Phonon anomaly in Sm$_2$BaNiO$_5$

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Abstract. We present low-temperature far-infrared study of Sm$_2$BaNiO$_5$. The lowest-frequency phonon of Sm$_2$BaNiO$_5$ generated by the motion of the Sm$^{3+}$ ion demonstrates anomalous behaviour at temperatures lower than the Néel temperature, $T_\text{N} < 55$ K. This phonon hardens at the magnetic ordering although its frequency shift does not follow the magnetic order parameter. The observed phenomenon is responsible for an unusual dielectric response of Sm$_2$BaNiO$_5$ reported in the literature. A correlation between the temperature behaviour of crystal-field levels and the phonon anomaly is discussed.

1. Introduction

Sm$_2$BaNiO$_5$ is a representative of a family of the rare-earth (RE) chain nickelates $RE_2$BaNiO$_5$ recognized to be model compounds for studying one-dimensional magnetism. In their $Immm$ crystallographic structure, Ni$^{2+}$ ions with the spin $S=1$ form straight chains directed along the crystallographic $a$ axis with RE ions interconnecting the chains. Y$_2$BaNiO$_5$ from this family is believed to be almost ideal Haldane magnet [1,2] and it does not order magnetically at least down to $T = 100$ mK. In the case when RE is a magnetic ion, nickelates experience a magnetic ordering at low temperatures ($13 – 62$ K depending on the particular RE ion). In particular, a magnetic ordering of Sm$_2$BaNiO$_5$ was detected at $T_\text{N} \sim 55$ K from the spectroscopically observed splitting of Kramers doublets of the Sm$^{3+}$ ion [3,4] and of the Er$^{3+}$ probe (Sm$_2$BaNiO$_5$:Er 1 at.%) [5] and from the anomaly in the temperature-dependent heat capacity [6].

Recently, the family of chain nickelates attracted attention also from the point of view of their multiferroicity [6-8]. Several mechanisms of a strong interactions between magnetic, charge, and lattice degrees of freedom are discussed. Spectroscopic study of some of representatives of $RE_2$BaNiO$_5$ also revealed specific spectral behaviour attributed to the magnetoelectric interactions in chain nickelates [9,10]. In particular, in Sm$_2$BaNiO$_5$, a dielectric constant exhibits a weak peak with increasing $T$ around 22 K [7, 8]. Authors of Ref. [7] explained this effect by the depopulation of the upper component of the exchange-split excited state of the ground Kramers doublet. The dielectric constant is closely related to vibrational properties. In this study we present results on the temperature behaviour of the low-energy phonon modes as well as of the Sm$^{3+}$ Kramers doublets, with the aim to find correlations between the vibrational, electronic, and dielectric properties of the samarium nickelate.
2. Experimental
Transmission spectra in a wide spectral range (25 – 15000 cm\(^{-1}\)) were measured using a Fourier spectrometer Bruker IFS125HR. For measuring in the spectral region with wavenumbers \(\sigma > 500\) cm\(^{-1}\), a tablet was prepared from a mixture of Sm\(_2\)BaNiO\(_5\) and optical-grade KBr powders. For \(\sigma < 500\) cm\(^{-1}\), a sample was prepared in the following way. Polycrystalline Sm\(_2\)BaNiO\(_5\) was ground in an agate mortar and mixed with ethanol. A droplet of the mixture was put on a diamond plate and dried. Low-temperature measurements were performed using an optical closed-cycle cryostat Cryomech PT403.

3. Experimental results and discussion
Transmission spectra in the far-infrared region (35 – 130 cm\(^{-1}\)) are presented in figure 1 for three temperatures, together with the black-white map showing changes in a wide temperature range. Three distinct absorption bands are clearly seen, namely, at 54, 100, and 114 cm\(^{-1}\). To attribute observed peaks to the vibrational modes we compare them with the data presented in reference [11], where the detailed analysis and infrared (IR) spectroscopic temperature-dependent study of an oriented Gd\(_2\)BaNiO\(_5\) single crystal was performed. It follows from group theory analysis that there are 14 (IR) – active modes in the \(Immm\) structure of \(RE\)\(_2\)BaNiO\(_5\) compounds:

\[
\Gamma_{IR} = 5B_{1u}(E||c) + 5B_{2u}(E||b) + 4B_{3u}(E||a) \tag{1}
\]

The observed peaks can be unambiguously attributed to the following symmetry representations, namely, the mode at 54 cm\(^{-1}\) (51 cm\(^{-1}\) in Gd\(_2\)BaNiO\(_5\) [11]) is the lowest-energy \(B_{3u}\) vibration; and correspondingly, the mode 100 (96) cm\(^{-1}\) is \(B_{2u}\), and the mode 114 (110) cm\(^{-1}\) is \(B_{1u}\).

![Figure 1. Anomalous behaviour of the lowest-energy phonon of Sm\(_2\)BaNiO\(_5\) in the vicinity of \(T_N = 55\) K. Transmission spectra at different temperatures (upper panel) and black-white intensity map (lower panel).](image)

From the temperature changes shown in figure 1 one can conclude that only the \(B_{3u}\) mode 54 cm\(^{-1}\) experiences noticeable changes at low temperatures in the region \(T < T_N\). The temperature shift of the maximum of this band is shown in more detail by black dots in figure 2. The energy of the discussed mode is almost constant in the temperature range 120 – 55 K. At temperatures lower than \(T_N = 55\) K the mode starts to harden and its temperature shift is almost linear with temperature.
With the aim to compare the temperature behaviour of the $B_{3u}$ phonon mode ($54$ cm$^{-1}$) with the order parameter of the second-order magnetic phase transitions we have measured optical transmittance spectra in the region of $f-f$ transitions of Sm$^{3+}$ ion. In the antiferromagnetic state Kramers doublets of the Kramers Sm$^{3+}$ ion split as it is shown in the upper insert of figure 2. An example of spectral line splitting is shown in figure 3 for the $^4F_{9/2}$ multiplet of the Sm$^{3+}$ ion. From the measured spectra we were able to restore the temperature dependence of the splitting of the ground Kramers doublet $\Delta_0(T)$, which is shown in figure 2 by stars.

Figure 2. The temperature dependence of the spectral shift of the lowest energy $B_{3u}$ phonon mode in Sm$_2$BaNiO$_5$ (dots), the splitting of the ground Kramers doublet $\Delta_0$ of the Sm$^{3+}$ ion (stars), order parameter (dashed line). Insets show the energy level scheme for two lowest Kramers doublets of the Sm$^{3+}$ ion in Sm$_2$BaNiO$_5$ in paramagnetic (PM) and antiferromagnetic (AFM) states (upper panel) and the temperature behaviour of the lowest-energy $B_{3u}$ mode in Gd$_2$BaNiO$_5$ according to reference [11] (lower panel).

Figure 3. Transmission spectra in the region of $F_{9/2}$ multiplet of the Sm$^{3+}$ ion at various temperatures. Splittings of the spectral lines are shown by arrows. Up-directed arrows denote transitions from the first excited Kramers doublet II (see the scheme in figure 2).

In a majority of magnets with interacting $d$- and $f$- magnetic subsystems, $d$-$d$ interactions are the strongest one. These interactions lead to the magnetic ordering of the $d$-magnetic subsystems at a critical temperature, while $f$-magnetic subsystem is magnetized in the effective field $B_{\text{eff}}$ created by ordered magnetic moments of the $d$-ions [12,13]. In the frame of such approach, one can write:

$$\Delta_0(T) = g\mu_B B_{\text{eff}}(T),$$

(2)
\[ B_{\text{eff}}(T) = \lambda m_{\text{Ni}}(T) \]  

(3)

Here, \( g \) is the magnetic \( g \)-factor of a single Sm\(^{3+} \) ion in the ground state, \( \mu_0 \) is the Bohr magneton, \( m_{\text{Ni}} \) – is the ordered magnetic moment of Ni\(^{2+} \) (in \( \mu_B/\text{atom} \)), \( \lambda \) - the molecular-field constant. The validity of equations (2) and (3) was proved for the members of the family of chain nickelates (see, e.g., [3,14,15], where \( \Delta_0(T) \) was compared to \( m_{\text{Ni}}(T) \) measured by the neutron scattering). Taking into account the relations (2) and (3) one can conclude that the splitting of the ground doublet \( \Delta_0 \) is proportional to the value of the \( m_{\text{Ni}} \), i.e. \( \Delta_0 \) in the ideal case can be used as the order parameter instead of the value of the magnetic moment.

The experimentally measured \( \Delta_0(T) \) is not zero at \( T=0 \) (see figure 2), i.e., it is not possible to use it as the order parameter directly. The matter is that, as was shown earlier [13], except for the relations (2) and (3) there exists another contribution to \( \Delta_0 \), connected with the existence of the magnetic correlations in the PM phase. This additional contribution is especially great in the case of low-dimensional magnetic systems [16], which is exactly the case of chain nickelates, and in all of the nickelates studied \( \Delta_0(T) \) has the so-called “tail” at \( T>T_N \) (see, e.g., [9,12,13,15]). However, in the same references it was shown that in the temperature region \( T<T_N \), \( \Delta_0(T) \) function is proportional to the \( m_{\text{Ni}}(T) \), i.e., in this part it can be used as the order parameter. The dashed curve in figure 2 shows how the order parameter behaves in Sm\(_2\)BaNiO\(_5\).

Comparing the shift of the phonon frequency and the order parameter, one can conclude that both values demonstrate totally different behavior. This means that the shift of the phonon mode 54 cm\(^{-1}\) cannot be connected with the direct influence of magnetic field \( B_{\text{eff}} \). Moreover, in another member of chain nickelates family, namely, in Gd\(_2\)BaNiO\(_5\), the same \( B_{3u} \) mode does not experience any shift in \( B_{\text{eff}} \) (see lower Inset in figure 2), which means that one has to find another reason for the low-temperature anomalous shift of the lowest-energy \( B_{3u} \) phonon mode in Sm\(_2\)BaNiO\(_5\).

One of the possible reasons could be the change of wave functions of the ground state. Really, in the case of Sm\(_2\)BaNiO\(_5\), the repulsion of energy levels was observed (see reference [4] and scheme in the upper insert of figure 2). The repulsion of the energy levels of the Sm\(^{3+} \) ion can occur only in the case of a strong interaction between two close levels, which leads to the intermixing of their wave functions:

\[ |\Gamma_i^f\rangle = c_1|\Gamma_i^i\rangle + c_2|\Gamma_i^2\rangle \]  

(4)

Here, \( |\Gamma_i^i\rangle, |\Gamma_i^1\rangle, \) and \( |\Gamma_i^2\rangle \) are the wave functions of the initial (i) and final (f) states of the first (1) and second (2) interacting levels. Such an effect of intermixing of wave functions was observed, e.g., in PrFe\(_3\)(BO\(_3\))\(_4\), which has led to the breaking of selection rules for optical transitions and to the appearance of new spectral lines for the forbidden transitions [17]. In the case of Sm\(_2\)BaNiO\(_5\), a change of wave functions could lead to the change of the Sm-O coupling constant and, as a result, to the hardening of the corresponding vibrational mode. Another reason could be electron-phonon interaction, see, e.g., [18].

Finally, we emphasize, that the observed phonon anomaly is responsible for the reported peculiarity at \( T = 22 \) K in the temperature behavior of the dielectric constant \( \varepsilon(\nu) \) [7] according to the relation:

\[ \varepsilon(\nu) = \varepsilon_\infty + \sum_i \frac{s_i^2}{\nu_{\text{TO},i}^2 - \nu^2 - i\nu\gamma_i} \]  

(5)

Here, \( \varepsilon_\infty \) is the high-frequency dielectric constant, \( s_i, \nu_{\text{TO},i} \), and \( \gamma_i \) are the oscillator strength, TO frequency, and damping constant for the \( i \)-th phonon, respectively.

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