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Crystal structure of the inversion-breaking metal $\text{Cd}_2\text{Re}_2\text{O}_7$

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Second harmonic generation (SHG) on the pyrochlore metal $\text{Cd}_2\text{Re}_2\text{O}_7$ indicates the presence of three order parameters setting in below an inversion breaking transition. Here, we explore a possible structural explanation and relate it not only to the SHG data, but also to neutron and x-ray diffraction, where we find that such a structural scenario can explain certain reflection extinctions observed in single crystal x-ray data. From this analysis, we suggest future experiments that could be done to resolve this matter. Finally, we comment on the Landau-violating nature of the inversion breaking transition and its relation to similar phenomena observed in improper ferroelectrics.

Although most pyrochlore oxides are insulating, $\text{Cd}_2\text{Re}_2\text{O}_7$ is a notable exception. It is a good metal and exhibits three phase transitions, one near 200 K (T_{s1}), another near 120 K (T_{s2}), and finally a low temperature superconducting transition (T_c) [1]. Structural data support the presence of inversion breaking at T_{s1} from a high temperature cubic phase ($\text{Fd}\bar{3}\text{m}$) to a tetragonal phase ($\text{I}\bar{4}\text{m}2$), whereas T_{s2} is claimed to be a weakly first-order transition to $\text{I}4_122$ [2]. There are several issues, though. First, x-ray [3] and neutron [4] data indicate very different atom displacements, these measurements being hampered by the fact that the structural distortion is weak. Second, single crystal x-ray diffraction [5] find reflection extinction conditions that are not consistent with $\text{I}\bar{4}\text{m}2$. Finally, second harmonic generation (SHG) data [6] are consistent with $\text{I}\bar{4}\text{m}2$, but are not consistent with its conversion to $\text{I}4_122$ below T_{s2} .

Subsequently, Liang Fu suggested the possibility that a novel spin nematic phase might set in below T_{s1} [7], motivated by the fact that large changes occur in the resistivity and susceptibility at T_{s1} despite the weak nature of the structural distortions. This in turn motivated new SHG experiments [8] that supported this picture, in that they found that the previously observed SHG signal was secondary in nature in regards to its temperature dependence (that is, it varied as $T_{s1} - T$). They found a new (but much smaller) signal that had a primary order parameter dependence ($\sqrt{T_{s1} - T}$). From the azimuthal and polarization dependence of the SHG signal, the secondary one (as before) was identified as having E_u symmetry relative to the high temperature cubic phase (consistent with $\text{I}\bar{4}\text{m}2$), but the primary one was identified as having T_{2u} symmetry. Given the known temperature dependences of the two SHG signals, this implies the presence of a third-order term in the Landau free energy. Since a product of three odd parity order parameters is not allowed, this indicates the presence of a third order parameter of even parity that also has a primary temperature dependence, identified as T_{1g} . These two primary order parameters were speculated to be associated with spin nematic order, with the secondary order parameter being a weak structural effect driven by the primary or-

der. The three together define a trilinear term in the Landau free energy.

In previous work [9], we did a detailed analysis of possible symmetries associated with the SHG data. We verified the structural origin of the secondary order parameter, finding that its SHG signature can be expressed in terms of an axial toroidal quadrupole (identified as well in later work [10]). We briefly mentioned a possible structural scenario for all three order parameters before turning to a possible magnetic one for the primary order parameters based on the known magnetic order observed in the closely related pyrochlore $\text{Cd}_2\text{Os}_2\text{O}_7$ [11]. But to date, there is no evidence from neutrons, Raman, nuclear magnetic resonance, or nuclear quadrupole resonance for either magnetic dipolar or spin nematic order.

All of the above motivates the present work, which instead studies the possibility of a structural origin for the primary order parameters. In that context, we note the possible relation to $\text{Cd}_2\text{Nb}_2\text{O}_7$, whose primary structural order parameter also has T_{2u} symmetry [12]. We then relate this to previous x-ray and neutron diffraction experiments, and suggest future experiments that could resolve this matter. Finally, we comment on the fact that condensing two primary order parameters at a second-order phase transition is a strong violation of the Landau theory of phase transitions, and connect this to equally puzzling data for improper ferroelectrics [13].

A possible structural scenario can be obtained by looking at all possible group-subgroup relations. From the Bilbao crystallographic server [14], the most likely structural scenario is $\text{I}\bar{4}$ as we mentioned before [9] (Fig. 1). The three space groups that feed into this are $\text{I}\bar{4}\text{m}2$ (E_u), $\text{I}\bar{4}2\text{d}$ (T_{2u}) and $\text{I}4_1/\text{a}$ (T_{1g}). The product of these three define a trilinear term in the Landau free energy as in Ref. 8 and summarized in Table I. By analyzing the atom displacements relative to the cubic phase consistent with these space groups [15], one can easily verify that $\text{I}\bar{4}2\text{d}$ (T_{2u}) gives rise to an xy axial toroidal quadrupole, and $\text{I}4_1/\text{a}$ (T_{1g}) to the z component of an axial toroidal dipole, with $\text{I}\bar{4}\text{m}2$ (E_u) giving rise to an $x^2 - y^2$ axial toroidal quadrupole. As a reminder, the antisymmetric combination of r (cubic atom positions relative to the in-

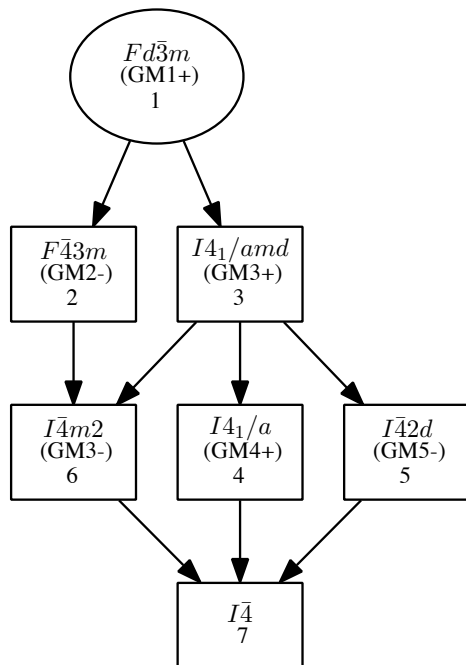


FIG. 1. Group-subgroup relations leading from $Fd\bar{3}m$ to $I\bar{4}$ [14]. Here, the cubic group representations are A_{1g} (Γ_1^+ , GM1+), E_g (Γ_3^+ , GM3+), T_{1g} (Γ_4^+ , GM4+), A_{2u} (Γ_2^- , GM2-), E_u (Γ_3^- , GM3-), and T_{2u} (Γ_5^- , GM5-).

TABLE I. The three order parameters (two primary, one secondary) that define the trilinear term in the Landau free energy in the two structural scenarios (with the space groups associated with them in parentheses). Note the order parameters for the first scenario have the same symmetries as those defined in the electronic scenario proposed by Harter *et al.* [8].

space group	primary-odd	primary-even	secondary-odd
$I\bar{4}$	T_{2u} ($I\bar{4}2d$)	T_{1g} ($I4_1/a$)	E_u ($I\bar{4}m2$)
F222	E_u ($I4_122$)	E_g (Fddd)	E_u ($I\bar{4}m2$)

version origin) and d (their displacements from r in the distorted phase) is the axial toroidal dipole ($g \equiv r \times d$, a polar vortex which preserves inversion). The symmetric combination of g and r form a pseudoscalar ($r \cdot g$) and five quadrupolar components (i.e., a pseudodeviator), all of which break inversion.

This brings us to the one single crystal x-ray diffraction study [5]. In the cubic phase, one has Bragg peaks at $(H,0,0)$, with $H=4n$ and $(0,0,L)$ with $L=4n$. In the tetragonal phase, new Bragg peaks appear at $H=4n+2$. But whether new Bragg peaks appear for $(0,0,L)$ at $L=4n+2$ depends on the space group. For $I\bar{4}m2$, they are allowed. But for $I\bar{4}2d$ and $I4_1/a$, they are not allowed. Indeed, Ref. 5 find no evidence for these new $(0,0,L)$ Bragg peaks, giving support to a picture where $I\bar{4}2d$ and $I4_1/a$ are primary and $I\bar{4}m2$ secondary.

To gain more insight, we turn to a discussion of the

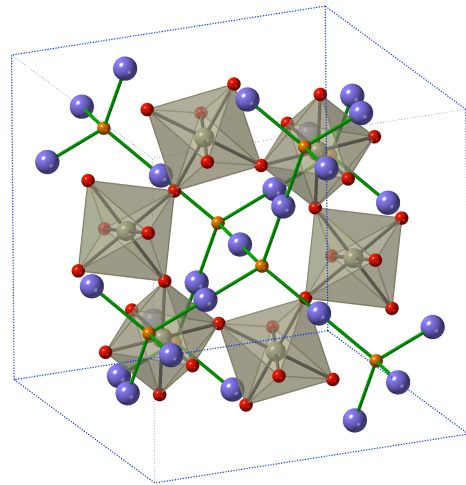


FIG. 2. Crystal structure of $Cd_2Re_2O_7$. Here, Re ions are in gray, Cd ions in purple, O(1) ions in red, and O(2) ions in orange. The crystal structure consists of corner sharing ReO_6 octahedra (the Re ions forming a pyrochlore lattice), interpenetrated by Cd_2O chains.

crystal structure of $Cd_2Re_2O_7$ (Fig. 2). It is composed of ReO_6 octahedra (the Re ligands are O(1) ions) and Cd_2O chains (these are O(2) ions). O(1) ions are displaced by all three of the above mentioned distortions, Re and Cd ions by only T_{2u} and E_u distortions, and O(2) ions not at all. Therefore, primary versus secondary could be associated with particular atom types. In that context, in most pyrochlores related to $Cd_2Re_2O_7$, the primary distortion is associated with the chains. This is clear in diffuse scattering studies of $Cd_2Nb_2O_7$ [16]. Interestingly, in $Pb_2Ir_2O_7$, it is known that the primary distortion is in the Pb_2O chains, but that the SHG arises from coupling of these distorted chains to the IrO_6 octahedra [17]. This can be understood from the fact that for the laser energy used, one is accessing excitations of the Ir d levels (similar considerations apply to the SHG data for $Cd_2Re_2O_7$, where one is probing excitations involving the Re d levels).

This can be looked into in more detail by analyzing the two studies, one x-ray [3] and one neutron [4], that attempted to determine atom displacements (a challenge given the weak nature of the distortions). To do so, we analyze these using AMPLIMODES [18]. The results are presented in Table II. In both cases, the atom displacements assumed by these authors was $I\bar{4}m2$. This leads to a primary mode of E_u symmetry, and secondary modes with symmetries E_g and A_{2u} . From Table II, one observes that both the mode amplitudes, and the individual atom type displacements, are significantly different for the two refinements. From x-rays, the ratio of the A_{2u} to E_u amplitudes is 57%, whereas it is only 21% for the neutrons. Moreover, the x-rays indicate a significant displacement of the Re ions that is not observed by neutrons.

TABLE II. Mode amplitudes (in \AA) and the relative weight by atom type [18] for $\text{Cd}_2\text{Re}_2\text{O}_7$ based on x-ray diffraction at 160 K [3] and neutron diffraction at 13 K [4], relative to the high temperature cubic phase, assuming an $\bar{I}4m2$ space group. For A_{1g} and E_g , only the O(1) ions displace, with mode amplitudes of 0.0230 and 0.0326 \AA from the x-rays, and 0.0171 and 0.0584 \AA from the neutrons. The O(2) ions do not displace relative to their cubic positions.

type	mode	Re	Cd	O(1)	total
x-ray	A_{2u}	0.060	0.341	0.599	0.0404
x-ray	E_u	0.097	0.043	0.860	0.1882
neutron	A_{2u}	0.002	0.132	0.866	0.1948
neutron	E_u	0.000	0.363	0.637	0.3410

This suggests a serious need to do a more careful study of the atom displacements, preferably supplemented by diffuse scattering studies. A challenge is the multi-domain nature of the samples, where the c -axis of the tetragonal phase can point in each of the three cubic directions. The domain structure is known to be rich, and also qualitatively changes across the lower (T_{s2}) transition [19]. Now, density functional theory studies have been done [20], but these have focused primarily on the O(1) ion displacements. It was found that E_u was unstable and T_{1u} not, but no other modes were commented on. We note that Raman data have claimed that the transition at T_{s2} is being driven by Cd ordering [21].

This brings up the question whether other structural scenarios are possible. The only other one that could be found is one with an F222 space group, noting that a general combination of $\bar{I}4m2$ and $I4_122$ forms this space group. On the other hand, a general F222 solution is not allowed [22] unless one couples E_u to other representations. The resulting group-subgroup relation is significantly more complex (Fig. 3). In this case, the three order parameters defining the trilinear term in the Landau free energy differ from the $\bar{I}4$ scenario as summarized in Table I. The primary order parameters are the second component of E_u (i.e., $I4_122$) and the second component of E_g (the first is from $I4_1/amd$ which also feeds into $\bar{I}4$, the second arises from Fddd), with again the first component of E_u being the secondary order parameter from $\bar{I}4m2$ (as before). $E_u(2)$ has the right angular symmetry to describe the primary order parameter seen by SHG [8]. And it also does not exhibit extra (00L) Bragg peaks, consistent with Ref. 5. As for $E_g(2)$, note that it is a secondary mode in the $\bar{I}4m2$ scenario [22] as shown in Table II. In general, available diffraction data indicates a body centered tetragonal space group which F222 is not. Moreover, a transition to F222 should be first-order in nature [22]. Altogether, we find this F222 scenario to be less likely than the $\bar{I}4$ one. Recently, though, Raman data have found evidence for a transition to F222 below 80 K [23].

In both structural scenarios, though, there are issues. The most obvious one is why the primary order parameters are structural in nature despite the small atom displacements, which is related to why the SHG signal is dominated by the secondary order parameter (which most likely is structural in origin). This is less of an issue in ‘electronic’ scenarios where the primary order parameters have a non-structural origin [7–9]. On the other hand, the SHG signal will be dominated by the Re d electrons, so the real issue is how the structural distortions couple to them. Without a microscopic model, this is not an easy question to address.

The more serious issue, though, applies to all scenarios for $\text{Cd}_2\text{Re}_2\text{O}_7$. In the electronic scenarios advocated by Fu [7], Harter *et al.* [8], and Di Matteo and Norman [9], and in both structural scenarios described here, the relevant term in the Landau free energy expansion is a trilinear one involving three order parameters (two primary, one secondary), each from a different group representation. It is hard to understand how two primary order parameters from different group representations can not only simultaneously condense, but in a second-order fashion as experimentally observed, since this violates the Landau theory of phase transitions. A similar issue is found in improper ferroelectrics which have a very similar trilinear term [13]. Although there has been significant theory work on the latter [24], the question raised above is still unresolved for these materials as well. Therefore, a solution to this problem could not only tell us much about $\text{Cd}_2\text{Re}_2\text{O}_7$, but about other materials where trilinear terms in the Landau free energy expansion also play a fundamental role [25]. Finally, resolving the nature of the phase transition at T_{s1} could potentially help us understand the origin of superconductivity in $\text{Cd}_2\text{Re}_2\text{O}_7$.

In conclusion, the relative merits of a structural scenario for the SHG data of $\text{Cd}_2\text{Re}_2\text{O}_7$ have been presented. From this, it is clear that single crystal studies of the structure are needed to determine what its actual space group is, and also the displacements of the various ions from their cubic positions in order to ascertain their potential impact on the nature of the SHG signal (x-rays being more sensitive to the heavier Cd and Re ions, and neutrons requiring isotopically enriched Cd to mitigate absorption). This could be aided by forcing the sample into a single domain by application of a magnetic field, given the anisotropy seen in the magnetic susceptibility below T_{s1} [19].

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[1] For a recent review, see Z. Hiroi, J.-i. Yamaura, T. C. Kobayashi, Y. Matsubayashi and D. Hirai, Phys. Soc.

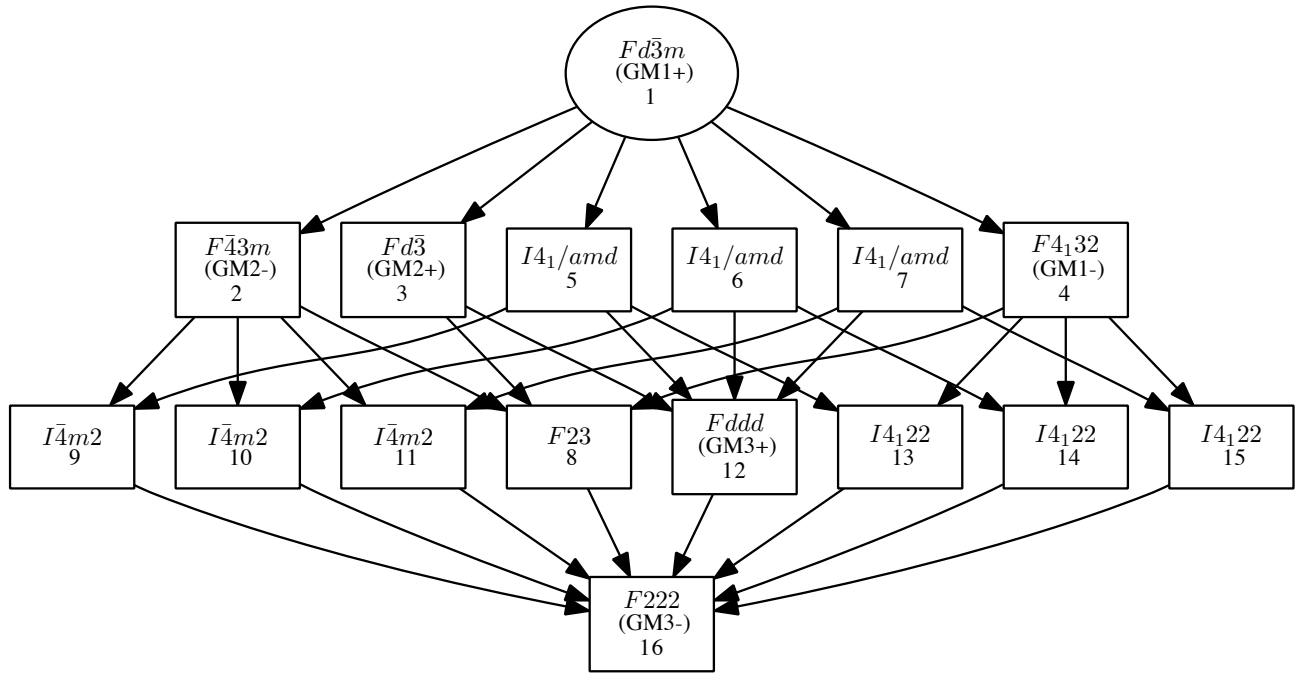


FIG. 3. Group-subgroup relations leading from $Fd\bar{3}m$ to $F222$ [14]. Here, the additional cubic group representations not listed in the Fig. 1 caption are A_{2g} (Γ_2^+ , GM2+) and A_{1u} (Γ_1^- , GM1-).

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