Ferroics: magnetic-compass lattice and optical phonon dispersions of dipolar crystals

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(Dated: September 3, 2018)

We report a simple safe and attractive pedagogic demonstration with magnetic compasses that facilitates an intuitive understanding of the concept that ferromagnetism and ferroelectricity do not result from dipole-dipole interactions alone. Phonon dispersion relations were calculated for a 3-dimensional simple-cubic dipole crystal and a 2-dimensional square-lattice dipole crystal. The latter calculation corresponds to the compass demonstration that confirm the antiferro ground state structure. A sum rule for the three optical phonon frequencies is discussed. A mathematical non-analyticity in the longitudinal optical phonon are also illustrated.

I. INTRODUCTION

Ferromagnetism and Ferroelectricity in crystals have occupied minds of physicists and chemists for a long time. Both are phenomena that involve temperature dependent symmetry breaking. Ferromagnetic and ferroelectric states have parallel alignments of magnetic and electric dipoles, respectively, in all unit cells of the crystal. Other possible orderings, e.g. antiparallel alignments of dipoles in neighboring unit cells, correspond to antiferro states. Ferromagnetic and ferroelectric (or antiferro) states having reduced symmetries are stable only up to a Curie (or Néel) temperature, above which the crystal typically transforms to higher-symmetry paramagnetic or paraelectric states. Energetic stability of the low-temperature state reflects the resolution of competition between various interactions. Ferromagnetism originates from a delicate balance between short-range bonding and long-range dipole-dipole interactions. In magnets, dipole-dipole interactions are relatively weak, and stability is governed mostly by short-range interactions, such as direct exchange, super exchange, double exchange, etc. Dipole-dipole interactions in magnets are important, however, in the energetics of domain formation.

Dipole-dipole interactions vary as $\frac{1}{r^3}$, where $r$ is dipole-dipole separation, and they are anisotropic. It is not straightforward for students to intuitively understand the role of dipole-dipole interactions in the stability of macroscopically ordered states, and that ferromagnetic and ferroelectric states are not the results of dipole-dipole interactions between atoms or sites. Here, we introduce an attractive demonstration with magnetic compasses which facilitates an intuitive understanding (Sec. II). In Sec. III we also introduce easy analytic and computational calculations of the phonon dispersion relations of dipole crystals, which: 1) demonstrates that the dipole-dipole interactions yield an antiferro ground state; 2) yields a simple picture of LO-TO splitting; 3) reveals a mathematical non-analyticity at the Γ point in the phonon spectrum that arises from infinite range interactions in crystals (this last point is not readily appreciated from standard text book treatments). Finally, we summarize in Sec. IV.

II. MAGNETIC COMPASS DEMONSTRATION

If one puts two magnetic compasses on a desk well separated from each other, both point north as pictured in Fig. IIa). As one brings them closer together, their dipole-dipole interaction dominates and below some critical distance, the influence of geomagnetism can be neglected. The compass needles align along the line between them, like $\langle SN \rangle < SN >$. As in Fig. IIc), if one puts three, four, or more compasses in a row, one also finds that they align according to $\langle SN \rangle < SN > < SN > \cdots$. If, however, one arranges the compasses on a square lattice, they order in a stable canted antiferro structure, which have zero total dipole moment, as shown in Fig.

We demonstrated this experiment to undergraduate
students and had them do it themselves. It generated a lot of interests in them and helped them to intuitively understand that ferromagnetic and ferroelectric ground states are do not occur a result of dipole-dipole interactions alone. One author, YS, originally invented this demonstration and displayed it in the Osaka Science Museum. It attracted children as well as adults seeding interest in the origin of magnetism in crystals.

This experiment is easier to perform when one uses magnetic compasses for car windshields, such as those shown in Figs. 1 and 2. Each compass has a transparent magnetic compasses for car windshields, such as those shown in Figs. 1 and 2. Each compass has a transparent bubble-like plastic container filled with oil, a suction cup for attaching it to a windshield, and a ferrite permanent magnet arrow that floats freely in the oil. Dimensions of the ferrite magnet are 8 $\times$ 3 mm. The 8 $\times$ 3 mm arrow sides are magnetic poles with surface magnetic fields $\approx$ 50 mT, that decay to 1.5 mT at the surface of the plastic container.

![FIG. 1: (a) Two car windshield magnetic compasses on a desk, sufficiently far apart that both point north. (b) Two compasses sufficiently close together that the dipole-dipole interaction dominates. (c) Five compasses in a row.](image)

![FIG. 2: Magnetic compasses in a 4 $\times$ 4 square lattice.](image)

III. PHONON DISPERSION OF DIPOLAR CRYSTALS

A system of classical dipoles on an array of sites is equivalent to a system of paired point charges $+Z^*$ and $-Z^*$ on the same sites overlappingly, in which the charges are allowed to move oppositely and infinitesimally: the dipole moment of the displaced charges is $\mu_i = Z^*u_i$, where $u_i$ is the displacement (separation vector) of $i$th pair point charges $\pm Z^*$. Along the displacement, the pair point charges do not shift their center of mass from their original site. The dipole-dipole interaction energy depends quadratically on the dipole moments $\mu_i$ and is directly related to harmonic phonon dispersion of the system. Using the analysis of phonon spectrum, we show the stability of the antiferro structure exactly and analytically.

It should be mentioned that there is a difference in degrees of freedom between displacement $u_i$ and a magnetic compass. The number of degrees of freedom of $u_i$ is three, though that of a magnetic compass is one, i.e., its rotation. However, as shown in the analysis of phonon spectrum for a 2-dimensional square-lattice dipole crystal in Sec. III B, there is a correspondence between the structure of phonon which has the minimum energy and the ground state of compass lattice.

A. 3-dimensional simple-cubic dipole crystal

Consider a 3-dimensional simple-cubic dipole crystal with lattice constant $a_0$. Dipoles are placed on lattice points and only the dipole-dipole interactions are considered,

$$V(u_i, u_j; r_{ij}) = \frac{Z^*}{\epsilon_{\infty}} \frac{u_i \cdot u_j - 3(\hat{r}_{ij} \cdot u_i)(\hat{r}_{ij} \cdot u_j)}{r_{ij}^3},$$

where: $Z^*$ is the Born effective charge; $\epsilon_{\infty}$ is the optical dielectric constant, refractive index squared; $u_i = u(r_i)$ and $u_j = u(r_j)$ are the displacements of dipoles $i$ and $j$; $r_{ij} = r_i - r_j$ is a vector between dipoles $i$ and $j$; and a hat indicates that the vector has a unit direction, e.g. $\hat{r} = r/|r|$. The dipoles $\{u\}$ in a super cell $Q_{\text{super}} = L_xa_0 \times L_ya_0 \times L_za_0 = Na_0^3$ under periodic boundary conditions are governed by the phonon Hamiltonian:

$$H(\{p\}, \{u\}) = \sum_{i=1}^{N} \sum_{\alpha} \frac{\{p_\alpha(r_i)\}^2}{2M^*} + \frac{1}{2} \sum_{i=1}^{N} \sum_{\alpha} \sum_{j=1}^{N} \sum_{\beta} u_\alpha(r_i) \Phi_{\alpha\beta}(r_{ij}) u_\beta(r_j),$$

where $M^*$ is the mass of the dipole, $\{p_\alpha(r_i)\}$ are the canonical conjugate momenta, $\Phi_{\alpha\beta}(r_{ij})$ are the interaction matrix elements, and $\{u\}$ are the canonical coordinate degrees of freedom.
where $\alpha$ and $\beta$ are independent Cartesian directions ($x$, $y$, and $z$), the $\alpha$ component of $r$ runs:

$$r_\alpha = 0, a_0, 2a_0, \cdots (L_\alpha - 1)a_0$$  (3)

$M^*$ is the effective mass for dipoles, $p(r_j) = M^* \dot{u}(r_j)$ is the momentum for $u(r_j)$, $\Phi_{\alpha\beta}(r_{ij})$ is the force constant matrix

$$\Phi_{\alpha\beta}(r_{ij}) = \frac{Z^2}{\epsilon_\infty} \sum_n \delta_{\alpha\beta} - 3(r_i + n)\alpha(r_j + n)\beta |r_{ij} + n|^2 ,$$  (4)

$$\Phi_{\alpha\beta}(r_{ij}) = \sum_n [\delta_{\alpha\beta}B(|r_{ij} + n|) - (r_i + n)\alpha(r_j + n)\beta C_{rr}(|r_{ij} + n|)]$$

$$+ \sum_{G} \sum_k \sum_{ij} \eta(k + G_\alpha(k + G)\beta \frac{4\pi}{\Omega_{\text{super}}} \exp \left(-\frac{|k + G|^2}{4\kappa^2} \right) \cos[(k + G) \cdot r_{ij}] - \delta_{ij}\delta_{\alpha\beta} \frac{2}{3\sqrt{\pi}} \kappa^3 ,$$  (6)

where $G$ is a reciprocal lattice vector, and $k$ is a reciprocal vector in a first Brillouin zone of the unit cell such as

$$G_\alpha = \cdots, -2\frac{2\pi}{a_0}, -\frac{2\pi}{a_0}, 0, \frac{2\pi}{a_0}, \cdots ,$$  (7)

$$k_\alpha = -L_\alpha - \frac{12\pi}{2L_\alpha} a_0, \cdots, -\frac{2\pi}{a_0}, 0, \frac{2\pi}{a_0}, \cdots ,$$  (8)

while the summation is not performed for the $G = k = 0$ case, as indicated in eq. (8) by $\sum'$. The Ewald summation is performed with decay functions

$$B(r) = \frac{\text{erfc}(\kappa r)}{r^3} + \frac{2}{\sqrt{\pi}} \exp(-\kappa^2 r^2) ,$$  (9)

$$C_{rr}(r) = \frac{3\text{erfc}(\kappa r)}{r^3} + \frac{2}{\sqrt{\pi}} \kappa^2 (2\kappa + \frac{3}{r^2}) \exp(-\kappa^2 r^2) ,$$  (10)

where $\kappa$ is a reciprocal decay length which one can determine arbitrarily.

It is well known that, by substituting

$$u_\alpha(r) = \frac{1}{N} \sum_k \bar{u}_\alpha(k) \exp(i k \cdot r) ,$$  (11)

$$p_\alpha(r) = \frac{1}{N} \sum_k \bar{p}_\alpha(k) \exp(i k \cdot r) ,$$  (12)

and

$$\Phi_{\alpha\beta}(r) = \frac{1}{N} \sum_k \bar{\Phi}_{\alpha\beta}(k) \exp(i k \cdot r) ,$$  (13)

$n$ is the super-cell lattice vector:

$$n_\alpha = \cdots, -2L_\alpha a_0, -L_\alpha a_0, 0, L_\alpha a_0, 2L_\alpha a_0, \cdots ,$$  (5)

and $\sum'$ indicates that the summation does not include terms for which $r_{ij} = n = 0$. In the 3-dimensional simple-cubic lattice, direct evaluation of sum in eq. (4) is difficult, because summation of $1/r^3$ in eq. (1) converges slowly. However, it can be evaluated by using the Ewald sum technique, as (in $Z^* = \epsilon_\infty = 1$ unit).

into eq. (2), the phonon Hamiltonian can be decomposed into the Hamiltonian which is local in $k$-space,

$$H_{k,\alpha} = \frac{\tilde{\omega}_\alpha(k) \tilde{p}_\alpha(k)}{2M^*} + \frac{1}{2} \sum_\beta \tilde{\Phi}_{\alpha\beta}(k) \tilde{u}_\beta(k) ,$$  (14)

where $\tilde{u}_\alpha(k)$, $\tilde{p}_\alpha(k)$, and $\tilde{\Phi}_{\alpha\beta}(k)$ are Fourier coefficients,

$$\tilde{u}_\alpha(k) = \sum_r u_\alpha(r) \exp(-i k \cdot r) ,$$  (15)

$$\tilde{p}_\alpha(k) = \sum_r p_\alpha(r) \exp(-i k \cdot r) ,$$  (16)

and

$$\tilde{\Phi}_{\alpha\beta}(k) = \sum_r \Phi_{\alpha\beta}(r) \exp(-i k \cdot r) .$$  (17)

Here, $\tilde{\Phi}_{\alpha\beta}(k)$ is a real function, because $\Phi_{\alpha\beta}(r)$ is a real even function in the simple cubic geometry. The second term of eq. (6) is transformed as

$$\tilde{\Phi}_{\alpha\beta}(k) = \sum_G (k + G)\alpha(k + G)\beta \frac{4\pi}{a_0^3} \exp \left(-\frac{|k + G|^2}{4\kappa^2} \right) ,$$  (18)

and terms in the summation of eq. (18) converge rapidly as a function of $k + G$. Therefore, with optimal $\kappa$ and fast Fourier transformation (FFT) for the first and third terms of eq. (4), $\Phi_{\alpha\beta}(k)$ can be evaluated by summing only $n_\alpha = -L_\alpha a_0, 0$ terms in real space and a $G = 0$ term in reciprocal space. For example, if $a_0 = 3.94$ Å and $L_x = L_y = L_z = 32$, $\kappa = 0.078$ Å$^{-1}$ gives sufficient accuracy in $\tilde{\Phi}_{\alpha\beta}(k)$ for double precision computations, as illustrated in Fig. 3.
because the trace of the matrix $\Phi(k)$ in eq. (1) is zero for all $r_{ij}$ and consequently the trace of $\Phi(k)$ also equal to zero for all $k$. 

In the long wavelength limit, $k \to 0+$ (with $L_x \to \infty$ in the present super-cell calculation), $\omega_1 = \omega_2$ converge to $\sqrt{\frac{1}{3} \sum_{i=1}^{3} \frac{\omega_i^2}{\omega_0^2}}$ and $\omega_3$ to $\sqrt{\frac{2}{3} \sum_{i=1}^{3} \frac{\omega_i^2}{\omega_0^2}}$. This frequency difference is called as the LO-TO splitting which has a non-analyticity (discontinuity) in a LO-branch at the $\Gamma$ point, $k = (000)$. The LO-TO splitting is analogous to the plasma-oscillation and corresponds to the longitudinal oscillations of dielectrics which obeys an equation of motion,

$$M \frac{d^2 u_z}{dt^2} = \frac{E_d}{\epsilon_{\infty}} Z^* = - \frac{4\pi P_z}{\epsilon_{\infty}} Z^* = - \frac{4\pi Z^2}{\epsilon_{\infty} \omega_k^4} u_z \ ,$$ (20)

where $E_d = -4\pi P_z = -4\pi Z^2 u_z/\omega_k^3$ is the depolarization field that is induced by the surface charges that are caused by the polarization $P_z$, as illustrated in Fig. 5. Along the $\Delta$ axis, the point group of $k$ is $C_{4v}$. Consequently, two TO phonon frequencies, $\omega_1 = \omega_2$, are degenerate, non-degenerate $\omega_3$ has to be the singly degenerate TO phonon, and their ratio has to be $\frac{\omega_3}{\omega_1} = \sqrt{\frac{2}{3}}$ to satisfy the sum rule (19). The singly degenerate TO phonon at the M point has the structure of oppositely z-polarized rods in a checker-board arrangement on an $xy$ plane. This antiferro structure has minimum energy. At the R point, oppositely directed dipoles align in NaCl structure and its three optical phonon frequencies become zero, $\omega_1 = \omega_2 = \omega_3 = 0$, because summing eq. (1) within nth neighbors gives zero. For instance, within 6 nearest neighbors,

$$\sum_{i \in (6 \text{ nearest neighbors})} V(u_i - u; r_{0i}) = 0 \ ,$$ (21)

and also within 12 second nearest neighbors,

$$\sum_{i \in (12 \text{ second nearest neighbors})} V(u_i; r_{0i}) = 0 \ .$$ (22)

### B. 2-dimensional square-lattice dipole crystal

The 2-dimensional square-lattice dipole crystal, which has $N = L_x \times L_y$ dipoles in a flat periodic super cell, is also governed by the Hamiltonian (24) and the force constant matrix (21), but there are no dipoles for $r_z \neq 0$ and $n_z \neq 0$. In the 2-dimensional case, summation in eq. (4) can be performed in real space. Calculated potential energies of phonons $u(r_i) = u_0 \exp(ik \cdot r_i)$ having wave vectors $k$ and constant amplitudes $u_0$ are shown in Fig. 6. Eigenmodes of polarization are $u_0 = (1,0,0)$, $u_0 = (0,1,0)$, and $u_0 = (0,0,1)$ for $k$ along $\Delta$ axis and $u_0 = (1,1,0)$, $u_0 = (1,-1,0)$, and $u_0 = (0,0,1)$ for $k$ along $\Sigma$ axis. The TO phonon energy minimum is at the $X$ point. There are two $X$ points, $k = (\pi/a_x,0)$ and $k = (0,\pi/a_y)$, in the first Brillouin zone of the 2-dimensional square-lattice crystal.
Another lowest-in-energy TO phonon of the 2-dimensional square-lattice dipole crystal, as functions of wave vector $k$ are plotted, along axes $M - \Sigma - \Gamma - \Delta - X$ in the first Brillouin zone. $N = L_x \times L_y = 64 \times 64$ is used for this calculation. This dispersion corresponds to TABLE II in Ref\textsuperscript{29}.

In the 2-dimensional infinite-size system, any linear combination of the two lowest-in-energy TO phonons form a “continuously degenerate manifold of antiferro ground states”\textsuperscript{9}. In finite-size systems, however, the continuous degeneracy breaks. The linear combination can be generally expressed with two coefficients $\cos \theta$ and $\sin \theta$:

$$u(r_i) = (0, 1, 0) \cos \theta \exp[i \pi a_0(r_i)_x]$$

$$+ (-1, 0, 0) \sin \theta \exp[i \pi a_0(r_i)_y], \quad (23)$$

and, in the finite-size system, its energy becomes a function of $L_x$, $L_y$, and $\theta$. In $L_x \times L_y = 2^n \times 2^n \ (n = 1, 2, \cdots)$ system, as shown in Fig. 8, $\theta = 0$ gives the simple antiferro structure (Fig. 7(b)), $\theta = \frac{\pi}{4}$ gives the lowest-in-energy cant antiferro structure (Fig. 7(d)), and $\theta = \frac{3\pi}{4}$ the highest-in-energy structure. Therefore, the cant antiferro structure is realized in the square lattice of magnetic compasses as described in Sec. III. This is because the cant antiferro structure minimizes leak flux outside the system. On the other hand, the highest-in-energy $\theta = \frac{3\pi}{4}$ structure maximizes leak flux. It can be also seen in Fig. 8 that, as the system size gets larger and consequently the finite-size effect get smaller, energy range becomes narrower and the energy converges to the value of infinite system ($\approx -2.549$), as the system size gets larger.
IV. SUMMARY

We introduced an attractive demonstration that uses magnetic compasses to facilitate an intuitive understanding of the fact that ferromagnetic and ferroelectric orderings in crystals are not the results of dipole-dipole interactions. It is an easy and safe experiment that may be a good prologue to lectures on ferromagnets and ferroelectrics. Phonon dispersion of 3-dimensional simple-cubic and 2-dimensional square-lattice dipole crystals are calculated to determine which antiferro structure is most stable, when dipole-dipole interactions alone are considered. For the 1-dimensional chain of dipoles, the Γ-mode with polarization along the chain is lowest in energy. For the 2-dimensional square-lattice dipole crystal, the antiferro X-mode with transverse polarization is lowest in energy. For the 3-dimensional simple cubic dipole crystal, the antiferro M-mode with a checker-board-arrangement of oppositely z-polarized rods is lowest in energy. The LO-TO splitting and a sum rule for the three optical frequencies was demonstrated in a simple way. This is also a good example of application of the Ewald summation technique commonly used in simulations of periodic systems of charged particles.

Acknowledgment

We thank International Frontier Center for Advanced Materials (IFCAM) of IMR who supported UVW to visit to Sendai and authors’ collaborative study in ferroelectrics. We would like to extend our gratitude to Professor Gyo Takeda (Emeritus Professor of University of Tokyo and Tohoku University) and Professor Noboru Takigawa (Department of Physics, Tohoku University) who showed TN the demonstration with magnetic compasses invented by YS. We also extend our gratitude to Professor Takayuki Hamaguchi (Nada Junior and Senior High School) who gave suggestive photos and comments of the compass lattices to the authors.

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10 Atomic-displacive waves in crystals accompanied by polarization are called optical phonons, because they absorb lights in crystals. The longitudinal-optical (LO) phonon has its atomic-displacive amplitude parallel to its wavevector. The transverse-optical (TO) phonon has that of perpendicular to its wavevector.