Elastic anomalies in HoNi$_2$B$_2$C single crystals

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We have measured temperature and magnetic field dependencies of the sound velocities and the sound attenuation in HoNi$_2$B$_2$C single crystals. The main result is a huge softening of the $C_{66}$ mode due to a cooperative Jahn-Teller effect, resulting in a tetragonal-orthorhombic structural phase transition. Anomalies in the behavior of the $C_{66}$ mode through various magnetic phase transitions permit us to revise the low temperature H–T phase diagrams of this compound.

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Holmium borocarbide HoNi$_2$B$_2$C is one of the most interesting members of the rare earth borocarbide family. The list of phenomena that have been found in this compound at low temperatures contains many of the mainstream research issues of solid state physics. Among them are the coexistence of superconductivity and magnetism, occurrence of multiple magnetic phases, including incommensurate spiral structures, and reentrant superconductivity (see for a review). In this work we uncover one more facet of complexity of HoNi$_2$B$_2$C: the presence of strong Jahn–Teller interactions.

Over the past decade almost all of the available arsenal of experimental tools has been used in the studies of borocarbides. However it seems that ultrasound methods did not receive the proper attention, and as a result the acoustic properties of these compounds are mostly “terra incognita” at present. In this work we have performed acoustic investigation of HoNi$_2$B$_2$C single crystals and obtained valuable data that are complementary to the known results. In particular, we have discovered a considerable softening of the $C_{66}$ elastic modulus that starts at temperatures as high as 100K. This is indicative of the strong Jahn–Teller interaction present in this compound. This interaction is the driving force of the tetragonal–orthorhombic structural phase transition. The magnetic phase transitions are accompanied by elastic anomalies which are most pronounced for the $C_{66}$ mode. By analyzing these features we were able to construct the H–T phase diagrams that added a few details to the existing phase diagrams (see for example).

Single crystals of HoNi$_2$B$_2$C were produced using the method described previously. Samples had the shape of plates of 0.2 mm thickness. The $c$ axis of the crystal was oriented perpendicular to the surface of the plate. The technique of working with submillimeter samples and the method of phase measurements are presented elsewhere. The characteristic feature of the method is the utilization of an electronically controlled phase shifter with a dynamical range that is practically unlimited. This, along with the use of a digital phase measuring device, allows to keep a very high resolution for large changes in the sound velocity. While the behavior of all pure modes of the crystal have been studied, we devote this paper mainly to the analysis of the most informative $C_{66}$ mode. The anomalies of the sound velocity of the $C_{44}$ mode are also briefly discussed at the end.

Shown in Fig. 1 are the temperature dependences of the sound velocity, $S$, of the $C_{66}$ mode both in the absence of an external magnetic field $H$ and when the field is oriented along main crystal directions. For $H = 0$ (curve 1) $S$ exhibits a considerable, about 35%, softening that starts showing up long before the onset of magnetic ordering found at $T \sim 10K$ by neutron diffraction experiment. At $T_{cr} = 5.23K$ there is a return to a stiffer state marked by a jump in $S$. If a magnetic field of $H = 4T$ is applied in the basal plane (curves 2 and 4) the magnitude of the softening is strongly reduced, though not eliminated completely. On the other hand, $S$ is affected very little if the field is applied along the $c$ axis (curve 3).
A wide temperature interval in which a softening of elastic constants takes place is the fingerprint of the Jahn–Teller interaction. The elastic constant of the lattice itself (background elastic constant $C^{(0)}$) increases very slowly with decreasing temperature. Much stronger temperature dependence comes from partially filled inner electronic shells of rare earth ions. For HoNi$_2$B$_2$C the crystal field splitting of the lowest J–multiplet of Ho$^{3+}$ ion is about 200 K, which explains why we do not see the pure background elasticity even at the highest temperatures used in our experiments (about 100 K). The localized electronic degrees of freedom are coupled to an extended degrees of freedom associated with the lattice. The elastic modulus of interest can be calculated as follows (see, for example): 

$$C_{66} = C_{66}^{(0)} - \frac{T}{v_{cell}} \frac{d^2}{d\varepsilon_6^2} \left[ \log \sum_i \exp \left( \frac{-E_i(\varepsilon_6)}{T} \right) \right]_{\varepsilon_6=0}$$

where $v_{cell}$ is the unit cell volume and $E_i$ are the eigenvalues of the single ion Hamiltonian $H_{ion} = V_{CF} + V_{JT}$ which operates within the lowest multiplet of Ho$^{3+}$ ion with J=8. The the crystal field Hamiltonian $V_{CF}$ has the form standard for tetragonal symmetry with the parameters determined by Gasser et al. The magnetic-ion–lattice (Jahn–Teller) interaction is taken in the simplest form $V_{JT} = -g\varepsilon_6 O_z^{-2}$, where $\varepsilon_6 = \varepsilon_{xy}$ is the relevant component of the strain tensor and $O_z^{-2}$ is the lowest order electronic quadrupole operator to which this strain couples by symmetry. Both $C_{66}^{(0)}$, assumed temperature independent, and the unknown coupling constant $g$ were determined from a fitting procedure in the temperature range where the system is paramagnetic. In Fig. 2 we show and the best fit (solid line), which corresponds to $g = 2.24$ meV/ion and $C_{66}^{(0)} = 1.63 \times 10^{12}$ dyn/cm$^2$, along with the experimental points (crosses) for $H = 0$. The agreement is quite good. The steep increase of $C_{66}(T)$ at $T_c = 5.23$ K is due to interactions with magnetic degrees of freedom, which we do not attempt to account for in this work.

The next conclusion is that Jahn–Teller interaction is in fact quite strong. If there were no other interactions in the system the crystal lattice would become unstable at about $T_{JT} = 2.89$ K as indicated by the vanishing of the calculated $C_{66}$ (see Fig. 2). Therefore, the Jahn–Teller interaction is the driving force of the structural phase transition from the tetragonal to orthorhombic phase that most probably takes place simultaneously with the stabilization of collinear antiferromagnetic ordering at $T_{cr} = 5.23$ K. Orthorhombic distortions of the crystal lattice have been observed previously at about 2 K and were associated with the magnetostriction.

Neither the sound velocity nor the sound attenuation, $\Gamma$, develop any visible anomalies at the superconducting phase transition ($T_c \approx 8$ K) in our experiments. At the same time magnetic phase transformations can be detected quite easily with the behavior of the $C_{66}$ mode. The typical shapes of the anomalies in the sound velocity and the sound attenuation are clearly seen in Fig. 1. The characteristic features are different for different branches are denoted by symbols of different shape; lines are guidance for eyes. Full symbols – results of $T$–sweeps with fixed $H$, open symbols – results of $H$–sweeps with fixed $T$.

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sound velocity at $T_1$ corresponds to a second order phase
transition of the improper segnetoelectric type.

Leaving such an analysis for a future publication we
present in Fig. 3 the obtained $H - T$ phase diagrams for
$H||[100]$ (top panel) and $H||[110]$ (bottom panel). Note
that we used two types of measurements: temperature
sweeps with fixed magnetic field and field sweeps with
fixed temperature. In all cases the external parameter
was kept increasing during sets of sweeps.

![Image](image-url)

FIG. 4: Temperature dependence of the attenuation (full
lines, right axis) and velocity (dotted lines, left axis) of the
$C_{66}$ mode for a) $H(0.45T)||[100]$, b) $H(0.6T)||[110]$ and c) $H(3T)||[001]$.

Let us discuss the case of $H||[100]$ (see Fig. 3, top
panel) in more detail. At $H = 0$ the temperatures of
the magnetic phase transitions practically coincide with
those found in the literature. The location of line 1 is
close to that of the other published data as well. Line 3
represents the position of a jump-like increase of the
sound velocity, which is steep at $H = 0$ but smears
considerably as $H$ grows. The attenuation always goes
through a maximum on line 3 (see insert on Fig. 1). At
$H \approx 0.4T$ line 3 splits forming a critical point. Shown
in Fig. 4a are the $S(T)$ and $\Gamma(T)$ curves at $H = 0.45T$
where the splitting of the line 3 is obvious. In the litera-
ture lines 3 and 3b are associated with the boundary of
a commensurate antiferromagnetic phase. Both line 3a
and line 3b represent an increase of the sound velocity
in the form of a smeared step. They are possibly bet-
ter detected as peaks in the attenuation (see Fig. 4a,
right vertical axis). Although it is in principle possible
that lines 3b and 3b stay separate from each other as the
magnetic field decreases all the way down to zero, we
were not able to observe any indications of such behav-
ior. Line 3 is not split as $H \rightarrow 0$ within the accuracy of
our experiments (see insert in Fig. 1).

![Image](image-url)

FIG. 5: Magnetic field dependence of the attenuation (full
lines, right axis) and velocity (dotted lines, left axis) of the
$C_{66}$ mode at $T = 5K$ for $H||[100]$.

The anomaly represented by line 2 is a step-like de-
crease of the sound velocity. At $H||[100]$ line 2 ap-
proaches line 3a as field increases, but disappears fur-
ther on. Over some range of magnetic fields line 2 coex-
ists with lines 3a and 3b (see Fig. 3, top panel). This
is demonstrated in Fig 4a where all three peaks in the
attenuation $\Gamma$ are clearly distinguishable. The simulta-
neous presence of all these three anomalies can also be
observed on an appropriate vertical cut of the $H - T$
plane in the top panel of Fig. 3. The magnetic field
dependence of $S$ and $\Gamma$ at $T = 5K$, shown in Fig 5, confirms
the coexistence of lines 2, 3a and 3b unambiguously.

In general, similar systematics holds true for $H||[110]$
as well (see Fig. 3, bottom panel). However, in the fields
larger than the value at which lines 2 and 3a merge one
can see a new feature on $S(T)$ and $\Gamma(T)$ curves (look up
$T_4$ in Fig. 4b). This suggests the existence of one more
line, line 4 in the bottom panel of Fig. 3, which could in
fact be a continuation of line 2.

For $H||[001]$ the $H - T$ phase diagram essentially co-
incides with the one published in the literature. We
do not present it again in this paper, but comment that
in high fields line 3 is possibly split as well. Indeed, in
fields as high as 3T (see Fig. 4c), we can readily define $T_{3a}$
and $T_{3b}$ on the attenuation temperature dependence
curve, $\Gamma(T)$.

Fig. 6 shows the temperature dependences of the ve-
locity of the $C_{44}$ mode in both Ho and Y borocarbides
that also exhibits slight softening. Notice that the mag-
FIG. 6: Comparison of the temperature dependence of the $C_{44}$ mode velocity for $YNi_2B_2C$ (top panel; $q||[001]$, $H||[001]$) and $HoNi_2B_2C$ (bottom panel; $q||[001]$, $H||[100]$).

The magnitude of the effect for this mode is three orders of magnitude smaller than for the $C_{66}$ mode in the $Ho$ compound (see Fig. 1). The $Y^{3+}$ ions in the other compound have all electronic shells completely filled, and therefore do not couple to the lattice by means of the mechanism discussed above. A softening of the $C_{44}$ mode velocity in $YNi_2B_2C$ for $H = 0$ has been observed recently by Isida et al., who associated it with the presence of a nesting feature of the Fermi surface.

Such anomalies have attracted a lot of attention in the 1970s in connection with superconductors of the A-15 crystal structure as a possible source of low temperature structural transformations. The theory predicts a logarithmic dependence of the active elastic modulus on temperature (for a given geometry). This is satisfied reasonably well for both compounds (see Fig. 6), providing the evidence of a measurable coupling of itinerant electrons to the lattice. In borocarbides this coupling is much weaker than in A-15 compounds, which could be due to a smaller contribution of 1D bands to the electronic spectrum.

Apart from a similar temperature dependence in the range of temperatures where softening takes place, the behavior of the $C_{44}$ elastic modulus in Y and Ho borocarbides with further decrease of temperature is very different. In the former compound the lattice softening stops upon stabilization of the superconducting phase, including the mixed state in magnetic fields (Fig. 6, top panel). In the latter compound the lattice starts growing stiffer only after magnetic ordering occurs while the onset of superconductivity does not produce any visible effect.

In summary, we demonstrated the presence of a Jahn–Teller interaction in $HoNi_2B_2C$ which is sufficiently strong to make the high temperature tetragonal crystal structure unstable (a cooperative Jahn–Teller effect). The details of $H – T$ phase diagram were clarified. We presented evidence in favor of the existence of critical points where several phase transition lines merge or perhaps intersect.

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