



Geometrical frustration, spin ice and negative thermal expansion – the physics of underconstraint

A.P. Ramirez^{a,*}, C.L. Broholm^b, R.J. Cava^c, G.R. Kowach^a

^aAT&T Bell Laboratories, Lucent Technologies 600 Mountain Ave., Murray Hill, NJ 07974-0636, USA

^bDepartment of Physics and Astronomy, Johns Hopkins University, Baltimore, MD, 21218, USA

^cChemistry Department, Princeton University, Princeton, NJ, 08540, USA

Abstract

The idea that some systems could have a thermodynamically large number of accessible ground states was presaged in the work of Pauling on ice (Pauling, Cornell University Press, Ithaca, NY, 1945) [1]. With the advent of spin glasses, the methodology for describing ground states changed dramatically, and in particular it was realized that the observed slow dynamics were due to relaxation among a large number of nearly degenerate ground states. Now the accepted wisdom is that both “frustration”, as well as structural disorder, is responsible for spin glass behavior. However, well before spin-glasses were identified as a distinct class of systems, it had been appreciated that even for structurally periodic systems, bond frustration could lead to a thermodynamically large number of states. There is now a well-defined class of magnets which display effects of macroscopic ground state degeneracy. This class of geometrically frustrated magnets presents some new paradigms with which to view condensed matter systems – marginal underconstraint and downward shift of spectral weight. We discuss possible realizations of these phenomena in both in spin ice and also outside the context of local-moment magnetism. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Geometrical frustration; Pyrochlore antiferromagnet; Negative thermal expansion

Ground state degeneracy of the type seen in ice is only one example of how solids sometimes do not fit together. Other manifestations of frustration are, for example, glass formation, the blue phase of cholesteric liquid crystals, and incommensurate states in general. Frustration is uniquely a solid state phenomenon, for it results from the symmetry-incompatibility of local and extended degrees of freedom and it is the extended degrees of freedom which differentiate solids from physical systems such as atoms, nuclei, and elementary particles. In systems with quenched random disorder, such as spin glasses, the nature of this symmetry-incompatibility varies on an inter-atomic length scale. In cholesteric crystals, for example, it results from the local desire to accommodate chirality on the intermolecular length scale and the tend-

ency to form long-range order [2–4]. In metallic glasses it results from the tendency of the metal atoms to form tetrahedra locally but to close-pack globally [5]. In the latter two examples, the systems yield to a state of lower energy by forming defects. The defects are allowed to form because frustration appears as the system is solidifying and defect formation is energetically possible. There are also systems where the symmetry-incompatibility is established at both a lower energy scale than the interaction among dynamical entities, as well as at a higher energy scale. An example of the first is common ice. Here the lattice freezes at 273 K (~ 0.03 eV) whereas the interaction among hydrogen atoms can be said to have an energy in the range of 1 eV. When the system freezes, the hydrogen motion is also frozen since there is no thermal energy to excite hydrogen-reorientation modes. In this paper, we will consider the converse – systems where the global symmetry is fixed at a very high temperature (a typical metal-oxide solidification temperature) compared to the interaction energies of the degrees

* Corresponding author. Fax: + 1-908-582-4702.

E-mail address: apr@bell-labs.com (A.P. Ramirez)

of freedom of interest, the atomic spins. This relationship between the two important energy scales holds the promise for qualitatively new collective behavior both in magnetic as well as nonmagnetic systems.

In geometrically frustrated magnets (GFM's), the symmetry incompatibility is between the local antiferromagnetic (AF) interaction, and the global symmetry imposed by a triangular crystal structure. The heuristic device illustrating this is AF Ising spins on a triangle, but frustration effects are more commonly observed for isotropic spins. There is now a class of materials which exhibit frustration effects and which have common microscopic properties [6]. Microscopically, they have triangle-based magnetic lattices, and isotropic spins (except for the special case of spin ice). The macroscopic effects of GFM's are for example (i) spin-liquid effects [7,8], (ii) spin-glass states for immeasurably small amounts of quenched disorder [9], and (iii) novel phase behavior in applied fields [10–12].

The other condition besides symmetry-incompatibility necessary for GFM's is under- or marginal-constraint. Underconstraint in dynamical systems can arise by rarefaction of interactions. In percolative systems, reduction of T_c is achieved by randomly reducing the mean-field coupling strength – experimentally one does this by preparing a dilute system, e.g., randomly placed magnetic spins in a nonmagnetic salt. There is also directed rarefaction, e.g. low-D systems. Random percolation is a trivial way to reduce T_c since the two-body interaction is also reduced. The object of studying GFM's is to reduce T_c while keeping the mean-field energy fixed. For nearest-neighbor interactions, a 2D Ising antiferromagnet on a square lattice will order. However, on a kagome lattice ordering does not occur, despite having the same mean field energy, which is defined by the exchange interaction, the spin value, and the number of nearest neighbors (nn), four in both cases. The difference lies in the connectivity of the next nearest neighbors (nnn). For the kagome case the nnn's are unique for each nn, while for the square lattice they are not and hence the system is overconstrained. So even though the spins are strongly interacting on the kagome lattice, the triangles can be thought of as isolated units to first approximation. These issues have been discussed by Moessner and Chalker using Maxwellian counting arguments [13].

The net result of geometrical frustration is large ground state degeneracy, and large $T = 0$ internal energy, compared to the unfrustrated case. The internal energy, however, depends on the spin-spin interaction – for instance, an ensemble of independent two-level centers with energy level splitting ε has $U(\infty) \propto N\varepsilon$ where N is the number of centers. The entropy, $S(T)$, on the other hand, is scale invariant – $S(\infty) = N \ln 2$ for the two-level ensemble. Thus, for identifying effects due solely to geometry, it is more useful to discuss the conserved quantity, entropy.

Most conventional magnetic systems undergo long-range order and lose entropy with the greatest rate dS/dT , in the vicinity of $T_c \sim \theta_w$. In low-D systems where T_c is suppressed by fluctuations, the entropy shows the largest rate of change at a temperature on the order of the Weiss constant. Physically this means that the majority of spins find themselves in correlated states involving a number of spins much less than N , but significantly greater than 1 well above T_c . So in both conventional magnets, as well as low-D systems, the entropy removal is dictated by the two-spin interaction energy. For a given class of excitations, the mean-field T_c is related to a characteristic energy scale for a generalized density of states. By contrast, GFM's are systems where, due to the large ground state degeneracy established locally by the frustrating triangle unit, spectral weight is dramatically shifted to temperatures lower than θ_w . The most obvious example of this effect is in ice and ice-like magnetic models which have finite entropy at zero temperature. Such systems have Ising-type local character and the degrees of freedom are frozen – ice-like zero-point entropy is more a measure of disorder than a measure of the number of thermally accessible states. An example of such an effect is shown below in the spin-ice behavior of $\text{Dy}_2\text{Ti}_2\text{O}_7$, and we will see that the field-induced behavior in these systems can be unusual. Most of the GFM's do not fall into this category and exhibit spectral weight shift from high energy, $\sim \theta_w$, to a lower energy scale which is dictated by the type of lattice, local anisotropy, and dimensionality. These considerations suggest a strong criterion for defining geometrical frustration. *Geometrical frustration causes spectral weight downshift to energies smaller than the individual two spin interactions.*

Ordinary water ice is probably the first realization of geometrical frustration. In the 1930s a discrepancy existed between value of entropy of water measured at 298 K measured spectroscopically, 45.10 cal/mol K, and that determined by integration of the specific heat divided by temperature of ice and water from $T \sim 10$ up to 289 K, 44.28 cal/mol K [14]. Pauling explained this discrepancy by appealing to the unusual structure of ice [1]. In ice (I_h), the oxygen atoms occupy a wurzite-type structure with four hydrogen ions placed in an approximate tetrahedral coordination around each O ion. Because the O–O distance is 2.76 Å, significantly greater than twice the O–H distance, 0.96 Å it was deduced that two H ions on each tetrahedra are closer than the other. There are many different arrangements by which this can happen – Pauling suggested this leads to a residual entropy of $R \ln 3/2 = 3.4$ J/mol K = 0.81 cal/mol K, which is in good agreement with the above difference of 0.82 cal/mol K. This entropy difference represents frozen-in orientational disorder among the OH_2 molecules. which results from the intrinsic interactions of

dynamical variables the symmetry of which is incompatible with the extended symmetry of the O atoms.

Harris et al. have used the similarity of water ice and the pyrochlore structure to suggest that there might exist distinct dynamics associated in a magnetic analogue [15]. They showed that a system of Ising doublets with FM interactions occupying the magnetic sites of a pyrochlore lattice maps onto the water ice problem. This is easily shown. If we stipulate a dipole–dipole interaction between two spins with moment μ and Ising axes joining the center and vertex of a tetrahedron, then the energy if both point either in or out is $1.67\mu^2/a \equiv \varepsilon$, where a is the length of a tetrahedron edge. For one spin in and one out, the energy is $-\varepsilon$. Thus, the lowest energy for four spins on the tetrahedron is -2ε , corresponding to two spins pointing in and two pointing out. The net moment of this state is $2\mu/\sqrt{3}$. This is compared to the AF configurations of all in, or all out, which have an energy of 6ε and no moment. We see that there are six possible two-in two-out state, and, in addition, the forcing of a particular configuration on one tetrahedron is not sufficient to specify the states on neighboring tetrahedra in the pyrochlore structure, which is a result of marginal constraint [13]. By comparison, if the all-in or all-out case has a lower energy, as might occur if superexchange exceeds the dipole–dipole interaction, then specifying one tetrahedron configuration fully determines a state of long-range order. Because the FM state has a large ground state degeneracy, it is more geometrically frustrated than the AF case. If the spin is due to a large-moment rare-earth ion, then dipole–dipole energies can easily exceed the superexchange interaction as we will see below.

The pyrochlore compounds $\text{RE}_2\text{Ti}_2\text{O}_7$, where RE is a rare earth ion, is an ideal system to study these effects. Here the Ti^{4+} ion is nonmagnetic and almost all the rare-earths can be substituted on the A-site. Special attention is paid to $\text{RE} = \text{Dy}$ and Ho since these are commonly observed to have Ising-type spins and are therefore possible realizations of Harris et al.'s spin ice. The susceptibility of $\text{Dy}_2\text{Ti}_2\text{O}_7$, was measured from 1.2 to 4.2 K [16] and shows a broad peak at 1.5 K. For $\text{Dy}_2\text{Ti}_2\text{O}_7$, $\chi(T)$ was extended to lower temperatures and a peak was found at 0.7 K with an inflection point at 0.6 K and a reduction to a small percentage of the peak value below 0.5 K [17]. For $\text{Dy}_2\text{Ti}_2\text{O}_7$, Blöte et al. noted the absence of long-range order in this compound and the small size of the specific heat, $C(T)$, peak in measurements which extend only up to ~ 1.5 K [17].

The $\chi(T)$ data of Harris et al. show that $\text{RE} = \text{Ho}$ has $\theta_w = +1.9$ K, i.e. FM. Ramirez et al. report $\theta_w = +0.5$ K for $\text{RE} = \text{Dy}$. Thus, both compounds are spin-ice candidates. Neutron scattering measurements of the crystal field levels for Ho^{3+} in $\text{Ho}_2\text{Ti}_2\text{O}_7$ show the first excited state above an Ising-like ground state doublet ($^5\text{I}_8, m_j = |\pm 8\rangle$) at 21 meV [18]. This is well

above the energy scale for spin–spin interactions, as inferred from θ_w . These authors point out that since the crystal structure varies little for different RE-substitutions, the crystal field parameters obtained from the $\text{RE} = \text{Ho}$ measurement allows an accurate determination of the splittings for the other compounds. In particular, a similar magnitude of splitting is found for $\text{RE} = \text{Dy}^{3+}$ ($^6\text{H}_{15/2}, m_j = |\pm 15/2\rangle$) and for both Ho and Dy, the easy axis is along the line joining the spin with the tetrahedron center.

Harris et al. performed elastic neutron scattering and μSR on $\text{Ho}_2\text{Ti}_2\text{O}_7$ [15]. They found no evidence of a magnetic transition in μSR down to 0.05 K. The neutron measurements showed no evidence for FM order in the temperature-dependence of the nuclear Bragg peak on cooling to 0.35 K but did show a broad ridge of scattering at $Q = (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ which sharpened on cooling down to 0.35 K. On applying a field in the $(1\bar{1}0)$ direction at $T = 0.35$ K, strong FM Bragg peaks do appear at $Q = (002), (111)$ and (220) , consistent with a magnetic structure possessing the same unit cell as the crystal structure. The intensity of these peaks depended on the sample history, whether it was cooled in finite or zero field, indicating spin freezing without long-range order, a rare occurrence in magnets without structural disorder, and suggestive of a new type of state, spin ice.

Thermodynamic evidence for an ice-like state was found in $\text{Dy}_2\text{Ti}_2\text{O}_7$. Ramirez et al. extended the $C(T)$ measurements of Blöte et al. to 12 K [19]. They found that the total integrated entropy amounted to only $(67 + 0.04)\%$ of $R \ln 2$, as shown in Fig. 1. Since Pauling predicted for ice a ground state entropy of $\ln 3/2$, normalized to O, this means the recovered entropy when normalized to H , is 70.7% of $R \ln 2$, and we see good agreement between the recovered entropy in both systems, which is strong evidence that $\text{Dy}_2\text{Ti}_2\text{O}_7$ has a finite ground state entropy. This suggests a ground state where the spin motif on each tetrahedron is two-in-two-out, but where there is no periodicity to the frozen state. This result is supported by $C(T)$ in a small magnetic field of 0.5 T (Fig. 1) which shows that roughly half of the ground state entropy is recovered up to 12 K. On application of larger fields, new transitions are observed in $C(T)/T$ in the form of three sharp peaks at $T = 0.34, 0.47$ and 1.12 K as shown in Fig. 2. These peaks are unusual in two respects. First, they represent only a few percent of the total spin entropy – this is most likely due to the polycrystalline nature of the sample, as discussed below. Second, and most surprisingly, the peak positions do not depend on the magnitude of the applied field. We note that, independent of the details of possible spin-ordering models, these peaks cannot be due to longitudinal spin fluctuations – they are still observable at $H = 6$ T where the Zeeman energy for longitudinal spins is ~ 55 K, i.e. a Boltzmann factor $g\mu_B \tilde{S}H/k_B T$ of 157 for the lowest-temperature peak.

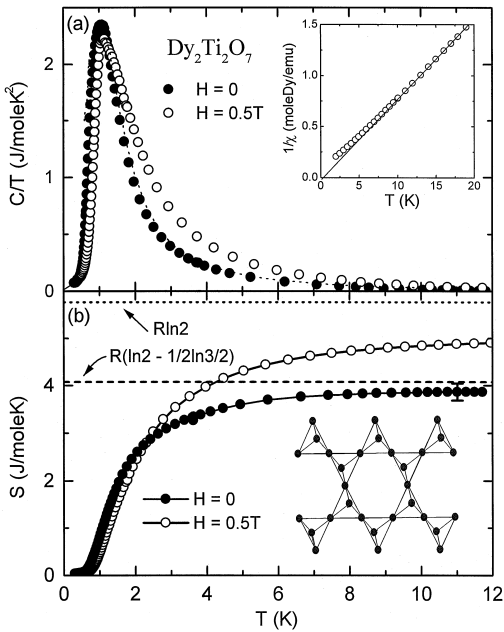


Fig. 1. (Top) Specific heat divided by temperature versus temperature, of the Ising pyrochlore $\text{Dy}_2\text{Ti}_2\text{O}_7$, for $H = 0, 0.5 \text{ T}$. The dashed line is the result of a Monte Carlo calculation in zero field. (Bottom) Entropy versus temperature for $H = 0, 0.5 \text{ T}$. The full entropy of this $S = \frac{1}{2}$ system is $R \ln 2$. The value $R(\ln 2 - 1/2 \ln 3/2)$ is the available entropy in ice predicted by Pauling. Upper inset: inverse susceptibility of $\text{Dy}_2\text{Ti}_2\text{O}_7$. Bottom inset: magnetic sites in the pyrochlore structure (reproduced from Ref. [19]).

The occurrence of sharp peaks in thermodynamic quantities in finite field when there were none in zero field is rare, and to our knowledge has been seen previously only in the frustrated magnet $\text{Gd}_3\text{Ga}_5\text{O}_{12}$ [12] and low-dimensional spin systems [20], the latter being an example of a singlet–singlet crossing. In contrast to both of these examples, the peak temperatures in $\text{Dy}_2\text{Ti}_2\text{O}_7$ are field-insensitive. This behavior is in contrast to that seen by Harris et al. in Monte Carlo simulations, where the temperature of the sharp peaks depend on the field magnitude, indicating a different type of transition than we observe in $\text{Dy}_2\text{Ti}_2\text{O}_7$ [21].

Ramirez et al. proposed that the $\text{Dy}_2\text{Ti}_2\text{O}_7$ $C(T)$ peaks are due to correlated motion among spins which do not couple to magnetic field, a situation realized for $\mathbf{H} \parallel (110)$ where half the spins have their Ising axis oriented perpendicular to \mathbf{H} . In this case, for $g\mu|\mathbf{H}| \gg k_B\theta_W$, the disorder of the ice state will be suppressed, leading to ordering on the sublattice of field-decoupled spins, which form chains. This scenario is supported by Monte Carlo calculations which show that for $\mathbf{H} \parallel (110)$, a sharp field-independent peak develops at a temperature corresponding to that of the upper peak in

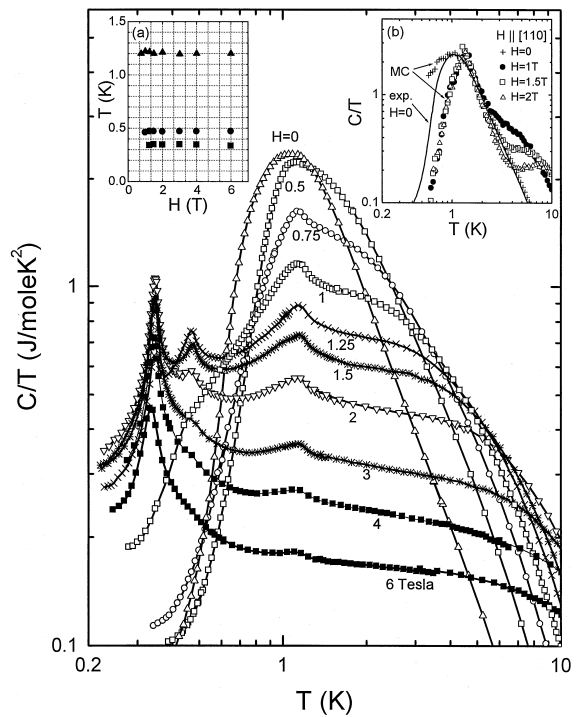


Fig. 2. Specific heat divided by temperature versus temperature, for a polycrystalline sample of the Ising pyrochlore system $\text{Dy}_2\text{Ti}_2\text{O}_7$ for several different field values. For fields above 0.5 T, sharp ordering-like features appear at 0.35, 0.47, and 1.2 K. The temperature at which these features appear does not change with field, as shown in the left inset, ruling out an origin in terms of longitudinal spins. Transverse spin ordering thus occurs as the result of the magnetic field reducing spin-ice disorder. The right inset shows Monte Carlo calculations of $C(T)/T$ for a single crystal with field applied along the (110) direction, yielding a peak similar to that seen at 1.2 K (reproduced from Ref. [19]).

the $\text{Dy}_2\text{Ti}_2\text{O}_7$ data (Fig. 2) [19]. The observed lower- T transitions are possibly long-wavelength reordering processes which are not picked up in MC simulations due to the small MC-sample size. The peak heights in the orientationally averaged powder sample of this experiment are significantly less than expected from ordering among half the spins. This suggests that there will be stringent tolerances on the sample orientation in experiments on single crystals.

As was already emphasized, ground state degeneracy and associated spectral weight down-shift is a key signature of frustrated interactions. Recently, ZrW_2O_8 has been observed to display negative thermal expansion which is large ($\alpha \equiv (\partial \ln L / \partial T)_P \cong 10^{-5} \text{ T}^{-1}$), isotropic, and constant between 50 and 420 [22]. This is remarkable behavior and is a possible structural realization of the same physics as found in GFMs.

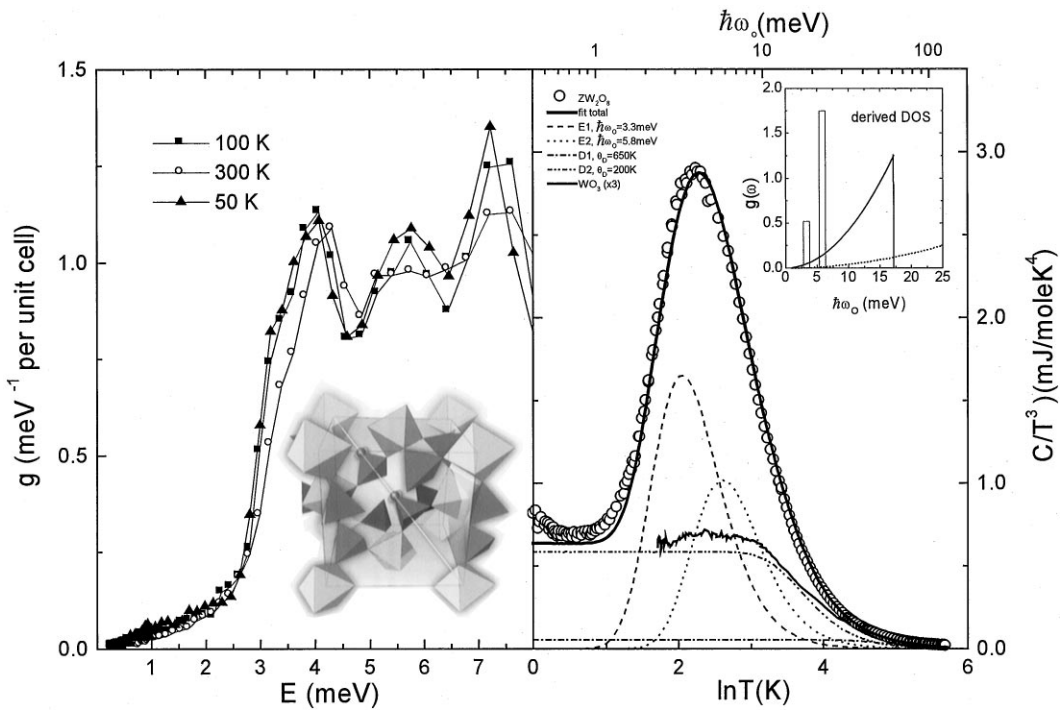


Fig. 3. Left panel: Neutron scattering density of states of ZrW_2O_8 at three different temperatures. Right panel: Specific heat divided by T^3 of ZrW_2O_8 . Lines are the result of fits to Debye terms and Einstein terms, with the optical energy and Debye energies of these terms shown. Left inset: ZrW_2O_8 unit cell, with the unshared WO_4 vertices highlighted. Right inset: The density of states extracted from the fits. (Reproduced from Refs. [26,27]).

The structure of ZrW_2O_8 , is comprised of ZrO_6 octahedra and WO_4 tetrahedra (Fig. 3). The unusual feature in this cubic material is that every WO_4 tetrahedron has one unshared vertex, as shown in the inset of Fig. 3. The Debye–Waller factors for the corresponding oxygens, O_3 and O_4 sites, are several times as large as that of the other atoms in the unit cell [23], indicating that modes incorporating these atoms will be highly anharmonic. Materials such as ZrW_2O_8 where the atoms are represented as rigid units such as octahedra and tetrahedra frequently exhibit soft mode transitions [24]. Such a transition is a common response to anharmonic motion, which suggests that ZrW_2O_8 might exhibit a soft mode transition. However, using a dynamical matrix method, Pryde et al. show that the low-energy modes of ZrW_2O_8 do not possess high symmetry features in reciprocal space [25]. Such features have been used in other rigid unit materials to predict the symmetry of soft modes. The absence of soft modes is also a statement of the inability of the system to realize a particular lower symmetry state into which it can transform to remove the anharmonicity, and in fact ZrW_2O_8 does not exhibit any structural transformations below 420 K.

The inability of ZrW_2O_8 to undergo a soft mode transformation is similar in spirit to the inability of

a GFM to order into an AF state. Following the above discussion on frustration and underconstraint, it is useful to ask whether there is a significant shift of spectral weight to low energies as a result of frustration. The dynamical matrix simulations that indicated low-symmetry modes also predicted a large density of states at low frequency [25]. Measurements of the specific heat of ZrW_2O_8 provided the first evidence of such low energy modes [26] (Fig. 3). These measurements revealed a contribution to the low-temperature $C(T)$ which is not only large, comprising ~ 6 oscillators/unit cell, but originates from a set of optical modes centered around 3–6 meV, an energy scale much lower than that observed in typical transition metal oxides. Direct measurements of the phonon density of states (Fig. 3) confirmed the $C(T)$ measurement, and showed how these low-energy states could lead to NTE [27]. It was found that the low-energy structure in the density of states could explain NTE assuming an average Gruneisen coefficient of -14 . Studies of related compounds will help determine the microscopic origin of low-energy modes in this material. Further measurements must be done to establish the origin of this low-energy scale and in particular the relevance of a GFM-like picture of frustrated soft modes.

I would like to thank my collaborators on the experimental work reviewed here, R.J. Cava, G.R. Kowach, C. Broholm, G. Ernst, B.S. Shastry, A. Hayashi, and R.D. Siddharthan.

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