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1999 J. Phys.: Condens. Matter 11 4157

(http://iopscience.iop.org/0953-8984/11/21/304)

J. Phys.: Condens. Matter **11** (1999) 4157–4162. Printed in the UK PII: S0953-8984(99)01547-7

Brillouin scattering and ultrasonic measurements of the elastic constants of $CuGeO_3$

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Received 3 February 1999, in final form 22 March 1999

Abstract. The sound velocities for longitudinal and transverse waves in single-crystalline $CuGeO_3$ have been measured using ultrasonic pulse-echo and Brillouin scattering techniques. The nine independent elastic constants have been determined. The elastic properties of this material are strongly anisotropic with an order-of-magnitude difference between the longitudinal elastic constants along the *c*- and *b*-axes.

1. Introduction

The quasi-one-dimensional Cu^{2+} ($S = 1/2$) antiferromagnet $CuGeO_3$ has recently been intensively studied [1]; this inorganic material exhibits a spin–Peierls transition (SP) which so far has been essentially found just among 1D magnetic organic materials. The spin–Peierls transition at $T_{SP} = 14$ K in $CuGeO_3$ is driven by the magnetoelastic interaction between the 1D antiferromagnetic chains and the 3D phonon field [1]. Several experimental studies of elastic constants have been published [2–4] but to our knowledge the determination of all of the elastic constants has not been reported. In the present investigation we report measurements of elastic constants by the Brillouin scattering and ultrasonic techniques. $CuGeO_3$ crystallizes within an orthorhombic structure. The lattice parameters are $a = 4.81$ Å, $b = 8.44$ Å and $c = 2.95$ Å. The magnetic chains are aligned along the c-axis. Therefore this system is characterized by nine independent elastic constants. The longitudinal constants are C_{11}, C_{22} and C_{33} corresponding to the a-, b- and c-axis respectively. The diagonal shear constants are C_{44}, C_{55} and C_{66} and the non-diagonal shear constants are C_{12}, C_{13} and C_{23}. The 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 [5].

2. Brillouin scattering

Brillouin spectra were recorded with a tandem arrangement of triple-pass Fabry–Perot interferometers of the Sandercock type [6]. Typical features of this system are a finesse of about 50 and a contrast larger than 10^{10}. The exciting wavelength 514.5 nm was chosen, to lie in the transparency region of the crystal. Different scattering geometries were used including the usual backscattering and right-angle scattering geometries and also a 'platelet' geometry where the angle between the incident and scattered beams is 90° outside of the sample. But since the angle of incidence on the surfaces is 45°, the actual scattering angle inside the crystal depends on the refractive index and this quantity cancels, in this case, in the general Brillouin shift formula:

$$\nu_B = \pm 2V \frac{\sqrt{(n_i^2 + n_s^2 - 2n_i n_s \cos 0)}}{\lambda}$$

where ν_B is the Brillouin shift, n_i and n_s the refractive indices for the incident and scattered beams, 0° the scattering angle, λ the laser wavelength and V the sound velocity. In each principal plane of the [100] type, the solutions of the Christoffel equation are given by

$$\det |C_{ijkl} n_j n_l - \rho V^2 \delta_{ik}| = 0$$

corresponding, for general directions, to a true transverse mode (T) polarized perpendicular to that plane and to quasi-longitudinal (QL) and quasi-transverse (QT) modes polarized within that plane. For example, in the [100] plane the different solutions are as follows:

$$\rho V^2 = C_{66} n_2^2 + C_{55} n_3^2$$

for the T mode and

$$\rho V^2 = \frac{1}{2}\Big\{(C_{22} + C_{44})n_2^2 + (C_{33} + C_{44})n_3^2 \pm \sqrt{[(C_{22} + C_{44})n_2^2 - (C_{33} + C_{44})n_3^2]^2 + 4n_2^2 n_3^2 (C_{23} + C_{44})^2}\Big\}$$

for the QL mode (with the + sign) and the QT mode (with the − sign).

The sample was an $(\boldsymbol{a}, \boldsymbol{b}, \boldsymbol{c})$ plate with dimensions of a few mm but with larger $(\boldsymbol{b}, \boldsymbol{c})$ cleavage faces of very good optical quality. Such a sample allows, in the 'platelet' scattering geometry, an easy determination of the velocity diagram for the quasi-longitudinal and quasi-transverse modes in the bc-plane. Additional directions were tested by rotating the sample around crystallographic axes. In the end, more than 70 sound velocities were measured in the principal planes.

The refractive indices of the crystals were estimated from the ratio of the Brillouin shifts for the backscattering and 'platelet' scattering geometries and from the ratio of the backscattering Brillouin shifts for different polarizations. If the absolute errors are large, the uncertainties on the index ratio are in the per cent range:

$$n_a = 1.80 \pm 0.1 \qquad n_b = 1.85 \pm 0.1 \qquad n_c = 2.0 \pm 0.1.$$

3. Determination of elastic constants

The determination of the diagonal elastic constants is based on experiments involving backscattering along the crystallographic axes. Off-diagonal constants are more difficult to determine since in the principal planes sound velocities always involve the absolute values of sums: $C_{\mu\mu\beta\beta} + C_{\mu\beta\mu\beta}$, where the elastic constants are not in the contracted Voigt notation. By a least-mean-squares procedure involving all of the measured sound velocities, the elastic constants were determined and, using the density of 5.1 kg m^{-3}, it is possible to give

$$C_{11} = 64 \text{ GPa} \qquad C_{22} = 37.6 \text{ GPa} \qquad C_{33} = 317.3 \text{ GPa}$$
$$C_{44} = 35.3 \text{ GPa} \qquad C_{55} = 35.3 \text{ GPa} \qquad C_{66} = 18.4 \text{ GPa}$$
$$|C_{12} + C_{66}| = 50.5 \text{ GPa} \qquad |C_{13} + C_{55}| = 82.2 \text{ GPa} \qquad |C_{23} + C_{44}| = 58 \text{ GPa}.$$

Among the possible solutions for the off-diagonal components, two sets of them satisfy the condition of a positive determinant as required by stability conditions with respect to an induced strain. In the first set all components are positive whereas in the second one only C_{12} is positive. By computing the elastic compliances from the elastic constants it is possible to estimate the principal components of the compressibility tensor which has already been investigated [7]. Taking into account the different labelling of axes in that work, the best agreement with those data is clearly obtained for the all-positive elastic constants set, yielding

$$C_{12} = 32.1 \text{ GPa} \qquad C_{13} = 46.9 \text{ GPa} \qquad C_{23} = 22.7 \text{ GPa}.$$

However, the agreement is not perfect for the linear compressibility value along $\boldsymbol{b}$, but it is reasonable.

Although it is difficult to assign accurate values to the errors on each elastic component, one can estimate the relative accuracy to be 2–3% for the diagonal components and to be more than 5% for the other components and perhaps up to 10% for C_{23} as indicated by the velocity diagrams in the principal planes plotted in figures 1–3. The relative errors on the elastic constants spread out for nearly all compliances with, for some of them, a heavy weighting. The more important weightings on $\Delta\beta_a/\beta_a$ occur for $\Delta C_{12}/C_{12}$ (about 10) and for $\Delta C_{22}/C_{22}$ (about 6). For $\Delta\beta_b/\beta_b$ the more important weighting is for $\Delta C_{22}/C_{22}$ but this weighting is smaller than 2, so a considerable relative uncertainty of more than 30% would be required in order to match with the compressibility values given by Adams *et al*. This is clearly outside

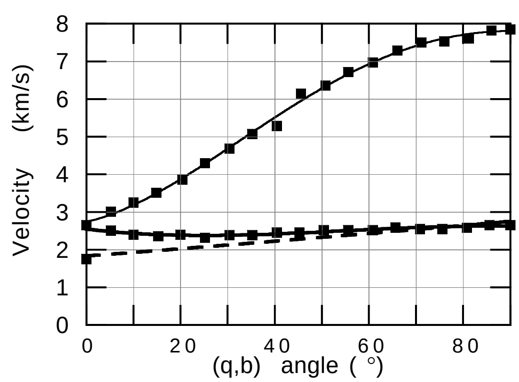

Figure 1. Sound velocities in the *bc*-plane. The ■ represent experimental data whereas - - - - and —— correspond to the best fits of elastic constants.

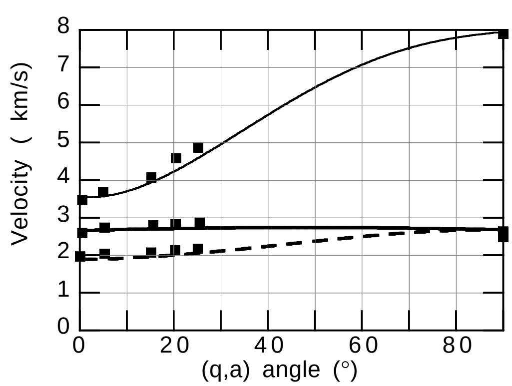

Figure 2. Sound velocities in the *ac*-plane. The ■ represent experimental data whereas - - - - and —— correspond to the best fits of elastic constants.

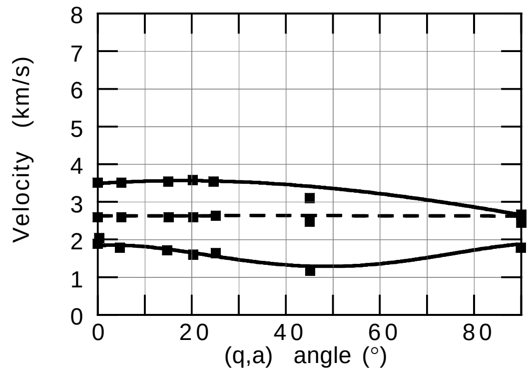

Figure 3. Sound velocities in the *ab*-plane. The ■ represent experimental data whereas - - - - and —— correspond to the best fits of elastic constants.

the range of the errors generated by ultrasonic and Brillouin scattering techniques and, if only a small error is admitted for this compressibility measurement also, then this difference should have a physical meaning, but the magnitude of the difference also seems beyond the possibilities for some relaxation process. However, when one considers the raw data given by Adams *et al* in their figure 5, one notices that the scattering of points allows for some uncertainties, in particular in the vicinity of atmospheric pressure where anvil pressure cells can generate non-hydrostatic and somewhat inhomogeneous pressures. The values that we report in table 1 are obtained from the extreme slopes of figure 5 of Adams *et al*, which can be extrapolated close to atmospheric pressure, taking into account the different crystallographic group labelling.

Table 1. Comparison of the values of the linear compressibility along the principal axes from Adams *et al* [7] and this work.

β_x (10^{-3} GPa^{-1})	Adams *et al* [7]	This work
β_a	4.1 ± 1.9	3.3 ± 2.9
β_b	14 ± 3	23.2 ± 2.6
β_c	3 ± 2	1.06 ± 0.6

4. Ultrasonic measurements

The standard pulse-echo technique was used in the ultrasonic measurements with $LiNbO_3$ transducers and the sound velocity was measured at 15 MHz by phase-coherent detection. Previous results for the longitudinal constants C_{11}, C_{22} and C_{33} have been given in [3, 4]. The values of the shear constants C_{44}, C_{55} and C_{66} are reported in table 2. The temperature dependences of the sound velocities of the shear modes C_{55} and C_{66} around the spin–Peierls transition are reported in figure 4. In contrast with the case for the longitudinal modes, no discontinuity in the sound velocity is observed at $T_{SP} = 14$ K. But a discontinuity in the temperature derivative is observed at T_{SP}. The thermodynamical analysis [8] of a second-order phase transition relates such a discontinuity to the specific heat anomaly [9] and the second stress derivative $\partial^2 T_c/\partial\sigma^2$:

$$\Delta \frac{1}{V}\,\frac{\mathrm{d}V}{\mathrm{d}T} \approx \frac{1}{2} C_{ij}\,\Delta C_p\,\frac{\partial^2 T_c}{\partial\sigma^2}.$$

Our estimates of $C_{ii}^2\, \partial^2 T_c/T_C\, \partial\sigma^2$, with $\Delta C_p = 2$ J mol^{-1} K^{-1} [9], are 40 and 60 for the modes C_{55} and C_{66} respectively. Large second temperature derivatives $\partial^2 T_C/\partial\sigma^2$ equal to 0.2 and 2 K GPa^{-2} are deduced for the C_{55}- and C_{66}-modes.

Table 2. Elastic constants of $CuGeO_3$ in GPa. Mass density is 5.1 g cm^{-3}.

	Brillouin values	Ultrasound values
C_{11}	64	71
C_{22}	37.6	34.5
C_{33}	317.3	343
C_{44}	35.3	37
C_{55}	35.3	33
C_{66}	18.4	22
C_{12}	32.1	
C_{13}	46.9	

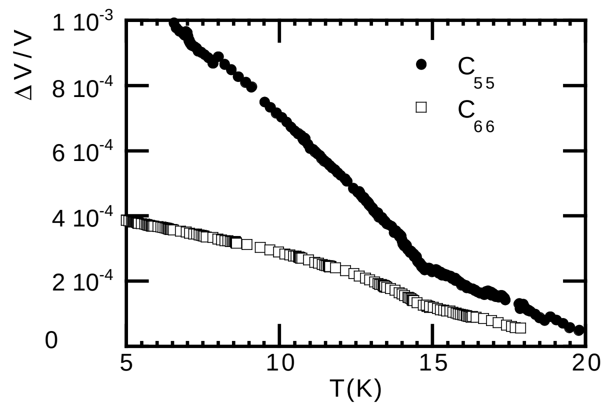

Figure 4. Temperature variation of the sound velocities of the shear modes C_{55} and C_{66}.

5. Discussion

As already pointed out in the ultrasonic studies, the elastic properties of this material are strongly anisotropic with nearly an order-of-magnitude difference between the compression elastic constants along $\boldsymbol{c}$ and $\boldsymbol{b}$. It is also noteworthy that along the $\boldsymbol{b}$-direction the transverse sound velocity is almost equal to the longitudinal one; however, in contrast to what was first suggested on the basis of a former neutron scattering study [2], the transverse sound velocity along $\boldsymbol{b}$ does not exceed the longitudinal one, at least in the very close vicinity of the Brillouin zone centre.

The ultrasonic and the Brillouin scattering techniques agree as regards the determination of the diagonal elastic constants, but the Brillouin scattering technique is more convenient for determining the off-diagonal elastic components. The principal linear compressibility values are found to agree reasonably well with the evolution of the parameters under pressure obtained by x-ray determination [7].

The Debye temperature $\Theta_D = 330$ K has been obtained by means of specific heat measurements [9]. A mean sound velocity V_D of about 2600 m s^{-1} is deduced from the lattice contribution βT^3 to the specific heat ($\beta = 0.255$ mJ mol^{-1} K^{-1}) [9]. V_D is comparable to the mean average sound velocity deduced from the velocity of the longitudinal (V_l) and shear modes (V_s):

$$\frac{9}{V_D^3} \approx \sum_l \frac{1}{V_l^3} + \sum_s \frac{1}{V_s^3}.$$

In conclusion, the nine independent elastic constants of $CuGeO_3$ have been determined and all of the shear constants are smaller than the longitudinal ones. The second stress derivative of the transition temperature has been estimated from the temperature behaviour of the shear modes C_{55} and C_{66} at the spin–Peierls transition.

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