The 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. 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 \( (\text{Fd}3\text{m}) \) to a tetragonal phase \( (\text{I}4\text{m}2) \), whereas \( T_{s2} \) is claimed to be a weakly first order transition to \( \text{I}4\text{I}2\text{2} \) \(^2\). 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 \( \text{I}4\text{m}2 \).

All of the above motivates the present work, which 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 \( T_{s2} \) 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 the fact that condensing three order parameters at a second order phase transition is a strong violation of Landau theory, and connect this to equally puzzling data on improper ferroelectrics \(^13\).

A possible structural scenario can be obtained by looking at all possible group/subgroup relations. From the Bilbao crystallographic server \(^13\), the most likely structural scenario is \( \text{I}4 \) as we mentioned before \(^9\) (Fig. 1). The three space groups that feed into this are \( \text{I}4\text{m}2 \) \( (E_a) \), \( \text{I}4\text{d} \text{I}(T_{2u}) \) and \( \text{I}4\text{I}\text{a}(T_{1g}) \). By analyzing the atom displacements relative to the cubic phase consistent with these space groups \(^15\), one can easily verify that \( \text{I}4\text{d} \text{I}(T_{2u}) \) gives rise to an \( xy \) axial toroidal quadrupole, and \( \text{I}4\text{I}\text{a}(T_{1g}) \) to the \( z \) component of an axial toroidal dipole.

As a reminder, the antisymmetric combination of \( r \) (cubic atom positions relative to the inversion origin) and \( d \) (their displacements from \( r \) in the distorted phase) is the axial toroidal dipole \( (g \equiv r \cdot d, \text{a polar vortex which preserves inversion}) \). 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 \(^3\). In the cubic phase, one has Bragg peaks at \((\text{H},0,0)\), with \( \text{H}=4\text{n} \) and \((0,0,\text{L})\) with \( \text{L}=4\text{n} \). In the tetragonal phase, new Bragg peaks appear at \( \text{H}=4\text{n}+2 \). But
whether new Bragg peaks appear for (0,0,L) at L=4n+2 depends on the space group. For I4m2, they are allowed. But for I42d and I41a, they are not allowed. Indeed, Ref. 5 find no evidence for these new (0,0,L) Bragg peaks, giving support to a picture where I42d and I41a are primary and I4m2 secondary.

To gain more insight, we turn to a discussion of the crystal structure of Cd2Re2O7 (Fig. 2). It is composed of ReO6 octahedra (the Re ligands are O(1) ions) and Cd2O 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\textsubscript{2u} and E\textsubscript{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 Cd2Re2O7, the primary distortion is associated with the chains. This is clear in diffuse scattering studies of Cd2Re2O7 [10]. Interestingly, in Pb2Ir2O7, it is known that the primary distortion is in the Pb2O chains, but that the SHG arises from coupling of these distorted chains to the IrO6 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 on Cd2Re2O7, 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 I. In both cases, the atom displacements assumed by these authors was I4m2. This leads to a primary mode of E\textsubscript{u} symmetry, and secondary modes with symmetries E\textsubscript{g} and A\textsubscript{2u}. From Table 1, 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\textsubscript{2u} to E\textsubscript{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. 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\textsubscript{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\textsubscript{u} was unstable and T\textsubscript{1u} not, but no other modes were commented on. We note that Raman data have claimed that the transition at T\textsubscript{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 I4m2 and I41a2 forms this space group. On the other hand, a general F222 solution is not allowed [22] unless one couples E\textsubscript{u} to other representations. The resulting group/subgroup relation is significantly more complex (Fig. 3). In this case, the three or-
FIG. 3. Group/subgroup relations leading from Fd3m to F222 [14]. Here, the additional cubic group representations not listed in the Fig. 1 caption are A2g (GM2+) and A1u (GM1-).

TABLE I. Mode amplitudes (in Å) and the relative weight by atom type [18] for Cd2Re2O7 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 I4m2 space group. For A1g and Eg, only the O(1) ions displace, with mode amplitudes of 0.0230 and 0.0326 Å from the x-rays, and 0.0171 and 0.0584 Å from the neutrons. The O(2) ions do not displace relative to their cubic positions.

| type     | mode | Re  | Cd  | O(1) | total |
|----------|------|-----|-----|------|-------|
| x-ray    | A2g  | 0.060 | 0.341 | 0.599 | 0.0404 |
| x-ray    | Eg   | 0.097 | 0.043 | 0.860 | 0.1882 |
| neutron  | A2g  | 0.002 | 0.132 | 0.866 | 0.1948 |
| neutron  | Eg   | 0.000 | 0.363 | 0.637 | 0.3410 |

Order parameters differ from the I4 scenario. The primary order parameters are the second component of Eg (i.e., I4122) and the second component of Eg (the first is from I41/amd which also feeds into I4, the second arises from Fddd), with again the first component of Eg 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. [4]. As for Eg(2), note that it is a secondary mode in the I4m2 scenario [22] as shown in Table 1. 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 I4 one.

In both scenarios, though, there are issues. The most obvious one is why the SHG signal is dominated by the secondary order parameter. This is less of an issue in ‘electronic’ scenarios where the primary order parameters have a non-structural origin [8] [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 Cd2Re2O7. In the electronic scenario advocated by Harter et al. [8] and in both structural scenarios, the relevant term in the Landau free energy expansion is a trilinear one involving three order parameters, each from a different group representation. It is hard to understand how all three can simultaneously condense, in particular in a second-order fashion as experimentally observed. A very similar issue is found in improper ferroelectrics [13]. Although there has been significant theory work on the latter [23], this question is still unresolved. Therefore, a solution to this problem could not only tell us much about Cd2Re2O7, but also about other materials where trilinear terms in the Landau free energy expansion play a fundamental role [24].

In conclusion, the relative merits of a structural scenario for the SHG data of Cd2Re2O7 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 isotropically 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 $T_s$.[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. Japan 87, 024702 (2018).
[2] J.-I. Yamaura and Z. Hiroi, J. Phys. Soc. Japan 71, 2598 (2002).
[3] S.-W. Huang, H.-T. Jeng, J.-Y. Lin, W. J. Chang, J. M. Chen, G. H. Lee, H. Berger, H. D. Yang and K. S. Liang, J. Phys.: Condens. Matter 21, 195602 (2009).
[4] M. T. Weller, R. W. Hughes, J. Rooke, C. S. Knee and J. Reading, Dalton Trans. 2004, 3032 (2004).
[5] J. P. Castellan, B. D. Gaulin, J. van Duijn, M. J. Lewis, M. D. Lumsden, R. Jin, J. He, S. E. Nagler and D. Mandrus, Phys. Rev. B 66, 134528 (2002).
[6] J. C. Petersen, M. D. Caswell, J. S. Dodge, I. A. Sergienko, J. He, R. Jin and D. Mandrus, Nature Phys. 2, 605 (2006).
[7] L. Fu, Phys. Rev. Lett. 115, 026401 (2015).
[8] J. W. Harter, Z. Y. Zhao, J.-Q. Yan, D. G. Mandrus and D. Hsieh, Science 356, 295 (2017).
[9] S. Di Matteo and M. R. Norman, Phys. Rev. B 96, 115156 (2017).
[10] S. Hayami, Y. Yanagi, H. Kusunose and Y. Motome, Phys. Rev. Lett. 122, 147602 (2019).
[11] J. Yamaura, K. Ohgushi, H. Ohsumi, T. Hasegawa, I. Yamauchi, K. Sugimoto, S. Takeshita, A. Tokuda, M. Takata, M. Udagawa, M. Takigawa, H. Harima, T. Arima and Z. Hiroi, Phys. Rev. Lett. 108, 247205 (2012).
[12] T. Malcherek, U. Bismayer and C. Paulmann, J. Phys.: Condens. Matter 22, 205401 (2010).
[13] E. Bousquet, M. Dawber, N. Stucki, C. Lichtensteiger, P. Hermet, S. Gariglio, J.-M. Triscone and P. Ghosez, Nature 452, 732 (2008).
[14] http://www.cryst.ehu.es/
[15] http://iso.byu.edu/iso/isotropy.php
[16] M. Pasciak, M. Wolczyz, A. Pietraszko and S. Leoni, Phys. Rev. B 81, 014107 (2010).
[17] Y. Hirata, M. Nakajima, Y. Nomura, H. Tajima, Y. Matsubayashi, K. Asoh, Y. Kiuchi, A. G. Eguiluz, R. Arita, T. Suemoto and K. Ohgushi, Phys. Rev. Lett. 110, 187402 (2013).
[18] D. Orobengoa, C. Capillas, M. I. Aroyo and J. M. Perez-Mato, J. Appl. Cryst. 42, 820 (2009).
[19] Y. Matsubayashi, D. Hirai, M. Tokunaga and Z. Hiroi, J. Phys. Soc. Japan 87, 104604 (2018).
[20] I. A. Sergienko, V. Keppens, M. McGuire, R. Jin, J. He, S. H. Curnoe, B. C. Sales, P. Blaha, D. J. Singh, K. Schwarz and D. Mandrus, Phys. Rev. Lett. 92, 065501 (2004).
[21] C. S. Knee, J. Holmlund, J. Andreasson, M. Kall, S. G. Eriksson and L. Börjesson, Phys. Rev. B 71, 214518 (2005).
[22] I. A. Sergienko and S. H. Curnoe, J. Phys. Soc. Japan 72, 1607 (2003).
[23] N. A. Benedek and C. J. Fennie, Phys. Rev. Lett. 106, 107204 (2011).
[24] I. Etxebarria, J. M. Perez-Mato and P. Boulay, Ferroelectrics 401, 17 (2010).