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Local symmetry breaking in $K_2V_3O_8$ as studied by infrared spectroscopy

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We report the vibrational properties of quasi-two-dimensional $K_2V_3O_8$ as a function of temperature. Based on the splitting of the 990-cm^{-1} *c*-axis phonon mode into a doublet, we conclude that the 110-K transition is driven by a local distortion of the VO_5 square pyramids. At lower temperature, red shifting of two *ab*-plane phonon modes motivates us to identify an additional, more modest relaxation near 60 K. These observations are supported by an analysis of the electronic structure as well as other physical-property measurements including the permittivity, specific heat, and magnetization.

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I. INTRODUCTION

$K_2V_3O_8$ is a member of the fresnoite-type vanadium oxide family with the chemical formula $A_2V_3O_8$ ($A=$K, Rb, Tl, and NH_4), which are tetragonal antiferromagnets. These layered vanadates consist of slabs of corner-sharing VO_5 square pyramids and VO_4 tetrahedra,[1] with *A* ions lying between each layer. The role of the alkali-metal ion is thus to separate the magnetic layers. Note that the VO_5 square pyramids contain the magnetic V^{4+} ions with $S=1/2$, whereas the tetrahedra contain nonmagnetic $S=0$ V^{5+} ions.[2–5]

The $A_2V_3O_8$ family of materials has attracted attention due to their novel low-temperature magnetic properties.[4] In particular, $K_2V_3O_8$ is a two-dimensional (2D) $S=1/2$ antiferromagnet ($T_N\sim 4$ K) that shows an unusual field-induced spin reorientation. In addition to a conventional spin-flop transition with the magnetic field applied along the *c* axis, $K_2V_3O_8$ exhibits a striking continuous spin rotation when the magnetic field is applied in the basal plane.[2] More recently, Bogdanov *et al.* suggested that $K_2V_3O_8$ may have a chiral cycloid magnetic structure, with a modulated weak ferromagnetic moment; in this case, the spin reorientation is related to suppression of the modulated state by a magnetic field.[6] Complementary Raman measurements show a persistent two-magnon scattering signal up to $\sim 8\ T_N$, suggesting that the energy scale for magnetic excitations in $K_2V_3O_8$ is dominated by J rather than T_N.[7]

In addition to the aforementioned low-temperature magnetic properties of $K_2V_3O_8$, several exploratory transport and thermodynamic measurements have identified an anomaly of unknown origin near 110 K. In this investigation, we employ permittivity, specific heat, and susceptibility techniques to systematically characterize this feature for the first time and use temperature-dependent infrared spectroscopy to investigate the microscopic nature of this transition, which we attribute to a local distortion of the VO_5 square pyramids. In addition, our spectroscopic work points toward a second, much weaker relaxation near 60 K. We briefly discuss the role of these two higher-temperature transitions in determining the parent state of the novel low-temperature magnetism in $K_2V_3O_8$.

II. EXPERIMENTAL ASPECTS

Single crystals of $K_2V_3O_8$ were grown by cooling VO_2 in a molten KVO_3 flux in a platinum crucible sealed inside a silica container. Typical dimensions of the resultant crystals were $\approx 1\times 1\times 0.1\ cm^3$. The *ab* plane and the *c* axis are identified by the large crystal face and the normal to the plane, respectively.

Permittivity, heat capacity, susceptibility, and optical reflectance measurements were carried out directly on the aforementioned crystals. For transmittance measurements, a pellet was prepared by mixing 560 ppm of $K_2V_3O_8$ with KCl powder. Here, a small portion of $K_2V_3O_8$ was cut from a crystal, crushed and mixed with dry KCl powder, then pressed at 20 000 psi under vacuum. The resultant pellet was transparent with a dark purple color.

Permittivity measurements were performed from 20 to 300 K using a Hewlett-Packard 4284A Precision LCR Meter and a CTI Cryogenics closed cycle refrigerator. Heat capacity measurements were performed in a commercial heat-pulse calorimeter manufactured by Quantum Design. Magnetization measurements were performed in superconducting quantum interface device magnetometer manufactured by Quantum Design.

Infrared measurements were performed in both reflectance and transmittance modes using a Bruker Equinox 55 Fourier transform infrared (FTIR) spectrometer coupled with a Bruker IR Scope II equipped with MCT and InSb detectors. We covered the frequency range from 600 to 12500 cm^{-1}. Spectral resolution was 1 and 2 cm^{-1} in the middle- and near-infrared, respectively. Appropriate wire grid and film polarizers were employed as necessary. No polarization dependence was observed in the *ab*-plane spectra. For polarized reflectance measurements in the interlayer direction, the sample was mounted vertically, with the narrow side facing toward the incident beam. Low-temperature measurements were carried out with an Oxford Microstat He open-flow helium cryostat with KRS5 windows.

The optical conductivity spectra were obtained via Kramers-Kronig analysis of the reflectance spectra,[8] and the absorption spectra were calculated from the transmittances using $\alpha(\omega)=-(1/hd)\ln T(\omega)$, where h is the concentration

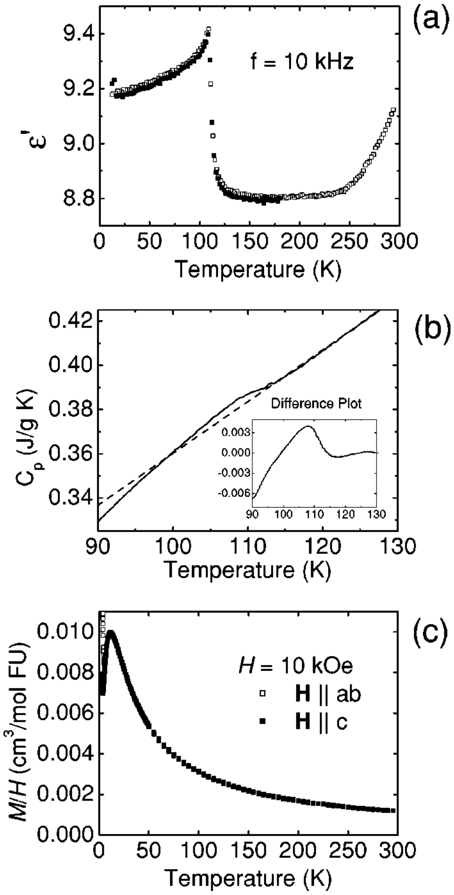

FIG. 1. Temperature variation of the (a) permittivity response in upsweep (solid square) and downsweep (open square) directions at 10 kHz, (b) specific heat (solid line) and an extrapolation based on a linear fit to the data above the 110 K anomaly (dashed line) and deviation of the data from the extrapolation line (inset), and (c) magnetic susceptibility with a magnetic field applied parallel to the *ab*-plane direction (solid squares) and to the *c* axis (open squares).

of $K_2V_3O_8$ in the KCl matrix, and *d* is the pellet thickness. In order to assign the center frequencies of various phonon modes, each peak was fit to a Gaussian lineshape, using a peak fitting program.

III. RESULTS AND DISCUSSION

A. Permittivity, specific heat, and magnetic response of $K_2V_3O_8$

Figure 1 displays the temperature dependence of the 10 KHz permittivity, specific heat, and magnetic susceptibility (M/H) of $K_2V_3O_8$. Both the permittivity and specific heat data show modest changes near 110 K, possibly related to a weak structural modification. The permittivity is low overall, with a characteristic signature at the transition temperature. It displays an increased polarizability in the low-temperature ground state compared with that above the transition temperature. The shape of the permittivity and specific-heat data near 110 K matches that expected for a continuous phase transition. The specific-heat data also shows an inflection point in this temperature regime. In contrast, the magnetic susceptibility[9] is not sensitive to the aforementioned changes near 110 K. As seen in Fig. 1(c), the susceptibility is the same for $H \| c$ axis and $H \perp c$ axis, at "high" temperatures (above $T \sim 15\,\mathrm{K}$). This isotropic response implies that the vanadium magnetic moment is insensitive to its environment; it does not feel the modified surroundings arising from the 110 K structural distortion. Consequently, χ is a smooth, continuous function of temperature. The susceptibility can be modeled by a Curie-Weiss temperature dependence with an effective magnetic moment of a single $S=1/2$ ion per formula unit, as described in Refs. 2, 4.

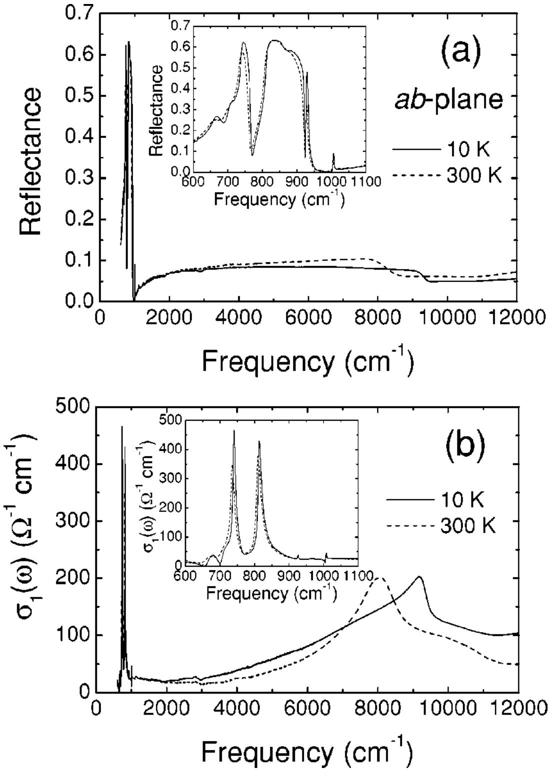

FIG. 2. Reflectance (a) and optical conductivity (b) spectra of $K_2V_3O_8$ in the *ab* plane at 300 (dashed line) and 10 K (solid line).

B. Vibrational properties

Figures 2(a) and 3(a) display the basal (*ab* plane) and interlayer (*c* axis) reflectance of $K_2V_3O_8$. Both sets of spectra show a typical semiconducting response, characterized by strong phonon modes and a low, flat background reflectance. The strong anisotropy between the *ab*-plane and the *c*-axis spectra demonstrates that $K_2V_3O_8$ is a two-dimensional optical material, consistent with expectation based upon the structure.

In the optical conductivity spectra [Figs. 2(b) and 3(b)], *ab*-plane phonon modes are found near 925, 820, 745, and 680 cm^{-1}, and *c*-axis phonon modes are observed near 995 and 940 cm^{-1}.[10] Longitudinal and transverse optic mode frequencies for these structures are tabulated in Table I. Previous investigations of vibrational modes in other vanadate based materials[11,12] allow us to assign the highest energy structure as a vanadium/apical oxygen stretching mode. This

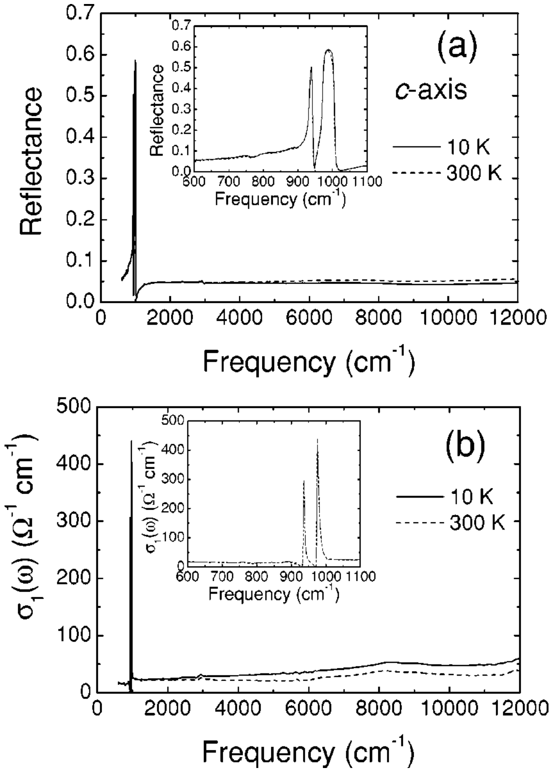

FIG. 3. Reflectance (a) and optical conductivity (b) spectra of $K_2V_3O_8$ in the interlayer (*c* axis) direction at 300 (dashed line) and 10 K (solid line).

assignment is based on the characteristically short bond lengths between transition metal ions and apical oxygens in the square pyramid building-block units of this class of materials; a short bond length translates into a tight "spring constant" and thus, a high resonance frequency. More specifically, Galy and Carpy[3] find that the bond lengths of V-O (apical) and V-O (*c* axis) are 1.582 and 1.628 Å for the VO_5 (square pyramids) and VO_4 (tetrahedra) in $K_2V_3O_8$, respectively. These are the shortest V-O bond lengths in the material. Thus, we expect stretching of these bonds to give rise to the highest-energy phonon modes in $K_2V_3O_8$. The *c*-axis polarization of the 995 and 940 cm^{-1} stretching modes follows directly from the orientation of the V-O (apical) and V-O (*c* axis) bonds for the VO_5 square pyramids and VO_4 tetrahedra, respectively, in the crystal structure. Using similar arguments, the *ab*-plane phonon structures are likely stretching modes of vanadium and basal-plane oxygens in the VO_5 and VO_4 building-block units.

TABLE I. Transverse and longitudinal optic phonon mode frequencies obtained by Kramers-Kronig transformation for the 10 K infrared reflectance spectra in *ab*-plane and *c*-axis polarizations.

Polarization	ω_{TO} (cm^{-1})	ω_{LO} (cm^{-1})
ab plane	745	766
	820	934
c axis	937	944
	977	1006

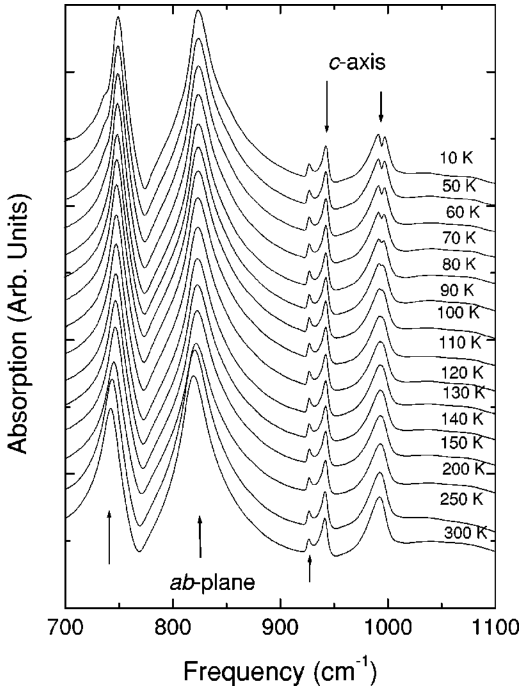

FIG. 4. Middle-infrared absorption spectra of $K_2V_3O_8$ in a KCl matrix at various temperatures. The spectra are offset for clarity.

For investigations of vibrational properties, a group theoretical analysis is useful to assign the experimentally observed infrared and Raman active modes. $K_2V_3O_8$ has a space group $P4bm$. Each unit cell contains two formula units, and a total of 26 atoms.[3,4] The total irreducible representation is $\Gamma_{\mathrm{total}} = 13A_1 + 9A_2 + 7B_1 + 11B_1 + 19E$. Here, only A_1 and E modes are infrared active. Excluding acoustic modes, there are 30 infrared active phonon modes: $\Gamma_{\mathrm{IR}} = 12A_1 + 18E$. A_1 modes are z (*c* axis) polarized, whereas the doubly degenerate E modes are *xy* (*ab* plane) directed. Because a symmetry reduction can lift the degeneracy of the E modes, *ab*-plane polarized features are expected to be most sensitive to formal, long-range symmetry breaking of the crystal.

Even though polarization information is lost in a transmittance experiment and subsequent calculation of the absorption spectrum, transmittance measurements often have the advantage of a higher sensitivity to small changes. Figure 4 displays the absorption spectra of $K_2V_3O_8$ as a function of temperature. Fortuitously, the aforementioned *ab*-plane and *c*-axis phonon modes do not overlap. As clearly shown in the absorption spectra (Fig. 4), the *c*-axis phonon mode near 990 cm^{-1} displays doublet character below 110 K. This effect is quantified in Fig. 5, where the center frequency of the 990 cm^{-1} mode (and three others) is plotted as a function of temperature. The 990 cm^{-1} mode splitting increases with decreasing temperature and saturates below 60 K, as shown in Fig. 5(d). Based upon our previous assignment of the 990 cm^{-1} mode as a V-O (apical) stretching mode in the VO_5 square pyramids, the splitting of this structure indicates a distortion of VO_5 square pyramids at 110 K. The slight displacement of the apical oxygen from the apex of a perfect square pyramid is a clear case of symmetry breaking. How-

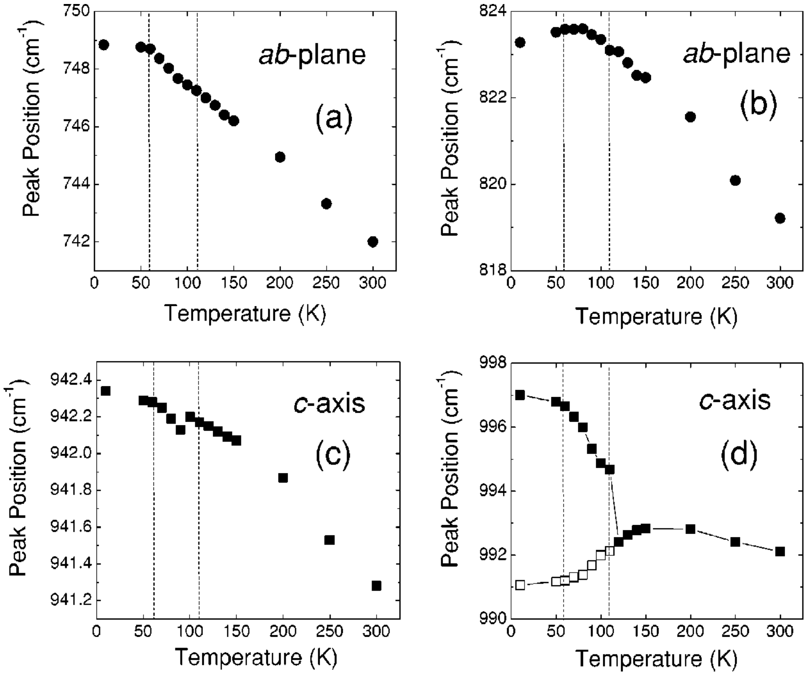

FIG. 5. Center frequency of selected phonon modes vs temperature. (a) and (b) are *ab*-plane phonon modes, and (c) and (d) are *c*-axis phonon modes. Vertical dashed lines denote transition temperatures. Error bars are on the order of the symbol size.

ever, based on the fact that only the 990 cm^{-1} *c*-axis phonon mode displays splitting in the low-temperature phase of $K_2V_3O_8$, we conclude that the symmetry breaking is fairly weak and local (rather than long range); it does not seem to alter the space group. That the distortion is a local phenomenon is also supported by the other center frequency vs temperature data in Fig. 5.

The *ab*-plane phonon modes displays only weak steps or inflection points in the vicinity of the 110-K transition, indicating only a slight sensitive to the distortion, and the *c*-polarized feature at 940 cm^{-1} does not show a strong connection to the transition within our resolution. Curiously, these results are in apparent disagreement with the aforementioned symmetry analysis, which predicts that symmetry breaking ought to influence the doubly degenerate phonon modes polarized in the 2D layer direction. The lack of formal, long-range symmetry breaking, as evidenced by the insensitivity of the *ab*-plane modes, thus supports a local rather than extended structural distortion in $K_2V_3O_8$ at 110 K.

The *ab*-plane phonon modes [Figs. 5(a) and 5(b)] blueshift with decreasing temperature until ~60 K. A similar blueshift is observed in the *c*-axis phonon modes near 940 cm^{-1} and 990 cm^{-1} (before splitting). However, the degree of blueshift observed in the *ab*-plane phonon modes is almost a factor of ten larger than that of the interlayer phonon modes. Thus, we anticipate that thermal contraction of $K_2V_3O_8$ occurs predominantly in the *ab* plane.

Below 60 K, the aforementioned blue shifting saturates: in the case of the 820 cm^{-1} feature, the mode actually redshifts with further temperature reduction [Fig. 5(b)]. The abrupt change in slope of the 820 cm^{-1} mode below 60 K [also observed more weakly in the 745 cm^{-1} structure, Fig. 5(a)] might be attributed to the saturation of thermal contraction and re-expansion of the crystal. More likely, it is the signature of a subtle relaxation near 60 K. These redshifts in the 820 and 745 cm^{-1} modes are quite pronounced considering the simultaneous insensitivity of the *c*-axis phonon modes to this relaxation. Thus, we conclude that the 60 K relaxation in $K_2V_3O_8$ is an *ab*-plane phenomenon, perhaps related to a basal plane distortion of the VO_5 building blocks. Upon careful examination, a small inflection point in the permittivity may be observed near 60 K [Fig. 1(a)], again suggesting the possibility of an additional relaxation at 60 K in $K_2V_3O_8$. In fact, this low-temperature relaxation has some similarities to that in other low-dimensional magnetic and molecular materials.[13–15]

C. Electronic properties

The 300-K *ab*-plane optical conductivity spectrum of $K_2V_3O_8$ shows a broad excitation near 8100 cm^{-1} [Fig. 2(b)]. Based on the vacuum-ultraviolet reflectance and photoemission study of vanadate compounds by Shin *et al.*,[17] this band is assigned as a $d \rightarrow d$ transition of vanadium ions in VO_5.[16] Excitations of this sort have also been assigned as Hubbard band-gap excitations.[18–20] In any case, this structure shifts strongly to higher energy with decreasing temperature; it is centered near 9200 cm^{-1} at 10 K. An overall blueshift of this excitation is in line with the aforementioned *ab*-plane thermal contraction effects, which cause the V 3*d* level splitting to increase due to a stronger crystal field at low temperature. At the same time, it is reasonable to anticipate that the electronic structure of $K_2V_3O_8$ may display some sensitivity to the 110 and 60 K changes, which are intimately related to the VO_5 and VO_4 building blocks, superimposed on this overall hardening trend.

In order to quantify changes in the electronic structure of $K_2V_3O_8$ through the 110 and 60 K changes, we plot the center peak position of the V $d \rightarrow d$ excitation as a function of temperature in Fig. 6. The graph clearly highlights not

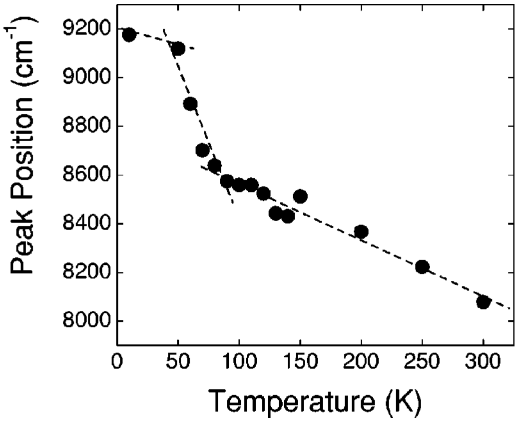

FIG. 6. Peak position of the $d \rightarrow d$ transition of V^{1+} as a function of temperature. Dashed lines guide the eye. Error bars are on the order of the symbol size.

only the overall blueshift of the band with decreasing temperature, but also three distinct temperature regimes: $T \geqslant 100\,\mathrm{K}$, $50\,\mathrm{K} \leqslant T \leqslant 100\,\mathrm{K}$ and $T \leqslant 50\,\mathrm{K}$. Near 100 K and again near 50 K, the center frequency vs temperature slopes change rapidly, indicating the possibility of phase transitions at these temperatures. While the overall blueshift is due to thermal contraction in *ab* plane, the rapid change in slope near 100 K (Fig. 6) indicates an additional change in crystal field, likely due to the distortion of the VO_5 square pyramid, because the transition temperature (100 K) is nearly coincident with that discussed earlier (at 110 K) and associated with the splitting of the 990 cm^{-1} *c*-axis phonon mode and the permittivity jump. In addition to the 110 K transition, the 50 K slope discontinuity also supports our finding of a weak *ab* plane related relaxation near 60 K. As mentioned earlier, it may be related to a minute basal plane distortion of the VO_5 square pyramids.

The distorted low-temperature structure of the VO_5 square pyramid is the parent state of the low-temperature magnetic properties. While the vanadium moment is unaffected by the distortion at 110 K, it is possible that the moment may be sensitive to the small local distortion in the VO_5 environment at very low temperatures (below 15 K), thus effecting both the spin flop and spin rotation in a magnetic field.

IV. CONCLUSION

We have carried out polarized infrared measurements on $K_2V_3O_8$ in order to explore the high-temperature properties in this prototypical magnetic material. Based on a splitting of the 990-cm^{-1} *c*-axis phonon mode, we conclude that the 110 K transition is driven by a slight distortion of the VO_5 square pyramids, whereas red shifting of two *ab*-plane phonon modes motivates us to certify an additional weak relaxation near 60 K. These observations are supported by an analysis of the electronic structure and are complemented by studies of other physical properties, including the permittivity, specific heat, and magnetization.

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[1] A tetrahedron is normally thought to be symmetric, however the VO_4 building block in $K_2V_3O_8$ is slightly distorted from the "perfect" tetrahedron, which results in unequal V-O bond lengths. On the other hand, the VO_5 square pyramids are symmetric (Ref. 3).

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[9] M/H is identical to χ except at the lowest temperatures, which are not the focus of this work.

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