Infrared phonons as a probe of spin-liquid states in herbertsmithite ZnCu$_3$(OH)$_6$Cl$_2$

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Abstract

We report on temperature dependence of the infrared reflectivity spectra of a single crystalline herbertsmithite in two polarizations—parallel and perpendicular to the kagome plane of Cu atoms. We observe anomalous broadening of the low frequency phonons possibly caused by fluctuations in the exotic dynamical magnetic order of the spin liquid.

Keywords: kagome, infrared, phonons, spin-phonon coupling

Supplementary material for this article is available online
(Some figures may appear in colour only in the online journal)
looking for signatures of magnetic fluctuations in infrared-active phonons of herbertsmithite.

Herbertsmithite [5] was first found in 1972 in Chile, synthesized in 2005 [6], and high-quality single crystals of millimeter size have been available since 2011 [59]. Neutron and synchrotron x-ray diffraction experiments on synthetic single crystals [59] found no obvious structural transition down to 2 K. In this paper, we report the temperature dependence of the infrared optical phonon spectra of a herbertsmithite single crystal. Our data show anomalous broadening of the low-frequency infrared phonons upon cooling.

Single crystals of ZnCu$_3$(OH)$_6$Cl$_2$ were grown as described elsewhere [59]. Fourier transform infrared reflectivity measurements were performed using a 2 mm in diameter aperture on the largest face of the single crystal. From polarization dependence of the reflectivity spectra, we found two orthogonal polarizations with distinct phonon resonances. We do not see mixture of the contributions between polarizations. This means that c-axis is sufficiently close to the face of the crystal for phonon study accuracy.

We determine the number of allowed infrared active phonons using the correlation method [60]. Space group of herbertsmithite crystal is $R3m$ with three formula units in hexagonal unit cell [6, 61, 62] which is reflected in the second column of table 1. However, the primitive unit cell is rhombohedral and it contains one formula unit which is reflected in the third column of table 1 where we divided the number of Wyckoff sites by 3. Thus, the total number of phonons is $3N = 54$, where $N = 18$ is the number of atoms in the primitive unit cell. The presence of two types of the unit cell settings in literature does not affect phonon calculation because Wyckoff sites $a$ and $b$ have the same site symmetry which is also valid for sites $d$ and $e$. Thus, for infrared active phonons, we expect to observe seven nondegenerate $A_{2g}$ modes in $e||c$ polarization, where $e$ is electric field of light and $c$-axis is perpendicular to the kagome plane, and 10 doubly degenerate $E_u$ modes polarized in the kagome plane. Raman-active phonon analysis is identical to the previously published results [22, 30].

The number of phonons observed in our reflectivity spectra is larger than predicted for the $R3m$ group. We do not consider the possibility of another space group because all structural studies result in one space group. The most probable origin of additional vibrational modes is crystal defects such as Cu/Zn counterdoping, vacancies, impurities. In general, any substitution ion in a lattice which differs by mass or spring constant results in new, localized modes [63]. Structural studies of our crystals show that the kagome plane consists of Cu ions only and 5 to 10 % of Cu reside in Zn plane [28, 29]. We do not study additional phonon modes here, instead, we focus on magnetic effects on phonons. The presence of additional modes does not affect our main result—the observation of unusual broadening of some phonons upon cooling. Both eigenmodes of an ideal crystal and additional local modes get narrower upon cooling. Only magnetic interactions in this compound can cause such broadening of phonons.

Figure 1 shows the measured reflectivity spectra of herbertsmithite together with the fit results over a broad frequency range. Modes seen in the frequency range approximately 100–3600 cm$^{-1}$ are phonons. Qualitatively, we can say that low frequency phonons are dominated by heaviest ions—Cu and Zn in this case, mid range phonons, say $a6$–$c9$ and $c3$–$c6$, are oxygen and chlorine dominated, and the highest modes $a10$ and $c7$ are hydrogen dominated. Magnetic effects are expected at low frequency phonons dominated by magnetic Cu$^{2+}$ ions. As the number of observed phonons is larger than predicted for the given space group, the assignment of phonons is somewhat arbitrary. We assign the strongest modes using the room temperature spectra where magnetic effects are minimal. We measured temperature dependence of reflectivity in two polarizations below 6000 cm$^{-1}$. Reflectivity spectra above 6000 cm$^{-1}$ were measured at room temperature without polarizer. A peak in the optical conductivity at 32000 cm$^{-1}$ (4 eV) is the optical gap.

Figure 2 shows temperature dependence of the measured reflectivity spectra of herbertsmithite in the bolometer frequency range. Phonon modes are usually sensitive to temperature and this property can help in identification of phonons among observed features in the reflectivity spectra. We assign the modes in panel (a) near 500 cm$^{-1}$ as two major phonons $a6$ and $a7$ which become clear at low temperatures. In spite

### Table 1. Allowed Γ-point phonons for herbertsmithite by Correlation method [60]. Space group $R3m$ ($\neq 166$), one formula unit ZnCu$_3$(OH)$_6$Cl$_2$ per rhombohedral primitive unit cell.

| Species | Wyckoff positions | For phonon calculation | Site symmetry | Vibrational modes |
|---------|-------------------|------------------------|---------------|------------------|
| Zn      | 3$a^a$ or 3$b^a$  | a or b                 | $D_{3d}$      | $A_{2g} + E_u$   |
| Cl      | 6$c$              | 2$e$                   | $C_{3v}$      | $A_{1g} + A_{2g} + E_g + E_u$ |
| Cu      | 9$d^a$ or 9$e^a$  | 3$d$ or 3$e$          | $C_{2h}$      | $A_{1u} + 2A_{2u} + 3E_u$ |
| O       | 18$h$             | 6$h$                   | $C_i$         | $2A_{1g} + A_{1u} + A_{3g} + 2A_{2u} + 3E_g + 3E_u$ |
| H       | 18$h$             | 6$h$                   | $C_i$         | $2A_{1g} + A_{1u} + A_{3g} + 2A_{2u} + 3E_g + 3E_u$ |
| Total:  | 5$A_{1g} + A_{1u} + 2A_{2u} + 8A_{2g} + 7E_g + 11E_u$ |

| Acoustic: | $A_{2u} + E_u$ |
| Infrared: | 7$A_{2u}(e||c) + 10E_u(e \perp c)$ |
| Raman:    | 5$A_{1g}(\alpha_{xx} + \alpha_{yy}, \alpha_{zz}) + 7E_u(\alpha_{xx} - \alpha_{yy}, \alpha_{zz})$, $(\alpha_{zz}, \alpha_{cc})$ |
| Silent:   | 3$A_{1u} + 2A_{2g}$ |

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$a$ From [6, 61].

$b$ From [62].
of its complicated line shape, we consider mode \( c_2 \) in panel (b) as one phonon and we fit it with one oscillator because it is expected to be a phonon singlet according to the symmetry analysis. Even without looking at the fit results, one can tell that phonons \( a_2 \) and \( c_1 \) show temperature behavior different from other phonons. Upon cooling, the reflectivity peaks of all other phonons grow while \( a_2 \) and \( c_1 \) phonons have the opposite trend because of broadening which is possibly of magnetic origin.

We do not assign broad features between 250 and 350 cm\(^{-1}\) in figure 2(b) as phonons because they do not depend on temperature and they are too broad to be phonons. This can be a low energy electronic transition but it should depend on temperature in this frequency range as well. We note that it is seen only in \( e \| c \) polarization. An asymmetric mode with Fano line shape and \( A_{1g} \) symmetry was observed at 230 cm\(^{-1}\) in Raman spectra [22, 30]. It was assigned as an additional lattice mode due to crystallographic disorder. Its Fano shape was explained as the result of interaction with a continuum of states, possibly, of spin fluctuations. Possibly, we are seeing that continuum in our infrared spectra. Another possibility— we observe this continuum as the electric dipole active excitation which means the first-order coupling between spin fluctuations and phonons similar to the electromagnon effect in noncollinearly ordered magnets [64].

Figure 3 is similar to figure 2 and it presents higher frequency phonons. We see extra phonons here in both polarizations. A group of phonons \( c_7 \) shows nonmonotonic temperature dependence. In two spectra taken at 20 and 30 K, they are stronger than in the 10 K spectrum. It is not likely that this is an experimental error. The two bottom panels show different frequency ranges of the same spectra. Thus, the nonmonotonic behavior of \( c_7 \) phonon group is real but not understood.

We extract phonon parameters by fitting the reflectivity spectra with the model of a sum of Lorentzian oscillators of the Reffit program [65]. The complex dielectric function \( \varepsilon = \varepsilon_\infty + \sum s_j \frac{\omega_j^2}{\omega_j^2 - \omega^2 - i\omega \gamma_j} \). (1)

Figure 3. Temperature dependence of the reflectivity spectra in the MCT detector frequency range. Grey lines are spectra at intermediate temperatures.

Figure 4 shows phonon fit parameters versus temperature for in-plane polarization. Usually, phonon parameters exhibit the following trend upon cooling. The resonance frequencies \( \omega_j \) harden, the spectral weight frequencies of the \( j \)th electric dipole active mode, respectively. The complex optical conductivity is related to the dielectric function by \( \sigma = \eta_1 + i\eta_2 = \omega\varepsilon/4\pi l \).

Figure 1. (a), (b) Room temperature reflectivity spectra measured and obtained from fits of the Lorentzian model (equation (1)). Electric field of light \( e \) is (a) in the kagome plane of Cu atoms, (b) perpendicular to the kagome plane. (c) Imaginary part of the dielectric constant obtained from fits for two polarizations. A peak at 32000 cm\(^{-1}\) (4 eV) is the optical gap. Resonances below 3600 cm\(^{-1}\) are phonons. \( a_1 \)–\( a_{10} \) and \( c_1 \)–\( c_7 \) are tentative assignments of phonons.
be a good example of such temperature behavior. Most of the other nine phonons behave in a similar way. Softening of the $a_2$ mode may also be a spin-phonon coupling effect but the $a_{10}$ hydrogen dominated mode also shows softening which is unlikely to be magnetic in origin. The $a_2$ phonon also shows very unusual broadening upon cooling which we can only understand as magnetic in origin. Splitting of a phonon doublet into two singlets by specific chiral magnetic ordering of Cu spins was predicted theoretically for a kagome plane of spins [32]. Phonon line shape looks like a single mode and fitting of the $a_2$ phonon line with two oscillators close in frequency results in rejection of one of the two oscillators by the Reffit program. Thus, we cannot detect possible splitting of the $a_2$ phonon although 4 cm$^{-1}$ spectral resolution of the measured spectra was sufficient for that task. This absence of detectable splitting does not rule out the whole model because the predicted splitting becomes zero at a certain range of the exchange parameters. For a VBS model, it was shown that competing VBS orders may contribute to all three optical phonon parameters [11]. The sign of the predicted frequency shift is unknown, the spectral weight may also change due to effective charge redistribution, and only additional broadening is the unambiguous prediction which we observe in the $a_2$ mode temperature dependence. Phonon $a_1$ shows quite small narrowing toward zero temperature which is surprising for such a low frequency phonon and also may be a sign of magnetic broadening competing with thermal narrowing of the phonon line. Phonon $a_9$ surprisingly broadens below 100 K and we cannot explain such a behavior. First-principle calculations of phonons for herbertsmithite may give us better understanding of the observed behavior by separating lattice effects from magneto-lattice ones.

Figure 5 shows the phonon fit parameters versus temperature for the polarization perpendicular to the kagome plane. Parameters of higher frequency phonons are shown in the supplemental material.

Spin liquid on a kagome lattice posses different types of spin dynamics in various temperature ranges [44] characterized by the ratio $k_B T/J$. In our temperature range, we possibly deal with paramagnetic regime at $T > J = 200$ K and with dipolar-like spin correlations below 200 K. Spin excitations can be probed by infrared spectroscopy directly at the frequencies of the spin excitations as magnetic dipole active or electric dipole (ED) active modes. To acquire electric dipole activity essentially magnetic spin excitations have to borrow ED activity from ED-allowed transitions, most probably from the infrared optical phonons—the effect known as electromagnon which was observed in some ordered frustrated magnets [66–68]. Spin orders can couple to phonons in the second order. This effect is called spin-phonon coupling [54, 55] and it leads to a magnetic shift (positive or negative) of the phonon frequency. In magnetically frustrated cubic spinel ZnCr$_2$O$_4$, accumulated magnetic energy leads eventually to a magneto-structural phase transition at 12 K. In the low temperature phase, the crystal structure becomes tetragonal,
one triply degenerate phonon splits into phonon doublet and singlet, and frequency splitting is proportional to the magnetic energy [55]. In herbertsmithite, there is no structural transition and we do not expect clear phonon splitting but rather broadening of a phonon line. Interestingly, the broadening of the α2 phonon is about 10% of its resonance frequency, as seen from figure 4, and phonon splitting predicted in [32] is also 10% of the resonance frequency.

We believe that the broadening effect on the α2 phonon is magnetic in origin and it has to do with valence-bond physics. At low temperature, the system may be settling into a spin-liquid regime, in which valence-bond singlets formed by neighboring Cu spins slowly move around. Bonds with and without singlets will tend to have different lengths and spring constants—the same effect as in ZnCr2O4 [55]. Thus a phonon will find that the lattice is a bit disordered and the phonon line will exhibit some broadening. Ab initio calculations similar to [69] would be very useful for further understanding of the spin-lattice dynamics in this material.

In conclusion, we report possible observation of magnetic broadening of at least one phonon mode in a herbertsmithite single crystal. This observation is in agreement with the prediction of one of the VBS models [11]. Further experimental and theoretical studies are needed to understand the origin of the magnetic effects on phonons, and to separate the eigenmodes of the R3m space group from the observed additional vibrational modes.

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