Metallic “Ferroelectricity” in the Pyrochlore $Cd_2Re_2O_7$

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A class of materials known as “ferroelectric metals” was discussed theoretically by Anderson and Blount in 1965 [Phys. Rev. Lett. **14**, 217 (1965)], but to date no examples of this class of materials have been reported. Here we present measurements of the elastic moduli of $Cd_2Re_2O_7$ through the 200 K cubic-to-tetragonal phase transition. A Landau analysis of the moduli reveals that the transition is consistent with $Cd_2Re_2O_7$ being classified as a ferroelectric metal in the weaker sense described by Anderson and Blount (loss of a center of symmetry). First-principles calculations of the lattice instabilities indicate that the dominant lattice instability corresponds to a twofold degenerate mode with E_u symmetry and that motions of the O ions forming the O octahedra dominate the energetics of the transition.

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Itinerant electrons screen electric fields and inhibit the electrostatic forces responsible for ferroelectric distortions. Therefore, in a metallic system one does not expect to find structural transitions similar to those found in insulating materials with a tendency toward ferroelectricity. The idea that metallic behavior and ferroelectricity may not always be incompatible had an early champion in Matthias [1]. A groundbreaking paper on this subject was written by Anderson and Blount (AB) in 1965 [2]. Applying Landau theory to a continuous cubic-to-tetragonal (C-T) structural phase transition, AB concluded that “a transition from cubic to tetragonal in which the only order parameter in Landau's sense is the unit cell shape, i.e., the strain, can be second order only with probability zero.” Applying these ideas to the C-T transition found in A-15 superconductors such as V_3Si and Nb_3Sn, AB concluded that “these and perhaps several other metallic transitions may be ‘ferroelectric’ in the sense of the appearance of a polar axis, or possibly at least involve the loss of a center of symmetry.” Ultimately, however, it was shown that the structural transitions in the A-15 compounds were not continuous but rather weakly first order, and that strain was indeed the appropriate order parameter [3]. As no other materials seemed to fit AB's criteria, ideas regarding metallic “ferroelectricity” have not been pursued over the past 38 years.

The pyrochlore $Cd_2Re_2O_7$ has attracted attention recently as an oxide superconductor on a geometrically frustrated lattice [4–8]. The normal state properties of $Cd_2Re_2O_7$ are also intriguing [9–15], particularly the C-T transition at 200 K that profoundly affects the electronic structure, transport, and magnetic susceptibility of this material. Evidence from resistivity, specific heat, nuclear quadrupole resonance, and x-ray diffraction [9,12,15–17] indicates that the 200 K C-T transition is continuous. Another, first-order, structural phase transition ($T_C = 120$ K) has been reported in $Cd_2Re_2O_7$ [18], but because the issues raised by this transition are secondary to the main focus of this Letter, we mention only this lower-temperature transition briefly in what follows. Despite several studies [15–17], the structure of $Cd_2Re_2O_7$ below 200 K has not been fully determined, mainly because the departure from cubic symmetry is extremely small and even high-resolution x-ray measurements [16,17] can barely detect the splitting of the cubic Bragg peaks. It has been shown, however, that there is no multiplication of the unit cell below the 200 K transition (the transition is ferrodistortive) and that a loss of threefold symmetry accompanies the transition [7]. There is also some evidence that inversion symmetry may be broken in the low-temperature phases [17]. $Cd_2Re_2O_7$, therefore, is a good candidate for becoming the first material to obey AB's criteria provided that strain can be ruled out as the primary order parameter for the C-T transition at 200 K.

Single crystals of $Cd_2Re_2O_7$ were grown from the vapor in sealed silica tubes using Cd metal (5N, Johnson Matthey) and Re_2O_7 (3N, Johnson Matthey) [6,9]. The measurements reported in this Letter were performed on a crystal cut into a rectangular parallelepiped with dimensions $1.2 \times 1.9 \times 2.3$ mm^3. The sample was oriented with all faces perpendicular to the

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crystallographic $\langle 100\rangle$ axes. The experimental density of the sample was 8.795 g/cm^3; this can be compared with the x-ray density of 8.814 g/cm^3.

Resonant ultrasound spectroscopy (RUS) measurements were performed as a function of temperature (5–300 K) to determine the elastic moduli of the sample. RUS is a technique developed by Migliori *et al.* [19] for determining the complete elastic tensor of a small single crystal by measuring its free-body resonances. This method has the advantage that all moduli can be determined simultaneously, thereby avoiding remounts of transducers and multiple temperature sweeps.

In Fig. 1 we plot the elastic moduli of $Cd_2Re_2O_7$ vs temperature for the three modes of elastic waves in the principal propagation directions in a cubic system [20]. Deep into the transition the ultrasonic absorption of the sample became so great that for several temperatures not enough resonances were observed to allow for an accurate determination of all three elastic moduli. However, the lowest frequency resonance depended almost exclusively on C_{44} and was visible throughout the entire transition.

If strain were the order parameter, we would expect at least one of these elastic constants to soften dramatically as expected for an elastic instability. This is not observed. The salient feature of Fig. 1 is the steplike change at 200 K in all of the moduli except C_{44}. This behavior of the moduli can be modeled using the order parameter proposed by Sergienko and Curnoe [21]. This order parameter involves collective atomic displacements corresponding to a long-wavelength phonon of E_u symmetry.

The minimal model for Landau free energy F which accounts for the anomalies of the elastic moduli should include a ferrodistortive energy F_d expanded in terms of the structural order parameter (η_1, η_2), the elastic energy F_{el}, and coupling between the order parameter and strain $F_{d-\mathrm{el}}$:

$$\begin{aligned}
F_d &= a_1(\eta_1^2+\eta_2^2) + a_2(\eta_1^2+\eta_2^2)^2 + a_3(\eta_1^2+\eta_2^2)^3 + b_1(\eta_1^3 - 3\eta_1\eta_2^2)^2,\\
F_{\mathrm{el}} &= 1/2C_{11}^0(e_1^2+e_2^2+e_3^2) + C_{12}^0(e_1e_2+e_2e_3+e_1e_3) + 1/2C_{44}^0(e_4^2+e_5^2+e_6^2),\\
F_{d-\mathrm{el}} &= \lambda_1(\eta_1^2+\eta_2^2)(e_1+e_2+e_3) + \lambda_2[(\eta_1^2-\eta_2^2)(e_1+e_2-2e_3) + 2\sqrt{3}\eta_1\eta_2(e_1-e_2)]\\
&\quad + \mu_1(\eta_1^2+\eta_2^2)(e_4^2+e_5^2+e_6^2) + \mu_2[(\eta_1^2-\eta_2^2)(e_4^2+e_5^2-2e_6^2) + 2\sqrt{3}\eta_1\eta_2(e_4^2-e_5^2)],
\end{aligned} \tag{1}$$

with $F = F_d + F_{\mathrm{el}} + F_{d-\mathrm{el}}$. Here C_{11}^0, C_{12}^0, and C_{44}^0 are the elastic moduli in the cubic phase ($\eta_1 = \eta_2 = 0$) and a_1, a_2, a_3, and b_1 are the Landau expansion coefficients, e_i is the strain, and λ_i and μ_i are coupling constants.

Terms up to fourth order in F_d are isotropic; therefore sixth-order terms are required to lift the degeneracy between ordered states. Since the phase transition at $T_C = 200$ K is second order, the coefficient a_2 must be positive. The elastic moduli in the tetragonal phase ($\eta_1 = 0$, $\eta_2 \neq 0$) can be calculated using Slonczewski-Thomas formalism [22]

$$C_{ij} = \frac{\partial^2 F}{\partial e_i \partial e_j} - \frac{\partial^2 F}{\partial \eta_2 \partial e_i}\frac{\partial^2 F}{\partial \eta_2 \partial e_j}\left(\frac{\partial^2 F}{\partial \eta_2^2}\right)^{-1},$$

where the equibrium values of η_2 and the strain tensor are calculated from the system of equations

$$\frac{\partial F}{\partial \eta_2} = \frac{\partial F}{\partial e_i} = 0, \qquad i = 1, \ldots, 6. \tag{2}$$

We obtain

$$\begin{aligned}
C_{11} &= C_{11}^0 - A^2/2a_2 + O(\eta_2^2),\\
C_{33} &= C_{11}^0 - B^2/2a_2 + O(\eta_2^2),\\
C_{12} &= C_{12}^0 - A^2/2a_2 + O(\eta_2^2),\\
C_{13} &= C_{12}^0 - AB/2a_2 + O(\eta_2^2),\\
C_{44} &= C_{44}^0 + O(\eta_2^2),\\
C_{66} &= C_{66}^0 + O(\eta_2^2),
\end{aligned} \tag{3}$$

where $A = \lambda_1 - \lambda_2$, $B = \lambda_1 + 2\lambda_2$. Higher-order terms can easily be calculated from the above equations by expanding in η_2, but the resulting expressions are cumbersome. Steps are therefore expected in the elastic moduli C_{11}, C_{33}, C_{12}, and C_{13} at the continuous transition, while the shear moduli C_{44} and C_{66} have continuous anomalies. The data in Fig. 1 are qualitatively consistent with these predictions [23].

In many respects the elastic behavior of $Cd_2Re_2O_7$ (CRO) resembles that of $SrTiO_3$ (STO), but there are some important differences. In STO the coupling is linear in all components of the strain but quadratic in the order parameter [19,22,24,25], whereas in CRO it is linear only in the diagonal components e_1, e_2, and e_3 of the strain tensor. It should also be kept in mind that STO is antiferrodistortive and inversion symmetry is not broken in the tetragonal phase. As in STO, the measured elastic anomalies of C_{11} and $(C_{11} - C_{12})/2$ in CRO are not true step functions but are broadened by several degrees. Lüthi and Moran [24] ascribe this behavior in STO to residual strain, and there is no reason not to expect this strain in CRO as well. The downward "dip" observed near T_C in the longitudinal elastic moduli has also been observed in STO and can be ascribed to order parameter fluctuations [25]. Domain formation below T_C introduces several difficulties into a quantitative analysis of the data, both because of the anisotropies associated with domains and because domain wall motions make

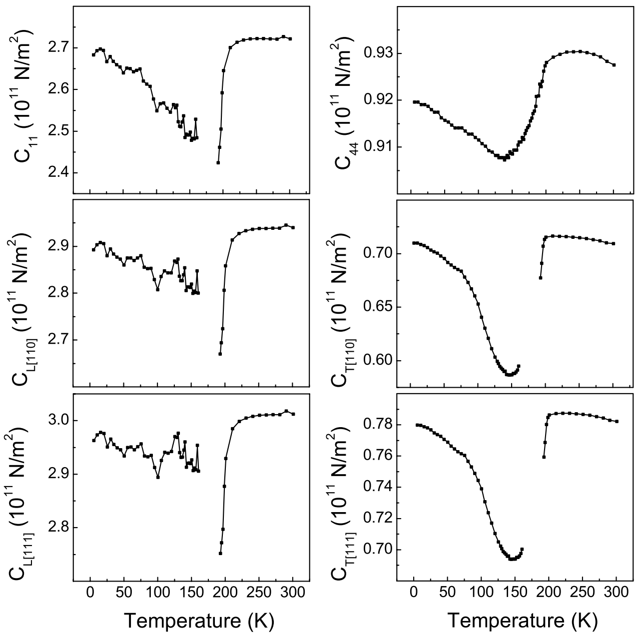

FIG. 1. Elastic moduli vs temperature obtained on a single crystal of $Cd_2Re_2O_7$ using RUS. The relationship between sound velocity and elastic moduli is given by $v_s = (C/\rho)^{1/2}$, where C is the effective elastic constant and ρ is the density. In a cubic crystal, longitudinal waves propagating in the [100] direction are governed by C_{11}, and both transverse waves are governed by C_{44}. In the [110] direction, longitudinal waves are governed by $C_{L[110]} = 1/2(C_{11} + C_{12} + 2C_{44})$, one transverse wave is governed by C_{44}, and the other by $C_{T[110]} = 1/2(C_{11} - C_{12})$. In the [111] direction, longitudinal waves are governed by $C_{L[111]} = 1/3(C_{11} + 2C_{12} + 4C_{44})$, and both transverse waves are governed by $C_{T[111]} = 1/3(C_{11} - C_{12} + C_{44})$. Note the small magnitude (2%) of the anomaly in C_{44} compared to the anomalies in the other moduli.

important contributions to the elastic moduli. To obtain elastic moduli below the transition we assumed a random domain distribution and that the sample retained a macroscopic cubic symmetry. Resolving these difficulties requires a detailed understanding of the microstructure of $Cd_2Re_2O_7$, and this knowledge is not yet available. However, none of these difficulties affects the phenomenology presented here.

To help elucidate the origin of the lattice instabilities, first-principles calculations were performed in the local density approximation (LDA) using the general potential linearized augmented plane-wave (LAPW) method [26] as described in Refs. [27,28]. Initially, scalar relativistic calculations of the atomic forces were performed for a sufficient number of small atomic displacements away from the equilibrium structure to determine the dynamical matrix for an 88 atom supercell. Then the full phonon dispersion relations were obtained by a direct method using the PHONON program [29]. At the zone center two very unstable modes were found, a twofold degenerate E_u symmetry mode and a threefold degenerate T_{1u} mode. Both of these modes involved breaking of inversion symmetry and have eigenvectors that are heavily dominated by the O(1) site (forming the O octahedra coordinating the Re ions). In addition, two more weakly unstable and several low frequency but stable modes involving Cd and Re atom shifts were found, many of them also breaking inversion symmetry.

Since the unstable modes were heavily dominated by O(1) motion, we neglected the minor components and calculated the energetics as a function of distortion amplitude with a tetragonal cell for the E_u and T_{1u} displacement patterns. These calculations were done relativistically, including spin orbit, which we find to significantly affect the energetics by reducing the tendency towards lattice instability. Nonetheless, we still find a substantial instability of the E_u mode and a marginal instability of the T_{1u} mode, as shown in Fig. 2. Clearly, the dominant instability corresponds to the E_u mode, and so we expect that the higher temperature phase transition is due to its freezing.

The lower-temperature transition might be associated with a change of symmetry into which this mode freezes (note that it is twofold degenerate), as in, e.g., the cubic-tetragonal-orthorhombic-rhombohedral transition sequence of $BaTiO_3$ under cooling. Freezing of the doubly degenerate E_u mode alone may result in three possible low symmetry structures $I\bar{4}m2$, $I4_122$, and $F222$ [21]. We have performed the LDA calculations for these three space groups and found that the energetics are nearly the same. This can be understood because terms up to fourth order in F_d are isotropic. In Fig. 2 we show the

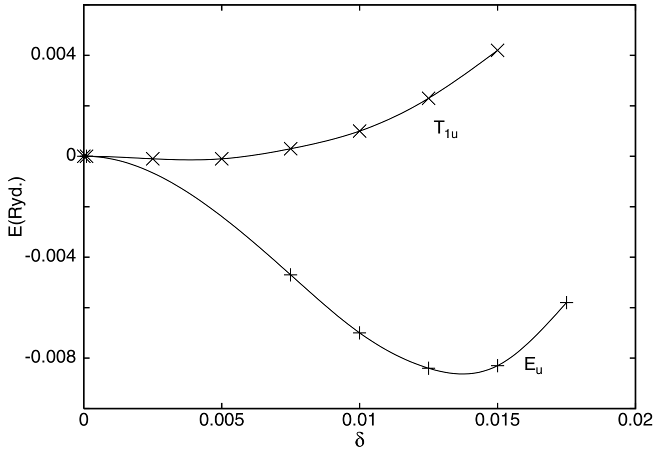

FIG. 2. Relativistic LDA energetics of lattice instabilities in $Cd_2Re_2O_7$. The coordinates of the O(1) atoms are in Cartesian coordinates, units of the lattice constant $a = 10.219$ Å: $(0.315 - \delta_E + \delta_T,\ 0.625,\ 0.625)$, $(0.935 + \delta_E + \delta_T,\ 0.625,\ 0.625)$, (0.625, 0.315, 0.625), (0.625, 0.935, 0.625), $(0.625,\ 0.625, 0.315 + \delta_E)$, $(0.625,\ 0.625,\ 0.935 - \delta_E)$, (0.375, 0.065, 0.375), (0.375, 0.685, 0.375), $(0.065 + \delta_E + \delta_T,\ 0.375,\ 0.375)$, $(0.685 - \delta_E + \delta_T,\ 0.375,\ 0.375)$, $(0.375,\ 0.375,\ 0.685 + \delta_E)$, $(0.375,\ 0.375,\ 0.065 - \delta_E)$, where E and T are the E_u and T_{1u} frozen-in amplitudes, respectively.

calculations, corresponding to the $I4_122$ structure, which was proposed to be the lowest temperature phase in Ref. [17]. In this case, soft modes associated with the T_{1u} could play an important role in the low-temperature superconductivity.

Alternately, we note that the two unstable modes are of different symmetry, and therefore do not interact at lowest order. Perhaps a mode related to the T_{1u} O(1) displacement but with additional metal and/or O(2) displacement is unstable enough to freeze in and give the lower-temperature transition.

The temperature dependence of the elastic moduli shown in Fig. 1 allows us to rule out strain as an order parameter in $Cd_2Re_2O_7$. The conclusions of Anderson and Blount [2] can therefore be applied to $Cd_2Re_2O_7$: the order parameter must be either (1) "some electronic mystery parameter" or (2) "some change in symmetry, such as the loss of the inversion center." At present, the evidence supports the second possibility with the most likely candidate for the order parameter being a small, coherent (hence ferroelectric) collective displacement of the atoms with E_u symmetry, dominated by the motion of the O(1) atom as discussed above. Even though, following AB, we use the term "ferroelectric," we stress that although inversion symmetry is broken there is no evidence that a polar axis is formed; indeed, our analysis is fully consistent with the $I\bar{4}m2$ space group proposed in Ref. [17], and this space group is piezoelectric, although because $Cd_2Re_2O_7$ is metallic, no piezoelectric coupling is possible here.

It is an open question whether the concept of a ferroelectric metal will be fruitful in explaining the anomalous physical properties at the 200 K transition in $Cd_2Re_2O_7$. In many ways, the 200 K transition is reminiscent of a charge density wave (CDW) transition such as that observed in $TaSe_2$, although CDWs in cubic materials such as pyrochlores are generally not expected. Moreover, electronic structure calculations indicate a nearly isotropic Fermi surface and no obvious nesting or CDW instability [26]. If $Cd_2Re_2O_7$ is indeed a ferroelectric metal, however, one can imagine a redistribution of charge within the material and physical properties that mimic a CDW transition. Also, the dramatic decrease of the electrical resistivity of $Cd_2Re_2O_7$ below 200 K finds a natural explanation in terms of reduced scattering from the unstable ions as they freeze in. It is hoped that the identification of $Cd_2Re_2O_7$ as a ferroelectric metal will stimulate theoretical development of the unique continuous phase transition found in this material.

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