Structural Order Parameter in the Pyrochlore Superconductor Cd$_2$Re$_2$O$_7$

I. A. SERGIENKO * and S. H. CURNOE

Department of Physics and Physical Oceanography, Memorial University of Newfoundland, St. John’s, NL, A1B 3X7, Canada

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It is shown that both structural phase transitions in Cd$_2$Re$_2$O$_7$, which occur at $T_{s1} = 200$ K and $T_{s2} = 120$ K, are due to an instability of the Re tetrahedral network with respect to the same doubly degenerate long-wavelength phonon mode. The primary structural order parameter transforms according to the irreducible representation $E_u$ of the point group $O_h$. We argue that the transition at $T_{s1}$ may be of second order, in accordance with experimental data. We obtain the phase diagram in the space of phenomenological parameters and propose a thermodynamic path that Cd$_2$Re$_2$O$_7$ follows upon cooling. Couplings of the itinerant electronic system and localized spin states in pyrochlores and spinels to atomic displacements are discussed.

KEYWORDS: pyrochlore, Cd$_2$Re$_2$O$_7$, structural phase transitions, order parameter

The pyrochlore structure with localized spins is a well known example of a three-dimensional geometrically frustrated system.\(^1\) Pyrochlore compounds with itinerant electrons have also recently attracted much interest due to the discovery of the first pyrochlore superconductor Cd$_2$Re$_2$O$_7$.\(^2\) Type-II superconductivity appears below $T_c=1.5$ K.\(^2-5\) In addition, Cd$_2$Re$_2$O$_7$, an ideal pyrochlore at room temperature (space group $Fd\bar{3}m$) exhibits two structural phase transitions, at $T_{s1}=200$ K and at $T_{s2}=120$ K. Both transitions are accompanied by anomalous transport properties. The electrical resistivity is weakly temperature dependent above 200 K, but shows a dramatic change in slope at $T_{s1}$, and then continues to decrease down to the onset of superconductivity.\(^2,3,6\) Hall coefficient measurements reveal that the conductivity is hole-like above $T_{s1}$ and electron-like below $T_{s1}$.\(^7\) Also, the magnetic susceptibility as a function of temperature drops below $T_{s1}$.\(^2,3,8,9\) Re nuclear quadrupole resonance experiments find no evidence of magnetic order in the low temperature phases of Cd$_2$Re$_2$O$_7$.\(^10\) The phase transition at $T_{s1}$ has been shown to be of second-order and specific heat measurements reveal a pronounced $\lambda$-type anomaly.\(^11\) Evidence of a first-order phase transition at $T_{s2}$ has been observed as a small but clear temperature hysteresis of electrical resistivity.\(^11\) The transition is also accompanied by small anomalies in the Hall coefficient and thermoelectric power but there is no change in the susceptibility.\(^7,12\)

The first x-ray diffraction study on Cd$_2$Re$_2$O$_7$ led to the conclusion that the space group symmetry for $T < T_{s1}$ is $Fd\bar{3}m$. But recent convergent-beam electron diffraction\(^13,14\) and x-ray diffraction experiments\(^15\) together with a Re NMR\(^10\) study clearly show that both inversion and three-fold symmetry is broken in both low temperature phases. Both phases are tetragonal and most probably the space group for $T_{s2} < T < T_{s1}$ (hereafter referred to as phase II) is $I4m2$, while that for $T < T_{s2}$ (phase III) is $I4_122$.\(^15\)

In this Letter we present a group theoretical analysis of phonons in pyrochlores and closely related spinels. We find that both structural phase transitions in Cd$_2$Re$_2$O$_7$ originate from an instability of the pyrochlore lattice with respect to the same long wavelength phonon mode, which is doubly degenerate in the room temperature phase (phase I). The I-II transition may be of second order despite the fact that $I4m2$ is not a maximal subgroup of $Fd\bar{3}m$. We model the phase transition sequence using Landau theory. Finally, we discuss the possibility of Jahn-Teller-like couplings of electronic band structure, as well as localized spin states in pyrochlores and spinels, to atomic displacements.

There is no multiplication of the pyrochlore primitive cell in the low temperature phases of Cd$_2$Re$_2$O$_7$,\(^15\) which implies that Brillouin zone-centered long-wavelength phonons are crucial for the phase transitions at $T_{s1}$ and $T_{s2}$. These phonons are most conveniently classified according to the irreducible representations of the point group $O_h$. Table I lists the long-wavelength phonons of the atomic displacements in pyrochlores and spinels. It is well established by x-ray studies that inversion symmetry is broken in both phases II and III.\(^6,11,15\) Therefore it follows that the structural phase transitions are due to a lattice instability with respect to odd phonon modes. Table II lists all low symmetry phases that can be described by order parameters (OP) spanning odd representations of $Fd\bar{3}m$ at the $\Gamma$ point of the Brillouin zone. We find in the following that both phases II and III are described by the $E_u$ OP, and there are no restrictions in principle for both of the I-II and I-III phase transitions to be of second order. On the other hand, the II-III phase transition can be of first order only, since there is no Table I. Brillouin zone centered phonon modes in (a) the pyrochlore Cd$_2$Re$_2$O$_7$\(^{(1)}\)O\(^{(1)}\)O\(^{(2)}\) and (b) a generic spinel compound $AB_2O_4$. The numbers in columns (a) and (b) are the number of atoms per fcc site.

|       | (a) | (b) | Modes                    |
|-------|-----|-----|-------------------------|
| 4 Re, 4 Cd | 4 B | $A_{2u} + E_u + 2F_{2u} + 2F_{1u}$ |
| 12 O(1) |     | $A_{1g} + A_{2u} + E_g + E_u + 2F_{1g} + 3F_{2g} + 3F_{1u} + 2F_{2u}$ |
| 2 O(2)  | 2 A | $F_{2g} + F_{1u}$                  |
|        | 8 O | $A_{1g} + A_{2u} + E_g + E_u + F_{1g} + 2F_{2g} + 2F_{1u} + 2F_{2u}$ |

* E-mail address: isergien@physics.mun.ca
Table II. Possible low-symmetry phases described by odd-parity OP’s at Γ point of Brillouin zone. Phases accessible from Fd3m by a single second-order phase transition are written in bold type. Plain type indicates phases, which can be accessed by a first-order phase transition or a sequence of phase transitions.

| A1u   | F4132  |
|-------|--------|
| A2u   | Fd3m   |
| E_u   | I42m, I4122, F222 |
| F1u   | I41md, R3m, Ima2, Cm, Cc, P1 |
| F2u   | I22d, R32, Ima2, C2, Cc, P1 |

group-subgroup relationship between symmetry groups of these phases.

We denote the two components of the E_u OP as (η₁, η₂) and consider the action of the Fd3m space group operations on the space spanned by η₁ and η₂ (see Fig. 1). The topology of this space coincides with the topology of the plane point group C₆ᵥ. There are two different special symmetry positions of the vector (η₁, η₂), corresponding to the distorted phases: II, (0, η₂) and III, (η₁, 0), with space groups I4m2 and I4122 respectively. Each of these two positions have five counterparts, which correspond to different domains. They are obtained by successively applying six-fold rotations in the OP space. The generic position of (η₁, η₂) corresponds to the F222 orthorhombic phase as shown in Table II.

In order to reveal the nature of the structural phase transitions, we decompose explicitly atomic displacements into irreducible representations. Fig. 2 shows two adjacent tetrahedra formed by Re atoms, as well as six oxygen atoms occupying the 48(f) Wyckoff position, which are the nearest neighbours of one of the Re atoms. We enumerate the four non-equivalent tetrahedral vertices, located at one fcc site as shown on Fig. 2. The coordinates in the ideal pyrochlore structure are (1/8, 1/8, 1/8), (1/8, −1/8, −1/8), (−1/8, 1/8, −1/8) and (−1/8, −1/8, 1/8) for Re atoms m = 1, 2, 3 and 4 respectively. The components of the displacement of the mth Re atom from its ideal position are denoted (xₘ, yₘ, zₘ). Then

\[ \eta_1 = (X - Y) / \sqrt{2}, \]
\[ \eta_2 = (X + Y - 2Z) / \sqrt{6}, \]

where \( X = (x_1 + x_2 - x_3 - x_4) / 2, Y = (y_1 - y_2 + y_3 - y_4) / 2 \) and \( Z = (z_1 - z_2 - z_3 + z_4) / 2 \).

To obtain the complete picture of atomic displacements in the ordered phases we also keep track of secondary OP’s, which are not critical but nevertheless become finite in the distorted phases due to coupling to the primary OP. In order to determine the representations corresponding to the secondary OP’s, we consider the second and third symmetric powers of the primary representation \( [E_u \otimes E_u] = A_{1g} \oplus E_g \) and \( [E_u \otimes E_u \otimes E_u] = A_{1u} \oplus A_{2u} \oplus E_u \) and find that \( A_{2u} \) and \( E_u \) phonons (listed in Table I) correspond to secondary OP’s (the breathing mode A₁g has been omitted). Of them, only \( A_{2u} \) involves Re atomic displacements. We denote the \( A_{2u} \) normal coordinate as \( \phi \) and obtain

\[ \phi = (X + Y + Z) / \sqrt{3}. \]

This mode couples to the the primary order parameter through the invariant combination \( (\eta_2^3 - 3\eta_1^2\eta_2)\phi \). Thus, in the first approximation, in phase II, \( \phi \) is proportional to \( \eta_2^3 \), and in phase III \( \phi \) is exactly zero. We have also found the normal coordinates for the other Re modes listed in Table I, which vanish exactly according to the symmetry of phases II and III. The inverse transformation yields:

\[ x_1 = x_2 = -x_3 = -x_4 = (\sqrt{3}\eta_1 + \eta_2 + \sqrt{2}\phi) / \sqrt{24} \]
\[ y_1 = -y_2 = y_3 = -y_4 = (-\sqrt{3}\eta_1 + \eta_2 + \sqrt{2}\phi) / \sqrt{24} \]
\[ -z_1 = z_2 = z_3 = -z_4 = (2\eta_2 - \sqrt{2}\phi) / \sqrt{24}. \]

It is worthwhile to note here the major difference between the tetrahedral network and a single tetrahedral molecule. In the latter, the normal coordinate (2) corresponds to the A₁ breathing mode and, unlike in crystals, may be omitted in most cases.

Thus we find that in phase II, \( x_1 = x_2 \approx -z_1 / 2 \) and in phase III, \( x_1 = -y_1 \) and \( z_1 = 0 \). The directions of the displacements are shown in Fig. 2. They are in complete accordance with the results of x-ray diffraction studies. In particular, in phase II, the two adjacent tetrahedra have different volumes, \( \Delta v = \sqrt{3}/8 \eta_2^3 \), and there are four different Re-Re bond lengths, \( \Delta l_{12} / l \approx (\pm \sqrt{2}/3 \eta_2 + 3\eta_2^3) \) and \( \Delta l_{34} / l \approx \pm 8/3 \eta_2^3 \). In phase III the volumes of the tetrahedra are the same and there are three different Re-Re bond lengths, \( \Delta l_{12} / l \approx (\pm \sqrt{2}/3 \eta_2 + \eta_2^3) \) and \( \Delta l_{34} / l \approx 4\eta_2^3 \).

The Cd atoms in Cd₂Re₂O₇ form a similar tetrahedral network shifted with respect to the Re network by a (1/2, 1/2, 1/2) translation. Thus the directions of the Cd atomic displacements in the distorted phases are exactly the same as those for Re atoms, although their absolute
values differ in general.

Similar considerations for the 12 oxygen O(1) atoms located at one fcc site yield

\[
\begin{align*}
x'_1 &= -x'_{10} = (\sqrt{3}\eta'_1 - \eta'_2 + \sqrt{2}\phi' + \xi'_1 + \sqrt{3}\zeta'_2)/\sqrt{24} \\
x'_4 &= -x'_{7} = (\sqrt{3}\eta'_1 - \eta'_2 + \sqrt{2}\phi' - \xi'_1 - \sqrt{3}\zeta'_2)/\sqrt{24} \\
y'_2 &= -y'_{11} = (-\sqrt{3}\eta'_1 + \eta'_2 - \sqrt{2}\phi' - \xi'_1 - \sqrt{3}\zeta'_2)/\sqrt{24} \\
y'_5 &= -y'_{8} = (-\sqrt{3}\eta'_1 - \eta'_2 + \sqrt{2}\phi' - \xi'_1 + \sqrt{3}\zeta'_2)/\sqrt{24} \\
z'_3 &= -z'_{12} = (2\eta'_2 + \sqrt{2}\phi' - 2\xi'_1)/\sqrt{24} \\
z'_6 &= -z'_{9} = (2\eta'_2 - \sqrt{2}\phi' + 2\xi'_1)/\sqrt{24},
\end{align*}
\]

while all of the other components of the displacements vanish. Fig. 2 shows six of the twelve oxygen atoms with their displacements in phases II and III. The undistorted coordinates of atom 1 are \((v, 0, 0)\), where the oxygen structural parameter is \(v \approx 0.192\). The coordinates of the \(n\)th atom \(n > 6\) are obtained by adding a \(1/4, 1/4, 1/4\) translation to the coordinates of atom \(n-6\). By analogy with the normal coordinates of the Re atoms, we denote the \(E_u\) and \(A_{2u}\) modes by \((\eta'_1, \eta'_2)\) and \(\phi'\) respectively. We also introduce normal coordinates for \(E_g\) \((\xi'_1, \xi'_2)\) since this mode is present in O(1) displacements (see Table I), which is a secondary OP, coupled to the primary OP as \((\eta'_1^2 - \eta'_2^2)\xi'_1 - 2\eta'_1\eta'_2\xi'_2\). It follows that \(\xi'_2 = 0\) and \(\xi'_1 \neq 0\) in both phases II and III.

A Landau-type model with \(C_{6\alpha}\) topology was first studied by Lifshitz, \(^8\) who considered a sixth-order expansion of the thermodynamic potential. Details of calculations and general formalism can be found in. \(^9, 20\)

Here we briefly summarise the results and apply them to CdoReO\(_2\). Only even-order polynomial invariants can be constructed from the OP components \(\eta_1\) and \(\eta_2\). There is only one isotropic fourth-order term \((\eta_1^2 + \eta_2^2)^2\), which does not lift degeneracy of ordered states. The first anisotropic term appears in sixth order, \((\eta_1^4 - 3\eta_1\eta_2^2)^2\), but as is easily seen from the following, the sixth-order model still fails to lift degeneracy between ordered phases along the line of the II–III phase transition. Hence we consider the eighth-order Landau expansion

\[
F = a_1(\eta_1^2 + \eta_2^2) + a_2(\eta_1^4 + \eta_2^4) + a_3(\eta_1^2 + \eta_2^2)^3 + b_1(\eta_1^4 - 3\eta_1\eta_2^2)^2 + a_4(\eta_1^2 + \eta_2^2)^4 + c(\eta_1^2 + \eta_2^2)(\eta_1^4 - 3\eta_1\eta_2^2)^2.
\]

Using standard minimization procedure, one finds that when \(a_1 = 0\) a second-order phase transition from phase I occurs to either phase II or III, depending on the sign of \(b_1\). In Fig. 3 we plot phase diagrams in the \(a_1b_1\) plane, obtained for \(a_2 > 0, a_3 > 0, a_4 > 0\) and different signs of \(c\). Overall stability of the potential (5) requires that \(a_1 + c > 0\). Contour plots of the potential as a function of \(\eta_1\) and \(\eta_2\) in phases II and III are shown in Fig. 3(c) and 3(d). One can clearly see for both phases six minima corresponding to six tetragonal domains.

The potential minima for phase II exist up to the line

\[
a_1 = 2a_2b_1/c - 3a_3((b_1/c)^2 + 4a_4(b_1/c)^3), \tag{6}
\]

and for phase III

\[
a_1 = 2a_2b_1/c - 3a_3((b_1/c)^2 + (4a_4 + c/2)(b_1/c)^3). \tag{7}
\]

Equating potentials of phases II and III, we obtain the line of the first-order II–III phase transition,

\[
a_1 = 2a_2b_1/c - 3a_3((b_1/c)^2 + (4a_4 + c/2)(b_1/c)^3). \tag{8}
\]

Fitting data about the I–II phase transition line from high pressure resistivity experiments\(^3\) to \(a_1 = 0\), we obtain \(a_1 = \alpha[T - 200 K + P - 40 K/GPa]\), where \(P\) stands for pressure and \(\alpha\) is an undetermined parameter. There is not enough data to determine unambiguously where the II–III transition line is located in the \(P-T\) phase diagram. However, we can speculate that the system follows, on cooling, the path indicated by the arrow in Fig. 3(b). It follows from Eqs. (6) and (7) that the width of the area where two phases II and III coexist is of third order of magnitude in distance from the triple point \(a_1 = b_1 = 0\), which is consistent with the smallness of temperature hysteresis observed in resistivity measurements.\(^11\)

In an applied magnetic field \(\mathbf{H}\) additional terms appear in the thermodynamic potential, resulting from magnetization energy and coupling between the magnetization \(\mathbf{M}\) and the structural OP

\[
\Delta F_M = \gamma(\eta_1^2 + \eta_2^2)\mathbf{M}^2 + \alpha \mathbf{M}^2 - \mathbf{M} \cdot \mathbf{H}, \tag{9}
\]
where we neglect higher-order terms of magnetic anisotropy. Then the magnetic susceptibility is

$$\chi^{-1} = \chi_0^{-1} + 2\gamma(n_1^2 + n_2^2),$$

(10)

where $\chi_0 = (2A)^{-1}$ is the susceptibility of the high-symmetry phase. Assuming $\gamma > 0$, this expression accounts for the susceptibility decrease observed in phases II and III.

Thus we have obtained the full description of atomic displacements occurring in Cd$_2$Re$_2$O$_7$ at the structural phase transitions at $T_{c1}$ and $T_{c2}$. The phenomenological treatment presented in this Letter is in complete agreement with experimental data available to date. On the other hand, a detailed account of the intriguing transitions, point to the importance of coupling of itinerant spin systems in pyrochlores and spinels. Yamashita and Ueda$^{27}$ considered a single tetrahedron of spin-1 atoms and found that the degeneracy of spin states can be lifted by a Jahn-Teller mechanism. It was possible due to presence in the Hamiltonian terms of type $(\partial J/\partial Q_{\alpha})Q_{\alpha} (s_is_j)_\alpha$, where $J$ is the direct exchange coupling between two tetrahedral vertices, $Q_{\alpha}$ is a linear combination of atomic displacements, corresponding to normal modes, and $(s_is_j)_\alpha$ stands for a symmetry adopted bilinear combination of spin-1/2 operators located at $i$ and $j$ vertices. Our analysis of phonon modes in the lattice of corner-shared tetrahedra shows that sum of two such terms for two adjacent tetrahedra vanishes since every vertex is a center of inversion $I$. This is because vertex located spins transform to equivalent spins under inversion: $I s_i = s_i, i = 1, \ldots, 4$ and thus their combinations are of even parity, while phonon modes of vertex atoms are odd under inversion.

On the other hand, there are still three possibilities for frustration removing due to spin-displacement coupling: (i) Unlike tetrahedra-corner atoms, oxygen O(1) displacements contain even phonon modes of $E_g$ and $F_{1g}$ symmetry ($A_{1g}$ is trivial breathing mode). We denote the normal coordinate corresponding to one of these modes by $Q_1$. Then the following coupling is possible: $(\partial J_1/\partial Q_1)Q_1 (s_is_j)$, where $J_1$ is the superexchange coupling via nearest-neighbouring oxygen atoms. (ii) The structural displacements or the spins are spatially modulated (non-zero wave vector), so that translations of the fcc lattice are not preserved. (iii) Spin states couple to quadratic a form of the tetrahedral displacements and play the role of secondary order parameters $(\partial^2 J/\partial Q_{m}Q_{n})Q_{m}Q_{n}(s_is_j)$. In this case, spin ordering may be driven by structural distortions but the mechanism cannot be classified as Jahn-Teller.

In summary, we have shown that the structural phase transitions in Cd$_2$Re$_2$O$_7$ at 200 K and 120 K can both be described by a single, two-component OP, which is the displacements of Re atoms transforming according to the representation $E_u$ of the point group $O_h$. We have also considered all secondary OP’s, which can couple to the primary OP. A Landau model with terms up to eighth order in the displacements is proposed in order to account for both phase transitions and the resulting phenomenology is in good agreement with experiments.

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