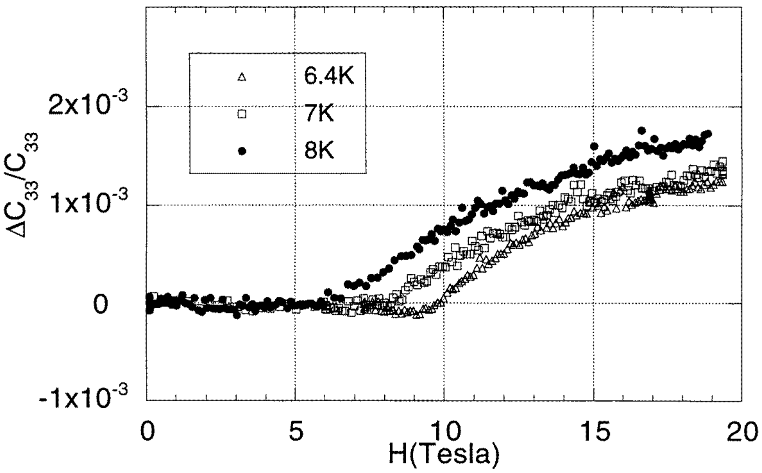

Figure 4. The magnetic field dependence of C_{33} of $Cu_{0.98}Zn_{0.02}GeO_3$ at different temperatures between 6 and 8 K with $H \parallel c$.

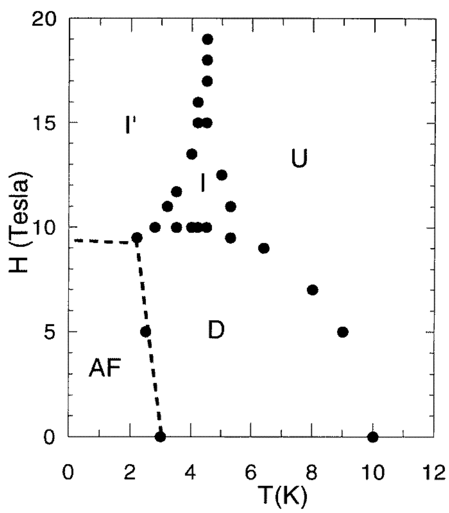

Figure 5. The magnetic phase diagram of 2% Zn-doped $CuGeO_3$, determined from C_{33} behaviour with field and temperature.

undoped crystal and which was attributed to the existence of soliton-like discommensurations [15].

Knowledge of the AF–I′ transition line cannot be deduced directly from the C_{33} measurements; however the existence of the softening at this transition line suggests that magnetic ordering which takes place at this transition line must be different from the magnetic order in the AF phase.

In conclusion, the magnetic phase diagram relating to the 2% Zn-doped $CuGeO_3$ has been determined from the elastic constant C_{33} as a function of temperature and magnetic field. The existence of two magnetic ordering phenomena is pointed out at low temperatures below 4 K:

(i) the antiferromagnetic (AF) phase which is stable at magnetic field values up to 10 T in good agreement with magnetic and neutron experiments [3–5];

(ii) a new I′ phase which appears at high magnetic fields above 10 T. The transition line between this I′ phase and the incommensurate I phase has been determined. We have shown that the I phase disappears at $H \sim 15$ T, above which a vertical transition line in the H–T diagram is observed between the I′ and uniform (U) phases. Magnetic and ultrasound measurements at high magnetic fields are under way in order to better understand this I′ phase.

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