Ultrasonic investigation of the magnetic ordering in the quasi-one-dimensional $S=\frac{1}{2}$ antiferromagnet $BaCu_2Si_2O_7$

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Magnetic ordering in the quasi-one-dimensional antiferromagnet $BaCu_2Si_2O_7$ is investigated with ultrasonic waves propagating along the chain axis. Transverse waves are found to couple most strongly with the magnetic properties. This is observed through an important velocity softening below 140 K and a sharp stiffening in the ordered state at $T_N=9.2$ K. We have mapped the *H-T* phase diagram by studying the stiffening anomaly in magnetic field oriented along the three crystal axes for values up to 8.5 T. The Néel temperature T_N decreases the most with increasing magnetic field oriented along the easy axis *c*; for this configuration two exotic spin-flop states could be identified at 2.1 and 4.7 T. Along the *b* axis, T_N decreases less with increasing field and a new phase transition is observed around 7.8 T. No field effects on T_N or additional transitions could be detected along the *a* axis. These transitions are discussed in relation with previously reported scenarios concerning the magnetic order.

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I. INTRODUCTION

The structural diversity of copper-oxide compounds make these materials very useful as model systems for fundamental studies of low-dimensional magnetism. Among these systems the quasi-one-dimensional (quasi-1D) $S=\frac{1}{2}$ antiferromagnet $BaCu_2Si_2O_7$ appears as an almost ideal material for, on the one hand, studying exotic spin dynamics in weakly interacting quantum spin chains[1–4] and, on the other hand, to investigate the ordered state in a magnetic field.[5,6] This silicate crystallizes in an orthorhombic crystal structure with space group *Pnma*.[7] The Cu^{2+} spins are strongly coupled antiferromagnetically along the crystallographic *c* axis by a strong superexchange interaction via the O^{2-} ions.[8] Weak interactions between the chains result in long-range antiferromagnetic ordering at $T_N=9.2$ K, as observed in bulk susceptibility and specific heat measurements.[1] The magnetic susceptibility shows a broad maximum around 150 K and a Bonner-Fisher[9] temperature profile with an intrachain coupling constant $J=24.1$ meV. In the ordered state the spins are parallel to the magnetic easy axis *c*. When nearest-neighbor spins along the *b* and *c* axes are aligned antiparallel relative to each other, nearest neighbors are ferromagnetically aligned along *a*.[1,3] Recently, it was shown that a magnetic field applied along the easy axis induces a spin-flop transition at 2.0 T followed by a second transition at 4.9 T.[5] These exotic two-stage spin-flop transitions were interpreted as resulting from a competition between Dzyaloshinskii-Moriya (DM) off-diagonal exchange interactions in the spin chains and isotropic exchange coupling between the chains. More recently, Zheludev *et al.*[6] have determined the magnetic structure of the various spin-flop phases; their results are inconsistent with the previously proposed model and the actual mechanism of the exotic two-stage spin-flop transitions still remains a mystery.

The ordered state of low-dimensional magnetic systems can also be investigated by ultrasonic waves. Indeed, acoustic phonons generally couple easily with spin degrees of freedom. This magneto-elastic coupling yields well-defined anomalies on the ultrasonic velocity[10,11] and a magnetic phase diagram is obtained by studying these anomalies in a magnetic field. We report in this paper such a study of the magnetic structure of a $BaCu_2Si_2O_7$ crystal. The most efficient coupling is obtained for transverse ultrasonic waves propagating along the easy axis. The elastic anomalies in the ordered state have been studied for a magnetic field applied along the the three crystal axes. Besides the two-stage spin-flop transitions already reported along *c*, we observed another magnetic transition along the *b* axis. These transitions are discussed in relation with the most recent magnetic structure reported in the literature.

II. EXPERIMENT

The $BaCu_2Si_2O_7$ single crystal was grown from the melt by a floating zone method associated with an image furnace. The crystal was cut into a rectangle with dimensions of $1.46\times1.76\times1.27$ mm^3, respectively, along the crystal axes *a*, *b*, and *c* as confirmed by an x-ray Laue backscattering experiment. We used a pulsed acoustic interferometer to measure the velocity of transmitted ultrasonic waves along the easy axis *c* with a sensitivity better than 1 ppm. Both longitudinal and transverse waves were generated at 30 MHz and odd overtones with $LiNbO_3$ piezoelectric transducers. A magnetic field up to 8.5 T could be applied along the three crystal axes. From the measurement of the ultrasonic velocity *V*, specific elastic constants *C* are obtained through the relation $\rho V^2=C$, where ρ is the density. Along the *c* axis, longitudinal waves yield C_{33} and transverse waves C_{55} and C_{44} for polarization along *a* and *b*, respectively.

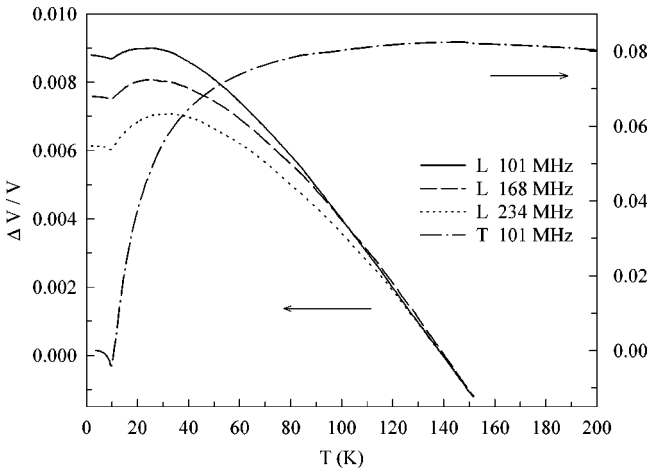

FIG. 1. Relative variation of the velocity as a function of temperature: longitudinal mode (left) and transverse mode (right).

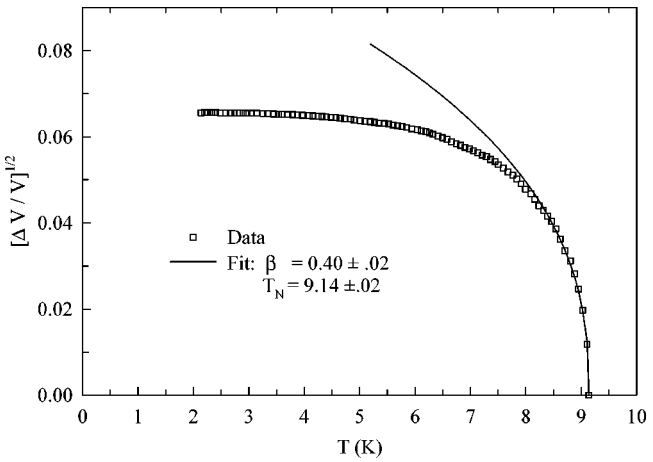

FIG. 2. Square root of the relative variation of the transverse velocity as a function of temperature below T_N: data (symbols) and best fit (line).

III. RESULTS AND DISCUSSION

The absolute values of the longitudinal and transverse waves propagating along the easy axis are 4200 m/sec and 2900 m/sec, respectively. We could not detect any measurable anisotropy effects for the two transverse waves. We present in Fig. 1 the relative velocity variation as a function of temperature in the range 2–200 K. For both acoustic modes, the velocity stiffens as the temperature is decreased below 200 K as expected for a typical solid. At low temperatures, however, the temperature profile presents a pronounced softening before entering the antiferromagnetic Néel state at 9.2 K where a sharp stiffening is obtained. For longitudinal waves, both the softening and stiffening anomalies are weak: when the softening which increases with frequency, as shown in Fig. 1, is around 0.1–0.3%, the stiffening is not frequency dependent at 0.01%. Although a maximum is observed around 30–40 K, frequency effects seem to extend up to 140 K at the highest frequency. In comparison, the relative transverse velocity variation is not dependent on frequency. It shows a maximum around 140 K and dramatically softens below 40 K by almost 9%; the sharp stiffening below T_N is a little larger than 0.5%. In summary, we observed elastic anomalies that are about 30–50 times larger for the transverse waves and for which there are no frequency effects. Moreover the softening of the velocity is accentuated below 40 K on both acoustic modes.

Magnetic susceptibility measurements[1] showed deviations from the Bonner-Fisher curves below 120 K, which were explained by the onset of three-dimensional spin correlations in this temperature regime. The softening of the ultrasonic velocity could likely be explained by a coupling to spin correlations which are extending up to 140 K, although the largest softening rate is obtained below 40 K in agreement with susceptibility data that show deviations from the Bonner-Fisher fit over this temperature range.[1] The time scale of these correlations seems, however, shorter along *c* than along the *ab* plane since frequency effects are observed on the longitudinal velocity in the 100 MHz range. This suggests that the spin correlation dynamics is anisotropic, and this unexpected existence of two spin dynamics could be consistent with both ferromagnetic and antiferromagnetic components of the magnetic structure.[5]

The sharp stiffening anomaly observed below T_N presents a temperature profile that can be associated with an order parameter. Indeed, such an elastic anomaly can be accounted for by a simple free energy Landau theory[12] using a biquadratic coupling term F_c between the elastic deformation e and the order parameter M, $F_c = he^2M^2$. This term leads to a stiffening of the elastic constant $C = C_0 + 2hM^2$, where h is the coupling constant and C_0 the elastic constant proportional to the square of the sound velocity. Using such a model, the square root of the velocity variation below T_N should be proportional to the order parameter M. These data for the transverse waves are presented in Fig. 2. In the vicinity of T_N the data are best fitted to a power law $(1 - T/T_N)^{\beta}$ with $T_N = 9.14 \pm 0.02$ K and $\beta = 0.40 \pm 0.02$, a value in better agreement with a 3D antiferromagnet than the one determined in neutron scattering experiments.[3]

The nature of the magnetic structure can be further investigated by the application of a magnetic field along the crystalline axes. The results presented below were obtained with the transverse waves because of a better sensitivity (larger acoustic anomalies) but identical ones were obtained with longitudinal waves. In Fig. 3 we present the relative variation of the velocity $\Delta V/V$ as a function of temperature, below 12 K, at different magnetic field values applied along the three crystal directions over the range 0–8 T. Several field behaviors can be deduced from these data of Fig. 3 and they will be discussed separately below.

First, we notice that a magnetic field shifts down the Néel temperature T_N if it is aligned along *b* and *c*, the largest shift being observed along the easy axis *c*. For the third axis (*a*), no shift could be detected up to 8.5 T. Such a downward shift of T_N over this field range could be an indication of additional magnetic phases in the ordered state. Along the *b* axis (lower panel of Fig. 3), the field modifies markedly the temperature profile of $\Delta V/V$ between 7 and 8 T, indicating a crossing of a phase boundary. Along the easy axis *c* (middle panel of Fig. 3), although the ordering temperature is shifted down by 0.2 K at 2 T, the overall stiffening anomaly is only

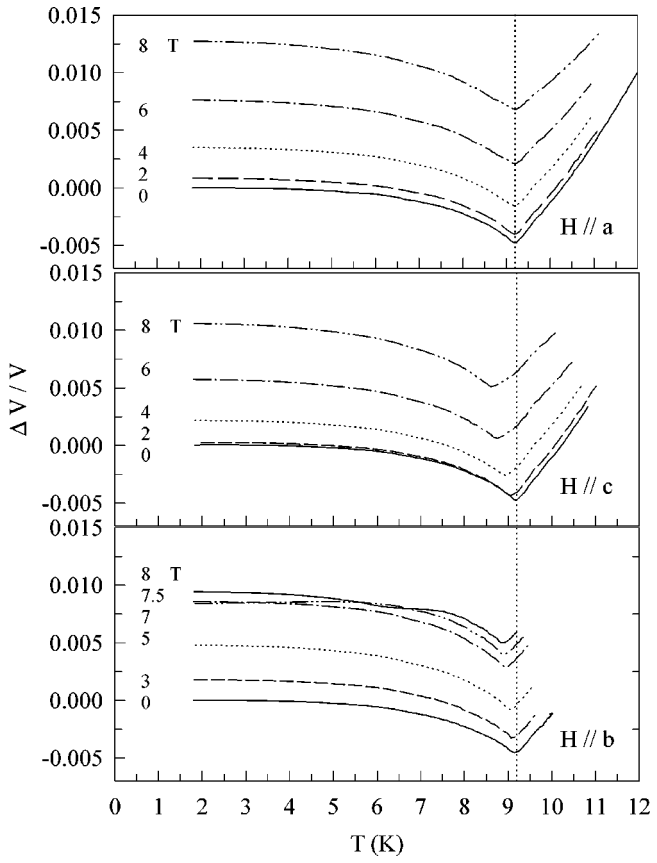

FIG. 3. Relative variation of the transverse velocity as a function of temperature, below T_N, for a magnetic field applied along the three crystalline axes.

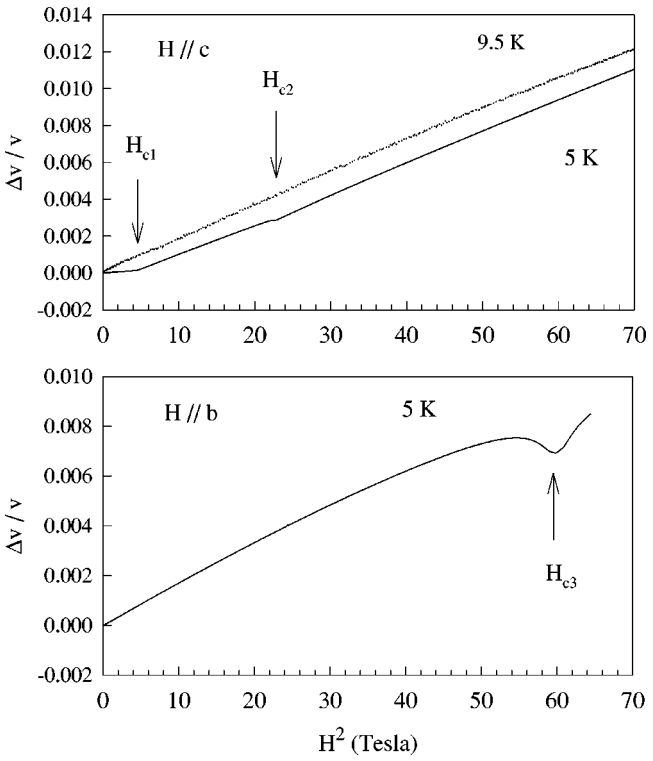

FIG. 4. Magnetic field dependence of the relative variation of the transverse velocity at fixed temperatures. The arrows indicate the anomalies.

weakly shifted upward with field in comparison with the one observed along the *a* axis (upper panel) at the same field. This could again indicate the proximity of a phase boundary. These new phases can be revealed more easily by examining the field dependence at fixed temperatures.

For the three crystalline directions, $\Delta V/V$ increases generally quasi-quadratically with field above T_N and, to emphasize this dependence, the relative velocity data will be presented as a function of H^2. This is exemplified in Fig. 4, along the easy axis *c*, where a near quadratic field dependence is clearly observed at 9.5 K (upper panel) up to 8.5 T. This dependence could result from a reduction of the spin correlations by a magnetic field leading to a reduction of velocity softening. Below the Néel temperature ($T=5$ K), although an overall quadratic dependence seems to emerge at the highest field values, two discontinuities are obtained: as the field is first raised from zero, the velocity variation increases very weakly, being almost constant up to $H_{c1}=2.1$ T where an abrupt slope variation is obtained. For higher field values, $\Delta V/V$ increases quasiquadratically with field up to $H_{c2}=4.7$ T where a weak but sharp downward anomaly is observed. When the field is further increased, the quadratic dependence is recovered. These two field anomalies are present at all temperatures below T_N, being less intense and smeared when the Néel temperature is approached. The two transitions seem to be first order since a clear hysteresis (0.05 T) is observed on both anomalies for increasing and decreasing fields. These anomalies have to be associated with the two stage spin-flop transitions observed in magnetization[5] and neutron diffraction experiments.[6] If the spin-flop transition at H_{c2} presents a field behavior of the velocity that is frequently observed in low-dimensional magnetic systems,[10,11] i.e., a sharp softening at the spin-flop field, the H_{c1} transition differs markedly, since an abrupt slope variation is rather obtained.

Along the *b* axis (lower panel of Fig. 4) at 5 K, $\Delta V/V$ increases also quasiquadratically with field up to 4 T where the growth rate starts to decrease. At higher field values, an intense dip is obtained at $H_{c3}=7.7$ T. This additional anomaly has to be considered as another phase transition: it is present for all temperatures below T_N and it possesses also the character of a spin-flop transition, being first order (hysteresis), showing an intense softening peak of the velocity at a spin-flop field that is almost constant with temperature.

In Fig. 5 we present the field and angular dependences of $\Delta V/V$ at 5 K; the curves have been shifted vertically for a clearer recognition of the angular dependence. These data were obtained by turning the sample in the magnetic field from the easy axis *c* ($H\|c$) to the *b* axis ($H\|b$). The three anomalies (indicated by arrows) are highly affected by a rotation of the field from the crystal directions: although their field positions are strictly constant, the anomalies are rapidly smeared and they completely disappear for angles between 10–20° from one or the other axis. This is again a behavior that is generally observed with spin-flop transitions.[13]

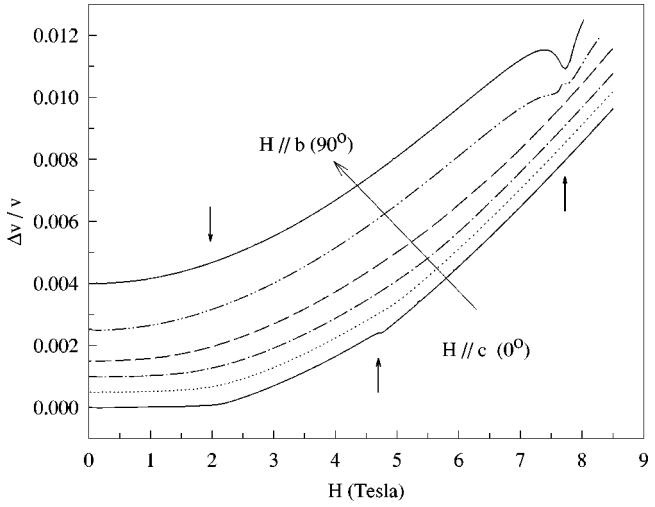

FIG. 5. Magnetic field dependence of the relative variation of the transverse velocity at 5 K: magnetic field oriented with angles 0°, 10°, 20°, 40°, 80°, and 90° from the *c* axis.

We have mapped out an *H-T* phase diagram for $BaCu_2Si_2O_7$ by using the temperature and magnetic field profiles obtained for different orientations of the magnetic field. This diagram is shown in Fig. 6. Along the easy axis *c*, the presence of the two spin-flop transitions at $H_{c1}=2.1$ and $H_{c2}=4.7$ T produces the largest reduction of T_N in comparison with the *a* axis where not a single field effect is observed. Both spin-flop transition lines have a small positive slope as a function of temperature. These lines are in agreement with the magnetization data.[5] When the field is oriented along *b*, another type of spin-flop transition is found at $H_{c3}=7.7$ T with a small positive temperature slope. This transition produces also a downward shift of the Néel temperature. Since the elastic anomaly revealing this transition is quite strong (Fig. 4), it has been possible to approach more precisely the temperature and field ranges where the different transition lines cross. We can see the curvature of the lines in

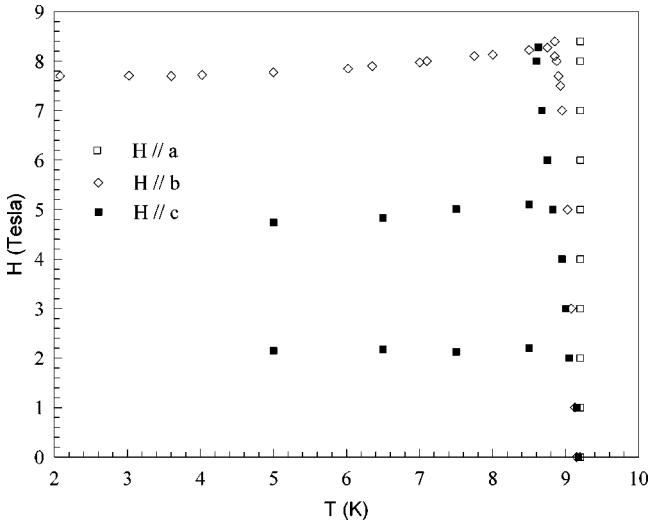

FIG. 6. *H-T* phase diagram of $BaCu_2Si_2O_7$ for field oriented along the three crystalline directions and values up to 8.5 T.

Fig. 6 merging at the critical point, $H_c=8.35$ T and $T_c=8.75$ K. Two similar critical points should exist along *c* and their existence can be guessed from changes of curvature in the shift of T_N; the anomalies are, however, too weak to permit their exact localization in the *H-T* plane.

The *H-T* phase diagram appears coherent with the recent magnetic structure reported by Zheludev *et al.*,[6] who have distinguished three phases labeled I, II, and III when the field is oriented along the easy axis. Phase I is characterized by spins parallel to the *c* axis, with nearest neighbor spins antiparallel along *b* and *c*, and parallel along *a*. With increasing field the ordered moment m_0 is growing weakly with a tilt angle α, which stays practically zero until near 2 T where it grows rapidly to 90°. In Fig. 4 (upper panel), this magnetic character is translated into an almost constant velocity variation up to H_{c1} where a sudden slope variation is observed, indicating that the moments have flopped along the *b* direction. Above H_{c1}, the magnetic structure of phase II is a slight distortion of a collinear one, all spins being parallel to the *b* axis but with a canting angle ϕ relative to the *a* axis and the same relative alignment of spins in adjacent chains ($H=0$). When the field is increased from H_{c1} to H_{c2}, although the ordered moment m_0 is increasing weakly, the canting angle varies almost linearly from 60° to 90°.[6] At H_{c2}, all the spins that were aligned along *b* flop along the *a* axis. Our ultrasonic data of Fig. 4 are again consistent with this scenario for phase II: the velocity variation is increasing monotonically with field, up to H_{c2}, where a sharp decrease is obtained when the spins flop along the *a* axis. Above H_{c2}, the magnetic structure is a collinear one, with all spins pointing along the *a* axis and the same relative alignment of spins in adjacent chains ($H=0$). In phase III the near-quadratic dependence of the velocity is progressively recovered (Fig. 4).

The new phase transition observed for a magnetic field oriented along the *b* axis is more unusual, since it involves, like the transition at H_{c2}, a spin rotation in the plane perpendicular to the magnetic field, but it can be reconciled with the magnetic structure of Zheludev *et al.*[6] In the lower panel of Fig. 4, we observe a quadratic dependence of the velocity variation as the field is increased, indicating a canting of the spins, away from the *c* axis, by the external field. Following such a canting of the spins in the *bc* plane, the free energy, including anisotropy effects together with interchain exchange coupling, is likely minimized by a spin rotation in the plane perpendicular to the field *H*. Because of the large amplitude of the acoustic anomaly and the high value of the field, we propose that the spins flop along the *a* axis at $H_{c3}=7.8$ T from phase I to phase III, which ensures minimization of the free energy for this field configuration. When the field is oriented along the *a* axis, minimum free energy is obtained by keeping the spins in phase I and no field effects could be obtained on the velocity, except for the reduction of the spin correlations giving rise to the quasiquadratic field dependence.

Finally, if we examine carefully the data of Fig. 3, we notice that, although a magnetic field shifts down the Néel temperature for the *b* and *c* directions, the stiffening anomaly amplitude relative to the value at T_N seems to increase qua-

siquadratically with field. Any conclusion about the field dependence of the order parameter is, however, difficult to make since a near-quadratic field dependence is observed at all temperatures below and above T_N.

IV. CONCLUSION

We have investigated the magnetic structure of the quasi-1D antiferromagnet $BaCu_2Si_2O_7$ with an ultrasonic velocity technique. It has been shown that transverse waves couple strongly with the magnetic structure. Elastic anomalies, observed both above and below the Néel temperature, reveal a coupling to spin correlations and to the antiferromagnetic order parameter. It has been found that a magnetic field applied along the three crystal axes decreases quadratically the velocity softening effects due to a reduction of spin correlations. Moreover, it has been possible to obtain an *H-T* phase diagram along the crystal axes by following the thermal and magnetic profiles of the elastic anomalies. The two stage spin-flop transitions along the easy axis have been identified and a third transition of a spin-flop type has been revealed along the *b* axis. Our data appear consistent with the magnetic structures of the various phases labeled I, II, and III and presented in a recent neutron diffraction paper.[6]

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