Hexagonal-to-base-centered-orthorhombic 4Q charge density wave order in kagome metals KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$

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I search for the ground state structures of the kagome metals KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$ using first principles calculations. Group-theoretical analysis shows that there are seventeen different distortions that are possible due to the phonon instabilities at the $M$ ($\frac{1}{2}, 0, 0$) and $L$ ($\frac{1}{2}, 0, \frac{1}{2}$) points in the Brillouin zone of the parent P6/mmm phase of these materials. I generated these structures for the three compounds and performed full structural relaxations that minimize the atomic forces and lattice stresses. I find that the Fmnm phase with the order parameter $M_1^+ (a, 0, 0) + L_2^- (b, b, 0)$ has the lowest energy among these possibilities in all three compounds. However, the Fmnm exhibits a dynamical instability at its $(0, 0, 1)$ point, which corresponds to the $A (0, 0, \frac{1}{2})$ point in the parent P6/mmm phase. Condensation of this instability leads to a base-centered orthorhombic structure with the space group Cmcm and 4Q order parameter $M_1^+ (a, 0, 0) + L_2^- (b, b, 0) + A_0^+(\frac{1}{4}c, \frac{\sqrt{3}}{4}c)$.

INTRODUCTION

KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$ are members of a new family of kagome metals recently discovered by Ortiz et al. [1]. These materials occur in a layered structure with the hexagonal space group P6/mmm. The kagome layers in these materials are made up of corner-shared V triangles interlaced with a hexagonal lattice of Sb ions. These are sandwiched by honeycomb layers of Sb ions such that the V ions are situated inside a face-shared lattice of Sb octahedra, which are then alternately stacked with hexagonal layers of A (= K, Rb, or Cs) ions to form the full three-dimensional structure.

First principles calculations predict that these materials host electronic bands that are both linearly dispersive and flat depending on the direction in the reciprocal space, and the Fermi level lies near Dirac points that are in the vicinity of van Hove singularities [1]. This electronic structure has been confirmed by angle resolved photoelectron spectroscopy (ARPES) experiments [2–14]. Calculations also show that these materials are $\mathbb{Z}_2$ topological metals with nontrivial surface crossings [3, 15], and there is evidence of topological surface states in ARPES measurements [8]. Although neutron scattering and muon spin resonance experiments find no evidence of localized electronic magnetic moments or long-range magnetic order [1, 16–18], large anomalous Hall effect has been observed in these materials [2, 19]. This has been attributed to a chiral flux phase [18, 20], but no such chiral flux current was found in spin-polarized scanning tunneling measurements [21].

All three compounds exhibit charge density wave (CDW) and superconducting transitions [3, 15, 22]. The CDW transition occurs at 78, 103, and 94 K, respectively, for KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$. The respective superconducting transition temperatures $T_c$ are 0.9, 0.9, and 2.5 K. Penetration depth and nuclear magnetic resonance (NMR) experiments find evidence for a nodeless s-wave superconducting gap [23, 24], but there are also experimental results that are suggestive of unconventional pairing [25–27]. Regardless, the superconducting state seems to have multiple Fermi sheets with different gaps [28–32]. Strain, pressure, doping, and sample thickness experiments indicate that there is competition between CDW order and superconductivity [26, 33–43].

The crystal structure of the CDW state has not been fully determined. An early scanning tunneling microscopy (STM) experiment found an in-plane $2 \times 2$ superlattice reconstruction in KV$_3$Sb$_5$ that is possibly chiral in nature [44]. Subsequent STM experiments have found evidence for $2 \times 2 \times 2$ as well as $1 \times 4$ charge order in the three materials [21, 31, 45–50]. X-ray scattering and NMR experiments support the presence of a $2 \times 2 \times 2$ charge order [4, 51], while one x-ray diffraction study finds evidence for a $2 \times 2 \times 4$ superstructure [29]. The $1 \times 4$ superlattice modulation that breaks the hexagonal symmetry has been argued to be a surface phenomenon [49, 50], but the c-axis resistivity only exhibits twofold symmetry in the presence of a rotating inplane magnetic field, suggesting that the $C_6$ rotational symmetry may also be broken within the bulk [52]. Optical and pump-probe spectroscopy experiments support both nesting-driven and unconventional scenarios for the CDW formation [53–56].

First principles calculations by Tan et al. predict that the $2 \times 2 \times 2$ order is caused by tri-hexagonal distortions within the V kagome layers [57, 58], whereas those by Ratchill et al. show that $C_6$ symmetry is broken by simultaneous condensation of the unstable phonons at the $M (\frac{1}{2}, 0, 0)$ and $L (\frac{1}{2}, 0, \frac{1}{2})$ wave vectors [59]. The charge, orbital and superconducting instabilities in these materials have been the subject of additional theoretical studies [20, 60–72]. Nevertheless, a detailed study that identifies the full crystal structure of these materials in their ground state, which is necessary to understand the mechanism underlying their CDW order and superconductivity, is still lacking.
In this paper, I use density functional theory based first principles calculations to search for the lowest energy structures of these materials among the possible structures that arise due to the phonon instabilities present in these materials. Group-theoretical analysis shows that there are seventeen different structural distortions possible due to the phonon instabilities at $M$ and $L$ points in the parent $P6/mmm$ phase of these materials. I generated these distorted structures for all three materials and performed full structural relaxations by minimizing the atomic forces and lattice stresses. I find that the $Fmmm$ phase with the order parameter $M^+_1(a, 0, 0) + L^-_2(0, b, b)$ has the lowest energy among these structures. However, the $Fmmm$ phase exhibits a phonon instability at the $Z(0, 0, 1)$ point in its Brillouin zone, which is equivalent to the $A(0, 0, \frac{1}{2})$ point of the $P6/mmm$ phase. This instability leads to a base-centered orthorhombic structure with the space group $Cmcm$, and it has the $4Q$ order parameter $M^+_1(a, 0, 0) + L^-_2(0, b, b) + A^+_4\left(\frac{1}{2}c, -\sqrt{3}c, 0\right)$ with respect to the $P6/mmm$ phase.

**COMPUTATIONAL APPROACH**

All structural relaxation and phonon calculations presented here were performed using the optB88-vdW exchange-correlation functional that accurately treats the van der Waals interaction [73]. The QUANTUM ESPRESSO package [74], which is a pseudopotential based planewave code, was used for the structural relaxations and the phonon calculations of the three compounds in the $P6/mmm$ phase. I used the pseudopotentials generated by Dal Corso [75] and energy cutoffs of 60 and 600 Ry for the basis-set and charge density expansions, respectively, in these calculations. An $8 \times 8 \times 4$ k-point grid and a Marzari-Vanderbilt smearing of 0.01 Ry was used for the Brillouin zone integration. The dynamical matrices were calculated on an $8 \times 8 \times 4 q$-point grid using density functional perturbation theory [76], and Fourier interpolation was used to obtain the phonon dispersions.

I used the ISOTROPY package to enumerate all possible structural distortions due to the phonon instabilities at $M$ and $L$ [77]. The calculated phonon eigenvectors were then used to generate the distorted structures on $2 \times 2 \times 2$ supercells of all three compounds. To minimize the consumption of computational resources, the VASP package was used to perform full structural relaxations of these supercells. A planewave cutoff of 400 eV, k-point grid of $8 \times 8 \times 4$, and Methfessel-Paxton smearing of 0.1 eV were used in these calculations.

Phonon calculations of the $Fmmm$ phase using density functional perturbation theory was not feasible with the available computational resources because of the large number of atoms in its primitive unit cell. Hence, the frozen-phonon approach as implemented in the PHONOPY package in combination with the QUANTUM ESPRESSO code as the force calculator was used to calculated the phonon dispersions of the $Fmmm$ phase of the three materials [78]. A 288-atom $2 \times 2 \times 2$ supercell and a $3 \times 3 \times 3$ k-point grid was utilized in these calculations. The frozen-phonon approach was also used to check for phonon instabilities at $Z(0, 0, \frac{1}{2})$ and $S(\frac{1}{2}, \frac{1}{2}, 0)$ points in the $Cmcm$ phase of CsV$_3$Sb$_5$ using 144-atom $1 \times 1 \times 2$ and $2 \times 1 \times 1$ supercells, respectively. These calculations used k-point grids of $6 \times 6 \times 2$ and $3 \times 6 \times 4$, respectively.

The spin-orbit interaction was neglected in all structural relaxation and phonon calculations. I made extensive use of the FINDSYM [79], AMPLIMODES [80], and SPGLIB [81] packages in the symmetry analysis of the relaxed structures.

The electronic structure of the $P6/mmm$, $Fmmm$, $Cmcm$ phases of KV$_3$Sb$_5$ was calculated using the generalized full-potential method as implemented in the WIEN2K package. I used the fully-relaxed structures obtained using the optB88-vdW functional but performed the calculations with the generalized gradient approximation of Perdew, Burke and Ernzerhof [82]. Muffin-tin radii of 2.5, 2.44, and 2.45 a.u. were used for K, V, and Sb, respectively. The planewave cutoff was set by $R_k^{\text{max}} = 7$, where $R_k^{\text{max}}$ is the planewave cutoff and $R$ is the smallest muffin-tin radius used in the calculations. $32 \times 32 \times 16$, $16 \times 16 \times 16$, and $16 \times 16 \times 8$ k-point grids were used for the $P6/mmm$, $Fmmm$, and $Cmcm$ phases, respectively. The density of states was calculated using $64 \times 64 \times 32$, $28 \times 28 \times 28$, and $24 \times 24 \times 12$ k-point grids, respectively. The spin-orbit interaction was included in these calculations.

**RESULTS AND DISCUSSION**

What is the lowest energy structure due to the phonon instabilities at $M$ and $L$?

**TABLE I. Calculated structural parameters of $AV_3Sb_5$ ($A = $ K, Rb, Cs) obtained using the opt88B-vdW functional in the high-temperature $P6/mmm$ phase.** The atomic coordinates are $A$ 1a $(0, 0, 0)$, $V$ 3g $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$, Sb1 1b $(0, 0, 0)\), and Sb2 4h $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$.

|      | $a$     | $c$     | $z_{\text{Sb}}$ | $a$      | $c$     | $z_{\text{Sb}}$ |
|------|---------|---------|-----------------|---------|---------|-----------------|
| K    | 5.4706  | 8.9370  | 0.7572          | 5.48213 | 8.95802 | 0.753           |
| Rb   | 5.4907  | 9.0910  | 0.7517          | 5.4715  | 9.073   | 0.74984         |
| Cs   | 5.5097  | 9.3065  | 0.7444          | 5.4949  | 9.3085  | 0.74217         |

* Ref. [1]

The calculated structural parameters of KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$ obtained using the optB88-vdW functional in the high-temperature $P6/mmm$ phase are given in Table I. These are in good agreement with the
The phonon dispersions of the three compounds obtained using these calculated structures are shown in Fig. 1, and they agree reasonably well with previous calculations. The phonon dispersions show a non-degenerate branch that is unstable along the path from \( M (0, \frac{1}{2}, 0) \) to \( L (0, \frac{1}{2}, \frac{1}{2}) \). Additionally, the phonon branch shows a much weaker instability near \( \Gamma \) and \( A (0, 0, \frac{1}{2}) \) in CsV\(_3\)Sb\(_3\). The unstable branch continuously connects to an acoustic mode near the Brillouin zone center. But all acoustic branches emerge with real velocities from the Brillouin zone center, indicating that an acoustic instability does not cause the structural transition in these materials. In all three materials, the instability at \( L \) is slightly larger than at \( M \). The strength of these instabilities increase as the atomic mass increases from K, Rb, to Cs. This is consistent with RbV\(_3\)Sb\(_3\) having a higher structural transition temperature than KV\(_3\)Sb\(_3\), but at odds with CsV\(_3\)Sb\(_3\) having a lower structural transition temperature than RbV\(_3\)Sb\(_3\). In CsV\(_3\)Sb\(_3\), the phonon instability is spread to a greater extent along the high-symmetry paths and the unstable branch is relatively flat along \( M-L \), which should both allow for more structural fluctuations, and this might explain the discrepancy.

The phonon branches in all three materials are relatively flat along the out-of-plane directions \( \Gamma-A \) and \( M-L \), indicating that the interlayer bonding in these materials is weak. This agrees with the lack of charge sharing between the alkali metal and V-Sb layers ascertained from electronic structure calculations [1]. The electronic structure calculations furthermore indicate that the alkali metal ions primarily act as electron donors, and the very similar phonon dispersions of the three compounds confirms this view.

The components of the displacement vector of the unstable phonon mode at \( L \) for the three compounds are given in Table II. As expected, the displacement vectors are qualitatively similar in all three compounds. I find that the nature of the displacement vector does not change along the out-of-plane \( M-L \) high-symmetry path, except that the alkali ions are fixed at \( M \) and for the presence of complex phase factors for the wave vectors that do not lie at the Brillouin zone corners. Within the \( ab \) plane, the unstable mode causes the V-V bonds orthogonal to the phonon propagation vector to dimerize. Additionally, the instability also causes out-of-plane motion of Sb ions that do not lie in the kagome plane.

Although the unstable phonon branch in these materials is non-degenerate at both \( M \) and \( L \), this instability can cause distortion along all three V-V chains present in the kagome lattice because the star of both \( M \) \( \{(0, \frac{1}{2}, 0), (\frac{1}{2}, 0, 0), (\frac{1}{2}, \frac{1}{2}, 0)\} \) and \( L \) \( \{(0, \frac{1}{2}, \frac{1}{2}), (\frac{1}{2}, \frac{1}{2}, 0), (\frac{1}{2}, \frac{1}{2}, \frac{1}{2})\} \) contain three elements. As a consequence, the irreducible representations (irreps) \( M^+ \) and \( L^- \) of the unstable phonon modes at \( M \) and \( L \), respectively, are three dimensional. I used the ISOTROPY

| atom | KV\(_3\)Sb\(_3\) | RbV\(_3\)Sb\(_3\) | CsV\(_3\)Sb\(_3\) |
|------|-----------------|-----------------|-----------------|
| A    | 0.00 0.00 0.01  | 0.00 0.02 0.01  | 0.00 0.03 0.03  |
| V(1) | 0.66 0.08 0.05  | 0.00 0.00 0.00  | 0.00 0.00 0.00  |
| V(2) | 0.66 0.08 0.05  | 0.00 0.00 0.00  | 0.00 0.00 0.00  |
| V(3) | 0.00 0.00 0.00  | 0.00 0.00 0.00  | 0.00 0.00 0.00  |
| Sb(1)| 0.00 0.03 0.17  | 0.00 0.04 0.16  | 0.00 0.07 0.16  |
| Sb(2)| 0.00 0.03 0.17  | 0.00 0.04 0.16  | 0.00 0.07 0.16  |
| Sb(3)| 0.00 0.03 0.17  | 0.00 0.04 0.16  | 0.00 0.07 0.16  |
| Sb(4)| 0.00 0.03 0.17  | 0.00 0.04 0.16  | 0.00 0.07 0.16  |
| Sb(5)| 0.00 0.00 0.00  | 0.00 0.00 0.00  | 0.00 0.00 0.00  |
FIG. 2. All possible isotropy subgroups and order parameters that can arise due to the $M^+_1$ and $L^-_2$ phonon instabilities of the $P6/mmm$ phase of the $AV_3Sb_5$ compounds. The 17 possible structures enumerated in the boxes in the middle row were generated for all three compounds, and full structural relaxations were performed on them. The boxes in the bottom row shows the final structure after the relaxation. Several low-symmetry initial structures relaxed to a higher-symmetry phase. For each phase, the space group symbol and number, order parameters of the $M^+_1$ and $L^-_2$ instabilities, and the total energy $E_{AV3Sb5}$ in meV per formula unit relative to the $P6/mmm$ phase are given in separate rows inside the boxes. The primary order parameter is given in bold face for the final structures. The structures with the same order parameter but different total energies are characterized by different atomic distances. The $Fmmm$ structure has the lowest energy in all three compounds.

software package to determine the distinct structural distortions that are possible in the six-dimensional order parameter subspace defined by the $M^+_1$ and $L^-_2$ instabilities. I found seventeen distortion vectors belonging to nine isotropy subgroups, and they are shown in Fig. 2. Using the calculated phonon displacement vectors, I generated all seventeen possible distortions corresponding to the isotropy subgroups on a 2×2 supercell of the parent $P6/mmm$ phase and fully relaxed these structures by minimizing both the atomic forces and lattice stresses.

In all three compounds, only distortions with the space groups $Immm$, $Fmmm$, $P6/mmm$, $Cmmm$, and $Pmmm$ could be stabilized, and their relative energies with respect to that of the undistorted phase are shown in Fig. 2. Interestingly, the relaxations resulted in several $P6/mmm$ structures with different $c$-axis periodicity and V-V distances that are characterized by dissimilar total energies. The relative energetic rankings of the structures belonging to different isotropy subgroups differ in the three compounds. However, the distorted structure with the space group $Fmmm$ is lowest in all three compounds. Symmetry-mode analysis using the AMPLIMODES program shows that primary order parameter of this phase is $(0, b, b)$ belonging to the the irrep $L^-_2$ and the secondary order parameter is $(a, 0, 0)$ belonging to the irrep $M^+_1$, which can also be surmised from the fact that the initial structure with a $M^+_1$ $(a, 0, 0)$ distortion does not relax to the $Fmmm$ structure but the initial structure with a $L^-_2$ $(0, b, b)$ distortion develops additional $M^+_1$ $(a, 0, 0)$ distortion during structural relaxation. My calculations not only confirm Ratcliff et al.’s result that the gain in energy due to a combined $M^+_1$ $(a, 0, 0)$ and $L^-_2$ $(0, b, b)$ 3Q distortion is larger than due to either $M^+_1$ $(a, a, a)$ or $L^-_2$ $(b, b, b)$ 3Q distortion [59], they also show that the $Fmmm$ structure with the order parameter $M^+_1$ $(a, 0, 0)$ and $M^+_1$ $(0, b, b)$ has the lowest energy among all possible structures due to the $M^+_1$ and $L^-_2$ instabilities.

The calculated structural parameters of the $Fmmm$ phase of the three compounds are given in Tables III, IV, and V in the appendix. The conventional unit cell of this face-centered orthorhombic phase is related to that of the parent hexagonal phase by the transformation matrix

$$T = \begin{pmatrix} 2 & 0 & 0 \\ 2 & -2 & 0 \\ 0 & 0 & 2 \end{pmatrix}.$$  

There are sixteen $AV_3Sb_5$ formula units per conventional unit cell of the $Fmmm$ phase, involving repetitions of 2, 4 and 2 along the $a$, $b$ and $c$ axes, respectively, with respect to the parent phase. The quadrupling along the $b$ axis also involves a shift of the structural motif along the $a$ axis. As a result, the structural distortion cannot be described as a reconstruction of the two-dimensional layers that preserve the angle between the lattice vectors. The $V_5Sb$ kagome plane in the $Fmmm$ phase is shown in Fig. 3. The colored solid lines in the figure indicate the V-V bonds that are contracted relative to the parent phase and different colors denote different bond lengths. The distortions involve the formation of a tri-hexagonal
Is the $Fmmm$ phase dynamically stable?

Synchrotron x-ray diffraction data measured by Ortiz et al. indicate a periodicity of four along the out-of-plane direction in the low-temperature phase of CsV$_3$Sb$_5$ [29]. However, the $Fmmm$ structure discussed above only exhibits a periodicity of two with respect to the $P6/mmm$ phase along the $c$ axis. I calculated the phonon dispersions of the three compounds in the $Fmmm$ phase to investigate whether this phase shows additional instability that leads to a $4c$ periodicity with respect to the parent phase, and the results are shown in Fig. 4. There is indeed an unstable branch in all three compounds, and the largest instability occurs at the $Z$ point $(0, 0, 1)$ with respect to the conventional lattice. The instability only occurs around $Z$ in KV$_3$Sb$_5$. In RbV$_3$Sb$_5$ and CsV$_3$Sb$_5$, this branch is unstable along the path $\Gamma-Z$. The instability at $\Gamma$ is small in RbV$_3$Sb$_5$, but it is almost as large as the instability at $Z$ in CsV$_3$Sb$_5$.

The $Z$ point of the $Fmmm$ structure is $A (0, 0, \frac{1}{2})$ in terms of the reciprocal lattice of the parent $P6/mmm$ phase. Therefore, this instability does not quadruple the periodicity along $c$.

The $Z$ point in the Brillouin zone of the $Fmmm$ structure has only one element in its star, and the unstable mode is nondegenerate with the irrep $Z_4^-$. The only isotropy subgroup of this irrep is $Cmcm$. So this instability causes a transition from a face-centered orthorhombic to a base-centered orthorhombic structure. I used the eigenvector of this unstable mode to generate 72-atom $Cmcm$ structures of all three compounds and performed full structural relaxations. The total energies of thus stabilized $Cmcm$ structures of KV$_3$Sb$_5$, RbV$_3$Sb$_5$ and CsV$_3$Sb$_5$ are 0.3, 0.3 and 0.9 meV per formula unit lower than that of the respective $Fmmm$ structures.

The calculated structural parameters of this phase for the three compounds are given in Table VI, VII, and VIII in the appendix. Fig. 5 shows its kagome layer where different V-V bond lengths of the triangles and hexagons are painted with different colors. Compared to the $Fmmm$ phase, the nearest-neighbor V triangles in the $Cmcm$ phase become inequivalent through alternate compression and expansion of their areas. There is additional differentiation of bonds in the V hexagons such that it is now composed of four different bond lengths. As a result, the individual kagome layers lose the mirror symmetry that is perpendicular to its $b$ axis, while the reciprocal lattice still exhibits this mirror symmetry because of the presence of a glide plane perpendicular to the $b$ axis in the $Cmcm$ phase.

The $Z_4^-$ instability of the $Fmmm$ phase corresponds to the $A_6^+$ irrep of the $P6/mmm$ phase. Remarkably, there are no unstable modes at $A (0, 0, \frac{1}{2})$ in the parent $P6/mmm$ phase. However, the lowest-frequency mode at $A$ has the irrep $A_6^-$. It has a small frequency of 11 cm$^{-1}$ and exhibits a strong dispersion characteristic of a soft mode. Apparently, the transition to the $Fmmm$ phase makes it unstable. This mode is doubly degenerate and structure-relationship analysis using the AMPLIMODES code shows that the order parameter has the direction $(\frac{1}{2}c, -\frac{\sqrt{3}}{2}c)$. Therefore, the $Cmcm$ phase can be characterized as having the 4$Q$ order parameter $M_1^* (a, 0, 0) + L_2^- (0, b, b) + A_6^+ (\frac{1}{2}c, -\frac{\sqrt{3}}{2}c)$.

Are there any structures lower in energy than the $Cmcm$ phase?

The magnitudes of the imaginary frequencies of the unstable phonon modes at $Z$ and $\Gamma$ in the $Fmmm$ phase of CsV$_3$Sb$_5$ are comparable. So it is possible that there are other structures lower in energy than the $Cmcm$ phase in this material. The unstable mode at $\Gamma$ has the irrep $\Gamma_4^-$. It is nondegenerate, and its only isotropy subgroup is $Fmm2$. The isotropy subgroup due to coupled $Z_4^-$ and $\Gamma_4^-$ instabilities is $Amm2$. I generated 144-atom conventional unit cells of these structures for CsV$_3$Sb$_5$ and fully relaxed them. The calculated total energies of
FIG. 4. Calculated phonon dispersions of fully-relaxed KV₃Sb₅, RbV₃Sb₅, and CsV₃Sb₅ in the Fmmm phase obtained using the optB88-vdW functional show all three materials have an unstable branch with largest instability at Z. The dispersions are plotted along the path Γ (0, 0, 0) → X (1, 0, 0) → Z (1, 1, 0) → Γ (0, 0, 0) → Y (0, 1, 0) → Z (1, 1, 0) → Γ (1, 1, 1). The coordinates are given in terms of the conventional reciprocal lattice vectors.

FIG. 5. The kagome layers in the Cmcm phase of AV₃Sb₅ compounds. The V-V bonds of different lengths within the triangles and hexagons are depicted using different colors. There are eight different dimerized V-V bonds in the Cmcm phase. Individual kagome layers in this phase lack the mirror symmetry perpendicular to the b axis, which is restored in the full lattice due to the presence of a glide plane.

the Fmm2 and Amm2 phases are 0.7 and 0.6 meV/f.u. higher than the Cmcm phase, respectively.

Congnizant of Ortiz et al.’s report of a 4c periodicity in CsV₃Sb₅ [29], I also studied the possibility that the instability at (0, 0, 1/2), i.e. the midpoint of the Γ–Z path of the Fmmm phase, produces a lower energy structure. Since (0, 0, 1/2) and (0, 0, -1/2) form a star, there are three possible distortions due to this instability. They correspond to a single-q, double-q with equal magnitude, and double-q with unequal magnitude condensations of the phonon instability. These structures have the space group Cmcm and exhibit 4c periodicity with respect to the parent P6/mmm phase. The calculated total energies of these structures are 0.5, 0.7, and 0.4 meV/f.u higher than that of the Cmcm phase due to the Z instability, respectively.

In principle, the Cmcm phase due to the Z instability may also exhibit phonon instabilities and might not be the lowest energy phase of these materials. The Cmcm phase has 72 atoms per primitive unit cell, and I did not have the computational resources to calculate its full phonon dispersions even using the frozen phonon approach as it requires at least a 2 × 2 × 2 supercell. However, frozen phonon calculations on the smaller 144-atom 2 × 1 × 1 and 1 × 1 × 2 supercells of CsV₃Sb₅ were feasible. These yield accurate phonon frequencies at the wave vectors commensurate to these supercells, and thus calculated phonon frequencies were all real. In particular, I did not find any instabilities that correspond to a quadrupling of the hexagonal cell along the c direction. Therefore, the synchrotron x-ray diffraction experiment of Ortiz et al. showing a periodicity of 4c in CsV₃Sb₅ at low temperatures remain a puzzle [29]. One possibility that could explain their observation is the presence of additional stacking disorder due to the broken m₆ symmetry of the kagome planes in the Cmcm phase. The occurrence of a substantial amount of 180° stacking faults can lead to peaks corresponding to a 4c periodicity in the diffraction data. It is worthwhile to note that such a 180° stacking fault is not possible for the Fmmm structure.

Electronic structure of the P6/mmm, Fmmm, and Cmcm phases of KV₃Sb₅

I now briefly discuss the electronic structure of KV₃Sb₅ in the P6/mmm, Fmmm, and Cmcm phases to illustrate how the structural distortions modify the electronic properties. Figs. 6 and 7 show the calculated electronic density of states (DOS) and band structures of the three phases, respectively. The band structure of the parent P6/mmm phase agrees with previous calculations [1, 12, 54, 57, 72], but the DOS shows noticeable qualitative and quantitative differences. In particular, previous results show that the Fermi level lies near a peak inside a valley. I instead find that the Fermi level lies on the shoulder of a peak outside the valley. Regardless, the calculated DOS at the Fermi level is relatively high with a value of 6.52 eV⁻¹ per formula unit both spin basis or 1.09 eV⁻¹/V per spin.
FIG. 6. Calculated electronic density of states of KV$_3$Sb$_5$ in the P6/mmm, Fmmm, and Cmcm phases.

The structural distortions strongly modify the electronic structure near the Fermi level. The valley formed by two peaks near the Fermi level widens and the Fermi level now lies near the bottom inside the valley. The DOS values are $\sim 3$ eV$^{-1}$ per formula unit both spin basis for the Fmmm and Cmcm phases. The V-V bond distances change by up to 5% as the P6/mmm phase distorts to the Fmmm structure, and the almost 50% concomitant decrease in the DOS shows that lattice couples strongly to the electronic states near the Fermi level. However, the electronic structure away from the Fermi level also shows significant changes. For example, the pair of close-lying peaks at $-0.71$ and $-0.56$ eV in the P6/mmm phase get reconstructed to a broader valley. Therefore, the structural transition from the P6/mmm to Fmmm phase cannot merely be ascribed to a Peierls instability and also has characteristics of a V-V bonding instability. On the other hand, the V-V distances change by at most 0.80% in the course of the Fmmm-to-Cmcm structural transition, and these structures have the same DOS value within the errors due to the coarseness of the k-point grid used in the calculations. In fact, the changes in the electronic structure away from the Fermi level are more noticeable even if they are relatively small. So this transition is mainly due to V-V bonding instability.

The band structure of the parent P6/mmm phase has three saddle points near the Fermi level at the M point. There are additional saddle points near $-0.7$ eV at M, $-0.5$ eV at $\Gamma$, and 0.2 and $-0.7$ eV at L. If one examines the folded bands at $\Gamma$ in the Fmmm phase, one can see that the van Hove singularities just below the Fermi level at M in the P6/mmm phase get strongly reconstructed. However, the van Hove singularities just above the Fermi level and at $-0.7$ eV persist at shifted positions. This suggest that CDW formation involves strong scattering mainly among the two saddle points just below the Fermi level. In the P6/mmm phase there are two electron band near the Fermi level around L, and only the one that forms smaller Fermi sheet gets completely reconstructed $\Gamma$ in the Fmmm phase. This shows scattering within van Hove singularities dos not fully capture the mechanism of CDW formation. The other electron band at L survives when it is folded to $\Gamma$, and such an electron band has been observed in ARPES experiments [9]. Interestingly, both the Fmmm and Cmcm phases exhibit saddle points close to the Fermi level, which implies that there are van Hove singularities near the Fermi level even in low symmetry phases. This is consistent with ARPES experiments on the low-temperature phase that observe emergence of new van Hove singularities [11].
SUMMARY AND CONCLUSIONS

In summary, I have explored the ground state structures of KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$ guided by the presence of phonon instabilities present in these materials. I used group-theoretical analysis to identify the seventeen different structural distortions that are possible due to the $M_1^+$ and $L_2^-$ phonon instabilities in the parent P6/mmm phase. I generated these structures for the three compounds and studied their energetics by performing full structural relaxations. The Fmmm phase with the order parameter $M_1^+ (a, 0, 0) + L_2^- (0, b, b)$ has the lowest energy in all three compounds among these seventeen possibilities. However, the three compounds in this phase exhibit a dynamical instability at the Z point, which corresponds to the A point in the parent P6/mmm phase. Condensation of this instability leads to a base-centered orthorhombic structure with the space group Cmcm and 4Q order parameter $M_1^+ (a, 0, 0) + L_2^- (0, b, b) + A_6^+ (\frac{1}{2} c, \frac{\sqrt{3}}{2} c)$.

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APPENDIX

Calculated lattice parameters and atomic positions of KV$_3$Sb$_5$, RbV$_3$Sb$_5$, and CsV$_3$Sb$_5$ in the Fmmm phase are given in Tables III, IV, and V, respectively. Those for the Cmcm phase are given in Tables III, IV, and V, respectively. These were obtained using the optB88-vdw exchange-correlation functional.

| TABLE III. Calculated atomic coordinates of KV$_3$Sb$_5$ in the Fmmm phase. Calculated lattice parameters are $a = 10.96216$, $b = 18.99453$, and $c = 17.88179$ Å. |
|---|---|---|---|
| atom | Wyckoff pos. | x | y | z |
| K | 8i | 0 | 0 | 0.24866 |
| K | 8f | 1/4 | 1/4 | 1/4 |
| V1 | 160 | 0.38111 | 0.12712 | 0 |
| V2 | 160 | 0.62362 | 0.37688 | 0 |
| V3 | 8g | 0.24645 | 0 | 0 |
| V4 | 8h | 0 | 0.74560 | 0 |
| Sb1 | 16m | 0 | 0.16668 | 0.63035 |
| Sb2 | 32p | 0.75060 | 0.41652 | 0.12735 |
| Sb3 | 16m | 0 | 0.66700 | 0.62709 |
| Sb4 | 4b | 0 | 0 | 0 |
| Sb5 | 8e | 1/4 | 1/4 | 0 |
| Sb6 | 4a | 0 | 0 | 0 |

| TABLE IV. Calculated atomic coordinates of RbV$_3$Sb$_5$ in the Fmmm phase. Calculated lattice parameters are $a = 10.98970$, $b = 19.03729$, and $c = 18.19619$ Å. |
|---|---|---|---|
| atom | Wyckoff pos. | x | y | z |
| Rb | 8i | 0 | 0 | 0.25132 |
| Rb | 8f | 1/4 | 1/4 | 1/4 |
| V1 | 160 | 0.12305 | 0.37708 | 0 |
| V2 | 160 | 0.88188 | 0.12732 | 0 |
| V3 | 8g | 0.74589 | 0 | 0 |
| V4 | 8h | 0 | 0.24532 | 0 |
| Sb1 | 16m | 0 | 0.83286 | 0.62440 |
| Sb2 | 32p | 0.75080 | 0.08356 | 0.12452 |
| Sb3 | 16m | 0 | 0.33334 | 0.62788 |
| Sb4 | 4b | 0 | 0 | 1/2 |
| Sb5 | 8e | 1/4 | 1/4 | 0 |
| Sb6 | 4a | 0 | 0 | 0 |

| TABLE V. Calculated atomic coordinates of CsV$_3$Sb$_5$ in the Fmmm phase. Calculated lattice parameters are $a = 11.01874$, $b = 19.08467$, and $c = 18.69718$ Å. |
|---|---|---|---|
| atom | Wyckoff pos. | x | y | z |
| Cs | 8i | 0 | 0 | 0.75120 |
| Cs | 8f | 1/4 | 1/4 | 1/4 |
| V1 | 160 | 0.38247 | 0.12750 | 0 |
| V2 | 160 | 0.62265 | 0.37734 | 0 |
| V3 | 8g | 0.24530 | 0 | 0 |
| V4 | 8h | 0 | 0.74501 | 0 |
| Sb1 | 16m | 0 | 0.33270 | 0.62051 |
| Sb2 | 32p | 0.25102 | 0.08364 | 0.12056 |
| Sb3 | 16m | 0 | 0.83336 | 0.62418 |
| Sb4 | 4b | 0 | 0 | 1/2 |
| Sb5 | 8e | 1/4 | 1/4 | 0 |
| Sb6 | 4a | 0 | 0 | 0 |

| TABLE VI. Calculated atomic coordinates of KV$_3$Sb$_5$ in the Cmcm phase. Calculated lattice parameters are $a = 10.96187$, $b = 18.99383$, and $c = 17.88307$ Å. |
|---|---|---|---|
| atom | Wyckoff pos. | x | y | z |
| K | 8e | 0.25016 | 0 | 0 |
| K | 8f | 0 | 0.25006 | 0.50138 |
| V1 | 8g | 0.11920 | 0.12292 | 1/4 |
| V2 | 8g | 0.11864 | 0.37716 | 1/4 |
| V3 | 8g | 0.37717 | 0.37333 | 1/4 |
| V4 | 8g | 0.37552 | 0.12708 | 1/4 |
| V5 | 4c | 0 | 0.00421 | 1/4 |
| V6 | 4c | 0 | 0.49543 | 1/4 |
| V7 | 8g | 0.25351 | 0.24950 | 1/4 |
| Sb1 | 16h | 0.24928 | 0.16648 | 0.37757 |
| Sb2 | 16h | 0.74551 | 0.16656 | 0.87713 |
| Sb3 | 8f | 0 | -0.08294 | 0.37732 |
| Sb4 | 8f | 0 | 0.41694 | 0.87684 |
| Sb5 | 8f | 0 | 0.41667 | 0.39043 |
| Sb6 | 8f | 0 | -0.08332 | 0.88024 |
| Sb7 | 8g | 0.24992 | -0.00003 | 1/4 |
| Sb8 | 4c | 0 | 0.74994 | 1/4 |
| Sb9 | 4c | 0 | 0.24991 | 1/4 |
TABLE VIII. Calculated atomic coordinates of RbV₃Sb₅ in the Cmcm phase. Calculated lattice parameters are \( a = 10.98897 \text{ Å}, b = 19.03705 \text{ Å}, \) and \( c = 18.19831 \text{ Å}\).

| atom | Wyckoff pos. | \( x \) | \( y \) | \( z \) |
|------|--------------|---|---|---|
| Rb   | 8e           | 0.25015 | 0 | 0 |
| Rb   | 8f           | 0 | 0.25006 | 0.50134 |
| V1   | 8g           | 0.11848 | 0.12275 | 1/4 |
| V2   | 8g           | 0.11781 | 0.37737 | 1/4 |
| V3   | 8g           | 0.37800 | 0.37323 | 1/4 |
| V4   | 8g           | 0.37585 | 0.12736 | 1/4 |
| V5   | 4c           | 0 | 0.00445 | 1/4 |
| V6   | 4c           | 0 | 0.49513 | 1/4 |
| V7   | 8g           | 0.25405 | 0.24932 | 1/4 |
| Sb1  | 16h          | 0.24904 | 0.16639 | 0.37479 |
| Sb2  | 16h          | 0.74935 | 0.16650 | 0.87422 |
| Sb3  | 8f           | 0 | -0.08278 | 0.37468 |
| Sb4  | 8f           | 0 | 0.41705 | 0.87409 |
| Sb5  | 8f           | 0 | 0.41665 | 0.37797 |
| Sb6  | 8f           | 0 | -0.08333 | 0.87775 |
| Sb7  | 8g           | 0.24989 | 0 | 0.00000 | 1/4 |
| Sb8  | 4c           | 0 | 0.74994 | 1/4 |
| Sb9  | 4c           | 0 | 0.24989 | 1/4 |

Table continued...

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