# Acoustic anomaly in the antiferrodistortive phase transition of $KHCO_3$ studied by Brillouin scattering

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Brillouin-scattering spectra of $KHCO_3$ have been observed as a function of temperature. The two pure transverse acoustic modes propagating along the $a^*$ and $b$ axes show an anomalous softening near the phase-transition temperature $T_N=318$ K. Their frequencies, however, are nonzero even at $T_N$. This incomplete softening behavior indicates an antiferrodistortive phase transition, though a ferroelastic transition was suggested by a previous ultrasonic study. A phenomenological discussion is given for the antiferrodistortive phase transition. [S0163-1829(97)03541-8]

Potassium hydrogen carbonate, $KHCO_3$, undergoes a structural phase transition at $T_N=318$ K.[1] Recently, Kashida and Yamamoto studied the crystal structure by x-ray analysis.[2] The structure is characterized by the orientational configuration of a planar $(HCO_3)_2$ dimer. In the high-temperature phase (phase I), each dimer is in a disordered configuration as shown in Fig. 1(a). The space group of the crystal is monoclinic $C2/m$. In the low-temperature phase (phase II), dimers are ordered in an antiphase configuration as shown in Fig. 1(b). The space group is monoclinic $P2_1/a$.[2–4] In phase II, the dimer takes one of two orientations as shown in Fig. 1(b). The change of the crystal structure strongly suggests that $KHCO_3$ undergoes an antiferrodistortive phase transition of the order-disorder type.

On the other hand, Haussühl performed an ultrasonic experiment and concluded that the phase transition of $KHCO_3$ is of ferroelastic type. This conclusion is based on the experimental fact that the elastic stiffness constant $c_{66}$, related to the pure transverse acoustic modes propagating along the $a^*$ and $b$ axes, shows an anomalous softening near $T_N$.[1] In the case of the ferroelastic transition, however, the spontaneous shear strain $x_{6s}$ appears with the freezing of any of these acoustic modes; that is, the frequency of such a soft mode should take a zero value at the transition point. In addition to this, the crystal structure should be triclinic $P1$ in phase II with the appearance of $x_{6s}$. This crystal structure $P1$ is inconsistent with the result of x-ray studies $P2_1/a$.[2–4]

The purpose of the present paper is to solve this inconsistency. All the acoustic modes propagating along the $a^*$, $b$, and $c$ axes were reexamined by a 90° Brillouin scattering system in the temperature range between 295 and 355 K. In particular, the anomalous behaviors of the pure transverse acoustic modes propagating along the $a^*$ and $b$ axes were carefully investigated near $T_N$ to elucidate whether the frequencies of these modes take zero values at $T_N$ or not. The present paper is a report of the Brillouin scattering of a $KHCO_3$ crystal.

A single crystal of $KHCO_3$ was grown from an aqueous solution by slow cooling. The crystal axes were confirmed by x-ray diffraction pattern analysis and also by the observation of the crystal habit. The rectangular prism shaped sample, $5\times5\times8$ mm$^3$, was obtained on referring to the dominant cleavage plane $(40\bar{1})$ and the natural rectangular plane (100). After the surfaces of the sample was polished up, the sample was mounted in a light scattering cell. The temperature of the sample was measured by a thermocouple placed near the sample and was controlled within $\pm0.05$ K. A longitudinal single-mode $Ar^+$ laser (Spectra-Physics, BeamLok 2060) was used as a light source. The wavelength and the output power of the laser beam were 514.5 nm and 80 mW, respectively. The scattered light from the sample was collected in the 90° Brillouin scattering geometry. A three-passed tandem Sandercock-type Fabry-Pérot interferometer was used as a spectrometer. The free spectral ranges employed here were 10 and 30 GHz. The finesse was maintained at more than 100 throughout the present experiment. The analyzed light was detected by a photomultiplier

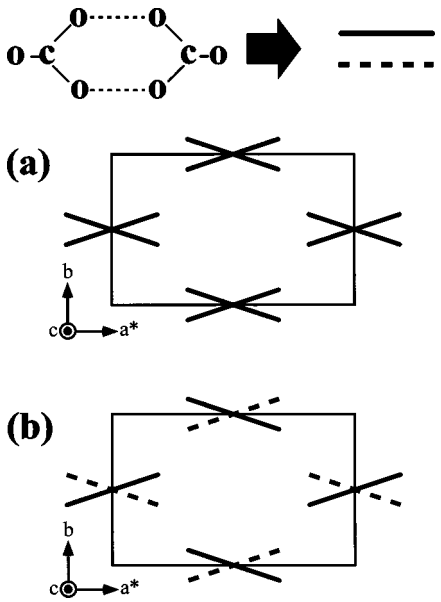


FIG. 1. The configuration of $(HCO_3)_2$ dimers on the $c$-axis projection. A dimer containing two hydrogen bonds ($O\cdots O$) is represented by a solid line or a dashed line. A unit cell is designated by a rectangle. (a) In the high-temperature phase (phase I), each dimer takes a disordered configuration. (b) In the low-temperature phase (phase II), dimers are ordered in one of two antiphase configurations expressed by a solid and dashed lines.

 

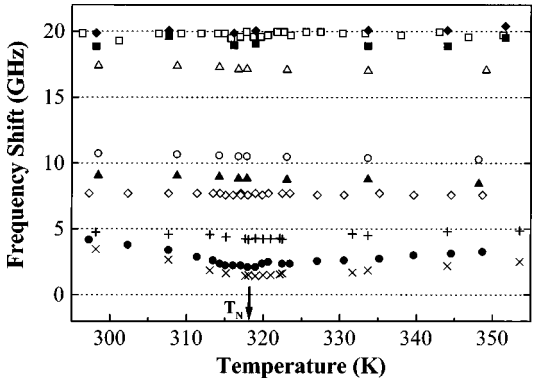


FIG. 2. The temperature dependence of the frequency shifts of the quasi-$c_{11}$ (□), the quasi-$c_{55}$ (◇), and the $c_{66}$ (●) modes propagating along the $a^*$ axis; the $c_{22}$ (◆), the quasi-$c_{44}$ (■), and the $c_{22}'''$ (×) modes propagating along the $b$ axis; the quasi-$c_{33}$ (△), the $c_{44}$ (○), and the quasi-$c_{55}$ (▲) modes propagating along the $c$ axis. The evaluated frequency $F(c_{46})$ (+) is also shown.

(Hamamatsu R585) and was accumulated in the memory of a multichannel analyzer. From the Brillouin scattering spectra obtained after 1200 time repetitions of accumulation, the frequency shift of the Brillouin peak was evaluated by the fit of the damped harmonic oscillator function.

All nine acoustic modes propagating along the $a^*$, $b$, and $c$ axes are observed precisely near $T_N$ by 90° Brillouin scattering. The frequency shift of each mode is plotted in Fig. 2 as a function of temperature. Two modes show remarkable softening behavior near $T_N$. One is the pure $c_{66}$ mode propagating along the $a^*$ axis and the other is the pure transverse acoustic mode, named the $c_{22}'''$ mode in Ref. 1, propagating along the $b$ axis. The typical spectra of these modes, which are measured with a high-frequency resolution of 0.1 GHz, are depicted in Figs. 3(a) and 3(b). The frequency shift data of these modes are plotted again in Fig. 4 on an expanded scale. Both of the $c_{66}$ and the $c_{22}'''$ modes soften toward $T_N$ as reported by Haussühl (Ref. 1). In addition to this fact, we found that their frequencies do not take zero values even at $T_N$: 2.1 GHz for the $c_{66}$ mode and 1.4 GHz for the $c_{22}'''$ mode. This incomplete softening behavior strongly indicates that the phase transition mechanism of $KHCO_3$ is not of ferroelastic type. This result disagrees with the conclusion of the previous ultrasonic study that a ferroelastic phase transition is expected.[1] The present result supports the x-ray result that $KHCO_3$ undergoes an antiferrodistortive phase transition.[2–4]

The origin of the incomplete softening of the $c_{66}$ and the $c_{22}'''$ modes is discussed. Hereafter, we employ the notation $F(c)$ to express the elastic stiffness constant $c$ in the frequency dimension as

$$F(c)=\left(\frac{|\boldsymbol{q}|}{2\pi}\right)\sqrt{\frac{c}{\rho}}. \tag{1}$$

Here $\boldsymbol{q}$ is the scattering vector and $\rho$ is the density of the sample. The elastic stiffness constant of the $c_{22}'''$ mode is expressed as

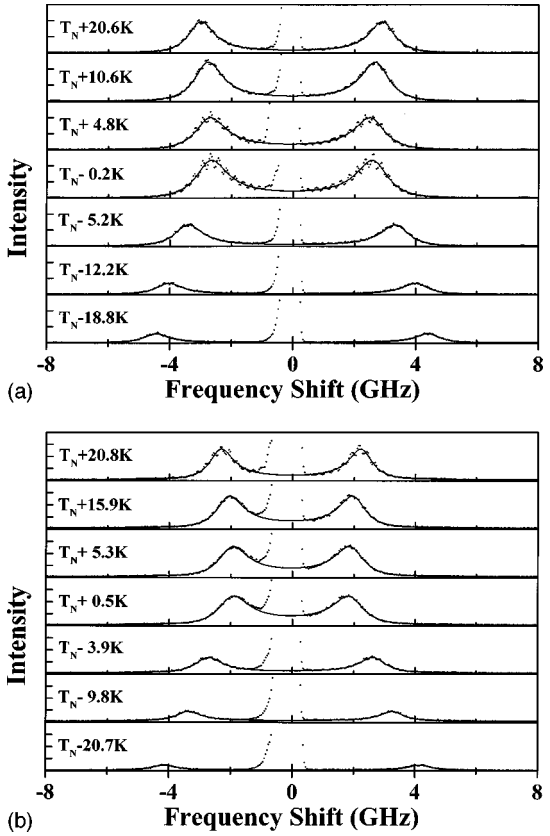


FIG. 3. The typical Brillouin scattering spectra of (a) the $c_{66}$ and (b) the $c_{22}'''$ modes at several temperatures near $T_N$=318 K. Thin curved lines indicate the result of the least squares fit of a damped-harmonic oscillator function.

$$c_{22}'''=\frac{c_{66}+c_{44}-\sqrt{(c_{66}-c_{44})^2+4c_{46}^2}}{2}. \tag{2}$$

By the use of Eqs. (1) and (2), $F(c_{46})$ can be evaluated directly from the frequency shift data of the observed $c_{22}'''$, $c_{44}$, and $c_{66}$ modes without the knowledge of $|\boldsymbol{q}|$ and $\rho$. Here we assume that there is no anisotropy in the refractive index

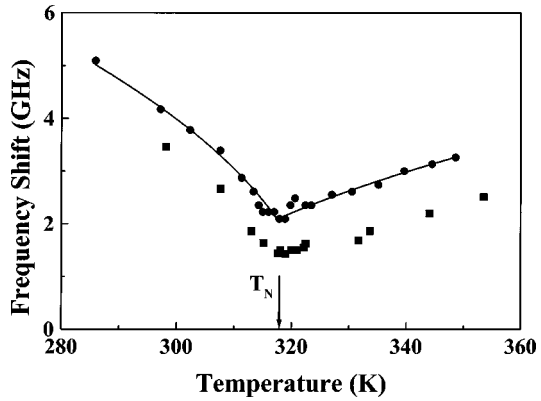


FIG. 4. The temperature dependence of the frequency shifts of the $c_{66}$ (closed circles) and the $c_{22}'''$ (closed squares) modes near $T_N$=318 K. The curved full lines indicate the result of the least squares fit of Eq. (5) to the frequency shift data of the $c_{66}$ mode.

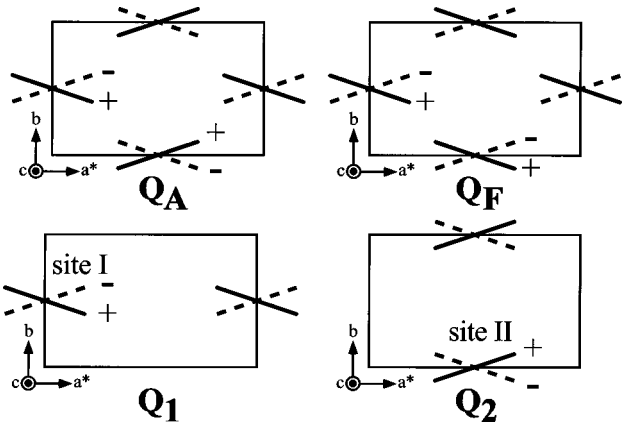


FIG. 5. The configuration of $(HCO_3)_2$ dimers (solid and dashed lines) corresponding to each of parameters $Q_A$, $Q_F$, $Q_1$ (at site I), and $Q_2$ (at site II) on the $c$-axis projection of the unit cell. The set of solid lines and that of dashed ones define the positive $(+)$ and negative $(-)$ signs of each parameter, respectively. The parameters $Q_A$ and $Q_F$ are related to $Q_1$ and $Q_2$ as $Q_A=(Q_1+Q_2)$ and $Q_F=(Q_1-Q_2)$.

$n$, though $|\boldsymbol{q}|$ directly depends on $n$. The temperature dependence of $F(c_{46})$ is added in Fig. 2. Since the frequency shift of the $c_{44}$ mode and $F(c_{46})$ are almost independent of temperature as seen in Fig. 2, one can deduce that the softening behavior of the $c_{22}'''$ mode is caused mainly by that of the $c_{66}$ mode. It is obvious that this deduction is not affected at all by the above assumption.

In order to explain the incomplete softening of the $c_{66}$ mode, we can employ the free energy $G$ expanded with the elastic strain $x_i$ ($i$ runs from 1 to 6) and with the parameters $Q_A$ and $Q_F$. Here $Q_A$ and $Q_F$ express the antiferrodistortive and ferrodistortive orders of the dimers, respectively, as shown in the upper half of Fig. 5. The parameter $Q_A$ should be the order parameter describing the antiferrodistortive phase transition of $KHCO_3$. It corresponds to the Brillouin zone boundary mode, the wave vector $\boldsymbol{k}$ of which is equal to the unit vector $\boldsymbol{a}^*$ of the reciprocal lattice in phase I.[2] This boundary mode belongs to the irreducible representation $\hat{\tau}_3$ of the space group $C2/m$ at $\boldsymbol{k}=\boldsymbol{a}^*$, where $\hat{\tau}_3$ is the notation given in Kovalev 's Table T4.[5] The parameter $Q_A$ corresponds to the Brillouin zone center mode belonging to the irreducible representation $Ag$ of the point group $2/m$ in phase II. On the other hand, the parameter $Q_F$ is related to the Brillouin zone center mode belonging to the irreducible representation $Bg$ of the point group $2/m$ in both phases I and II. The introduction of $Q_F$ into the free energy $G$ is essential for the explanation of the incomplete softening of the $c_{66}$ mode.[6] Because $Q_A$ and $Q_F$ are symmetrically nonequivalent, the temperature dependence of the coefficients of the $Q_A^2$ and $Q_F^2$ terms is not evident. The patterns $Q_A$ and $Q_F$ can be generated by new parameters $Q_1$ and $Q_2$: $Q_1=(Q_A+Q_F)/2$ and $Q_2=(Q_A-Q_F)/2$. The new parameters are symmetrically equivalent and independent in phase I as shown in the lower half of Fig. 5. The free energy $G$ in phase I is expanded by $Q_1$, $Q_2$, and $x_i$ according to the symmetry of the space group $C2/m$ as

$$G=\frac{1}{2}A(Q_1^2+Q_2^2)+\frac{1}{4}B(Q_1^4+Q_2^4)+\xi Q_1Q_2 + \eta(Q_1-Q_2)x_6+\frac{1}{2}c_{66}^0x_6^2. \quad (3)$$

Here $A$, $B$, $\xi$, and $\eta$ are the expansion coefficients and $c_{66}^0$ is the elastic stiffness constant at constant $Q_1$ and $Q_2$.[7] In this equation, only the lowest order of couplings among $Q_1$, $Q_2$, and $x_i$ are considered. Another lowest coupling term $(Q_1-Q_2)x_4$ can be included in Eq. (3), but it is neglected because the effect is estimated to be small by the observation of the $c_{44}$ mode as shown in Fig. 2. To discuss the temperature dependence of $c_{66}$, we assume that the coefficient $A$ has a linear temperature $T$ dependence as $A=\alpha(T-T_0)$ with positive constants $\alpha$ and $T_0$. The bilinear couplings among $Q_1$, $Q_2$, and $x_i$ ($i=1$, 2, 3, and 5) do not appear in Eq. (3) due to the crystal symmetry. This explains the present experimental fact that the $c_{11}$, $c_{22}$, $c_{33}$, and $c_{55}$ modes do not show any anomalous behaviors as seen in Fig. 2.

Three sets [cases (I), (II), and (III)] of the stable solutions of $\langle Q_1\rangle$, $\langle Q_2\rangle$, and $\langle x_6\rangle$ are obtained from the equilibrium condition $\partial G/\partial Q_1=\partial G/\partial Q_2=\partial G/\partial x_6=0$ and from the minimization of the free energy as follows.

Case (I): $\langle Q_1\rangle=\langle Q_2\rangle=\langle x_6\rangle=0$. This case corresponds to phase I.

Case (II): $\langle Q_1\rangle=\langle Q_2\rangle\equiv Q$ and $\langle x_6\rangle=0$, where $Q^2=-(A+\xi)/B$. This case corresponds to phase II. The minimum of G is calculated as $G=-(T_N-T)^2/2B$. The phase transition temperature $T_N$ is defined as $T_N=T_0-\xi/\alpha$.

Case (III): $\langle Q_1\rangle=-\langle Q_2\rangle\equiv Q$ and $\langle x_6\rangle=-2\eta Q/c_{66}^0\equiv x_{6s}$, where $Q^2=-(A-\xi-2\eta^2/c_{66}^0)/B$. The dimers align with ferrodistortive configuration $Q_F$ as shown in Fig. 5 and the space group should become triclinic $P1$. The minimum of $G$ is calculated as $G=-(T_C-T)^2/2B$. The phase transition temperature $T_C$ is defined as $T_C=T_0+(\xi+2\eta^2/c_{66}^0)/\alpha$. The spontaneous strain $x_{6s}$ appears and the $c_{66}$ mode takes zero frequency value at $T_C$. Since the antiferrodistortive phase transition in $KHCO_3$ is concluded in the present study, case (III) must be omitted. To be consistent with this result, the value of $G$ in case (III) should always be larger than the value of $G$ in case (II). This gives the relation $T_C<T_N$, which is equivalent to the condition

$$\xi+\frac{\eta^2}{c_{66}^0}<0. \quad (4)$$

The temperature dependence of the elastic stiffness $c_{66}$ is given finally as

$$c_{66}=c_{66}^0-\frac{2\eta^2}{\alpha(T-T_N)-2\xi}, \quad \text{for } T\geqslant T_N,$$
$$=c_{66}^0-\frac{2\eta^2}{2\alpha(T_N-T)-2\xi}, \quad \text{for } T\leqslant T_N. \quad (5)$$

The incomplete softening behavior observed in the present study is explained well by Eqs. (4) and (5). Especially, these equations assure that $c_{66}$ has a positive value of $c_{66}^0+\eta^2/\xi$ even at $T=T_N$. The frequency $F(c_{66}^0+\eta^2/\xi)$ is determined

experimentally to be 2.1 GHz at $T=T_N$. Expanding Eq. (5) in terms of $(T-T_N)$ and approximating it by the first term, it is rewritten in the unit of frequency and is used for the least squares fit to the frequency shift data of the $c_{66}$ mode. The fit is done simultaneously in both phases I and II under the assumption of the linear temperature dependence of $c_{66}^0$. The successful result is obtained and is drawn by the curved full lines in Fig. 4. There are two independent fitting parameters which correspond to $\alpha\eta^2/\xi^2$ and to the temperature gradient of $c_{66}^0$ through Eq. (1). The value of the parameter corresponding to $\alpha\eta^2/\xi^2$ and that to the temperature gradient of $c_{66}^0$ are determined to be $0.58\pm0.02$ GHz $^2$/K and $-0.08\pm0.01$ GHz $^2$/K, respectively.

In summery, we report here a Brillouin scattering study of $KHCO_3$. It is elucidated by a careful experiment that the $c_{66}$ and the $c_{22}'''$ modes never take zero frequency values even at $T_N$. This supports the result of x-ray study which suggests an antiferrodistortive phase transition of $KHCO_3$. By the present result, we solved the early inconsistency between the ultrasonic and x-ray studies. The softening behavior of the $c_{22}'''$ mode is explained by the temperature dependence of the $c_{66}$ mode. The incomplete softening of the $c_{66}$ mode is discussed phenomenologically and explained well quantitatively.

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[6] If the free energy $G$ is expanded in powers of $Q_A$ and the elastic strains $x_i$ as

$$G=\frac{1}{2}aQ_A^2+\frac{1}{4}bQ_A^4+\sum_{i=1,2,3,5}\eta_iQ_A^2x_i+\frac{1}{2}\sum_{(i,j)}c_{ij}^0x_ix_j,$$

one cannot explain the anomalous behavior of the $c_{66}$ mode. Even if higher order terms related to the elastic strain $x_6$ are added to $G$, the softening behavior of the $c_{66}$ mode above $T_N$ cannot be explained. These results are caused by the neglect of $Q_F$.

[7] One can express the free energy $G$ with $Q_F$ and $Q_A$ as

$$G=\frac{1}{2}\left(\frac{A+\xi}{2}\right)Q_A^2+\frac{1}{4}\left(\frac{B}{8}\right)Q_A^4+\frac{1}{2}\left(\frac{A-\xi}{2}\right)Q_F^2+\frac{1}{4}\left(\frac{B}{8}\right)Q_F^4$$
$$+\frac{1}{4}\left(\frac{3B}{4}\right)Q_A^2Q_F^2+\eta Q_Fx_6+\frac{1}{2}c_{66}^0x_6^2.$$

The distinct feature is that both coefficients of $Q_A^2$ and $Q_F^2$ depend on temperature through $A=\alpha(T-T_0)$. It is apparent that $Q_F$ causes the $c_{66}$ mode softening through the bilinear coupling $\eta Q_Fx_6$. This form of $G$ is obtained from Eq. (3) by the use of relations $Q_1=(Q_F+Q_A)/2$ and $Q_2=(Q_A-Q_F)/2$.