

**Orbital-ordering-induced phase transition in LaVO<sub>3</sub> and CeVO<sub>3</sub>**

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The structural phase transition in the orthovanadates LaVO<sub>3</sub> and CeVO<sub>3</sub> has been studied with high energy synchrotron x-ray diffraction. LaVO<sub>3</sub> undergoes a second order phase transition at  $T_N=143$  K and a first order transition at  $T_t=141$  K, while in CeVO<sub>3</sub> there are phase transitions occurring at  $T_0=154$  K of second order and at  $T_N=134$  K of first order. These phase transitions are confirmed by specific heat measurements. The phase transition at  $T_t$  in LaVO<sub>3</sub> or  $T_0$  in CeVO<sub>3</sub> is due to a *G*-type orbital ordering which lowers the structure symmetry from orthorhombic *Pbnm* to monoclinic *P2<sub>1</sub>/b11*. The structure change at  $T_N$  in CeVO<sub>3</sub> is ascribed to an orbital ordering enhanced magnetostrictive distortion, while that at  $T_N$  in LaVO<sub>3</sub> is most probably due to an ordered occupation of the vanadium *3d t<sub>2g</sub>* orbitals associated with an antiferromagnetic ordering. We propose that the first order phase transition at  $T_t$  in LaVO<sub>3</sub> should be associated with a sudden change of both spin and orbital configurations, similar to the phase transition at  $T_s=77$  K in YVO<sub>3</sub> [Ren *et al.*, Nature (London) **396**, 441 (1998)], causing a reversal of the net magnetization. However, the ordered state above  $T_t$  in LaVO<sub>3</sub> is identical to that below  $T_s$  in YVO<sub>3</sub>. It is found that, with increasing lanthanide ionic radius, the Néel temperature  $T_N$  increases while the orbital ordering onset temperature decreases in these orthovanadates.

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**I. INTRODUCTION**

In transition metal oxides strong correlations between spin, orbital and charge degrees of freedom and lattice distortion play a crucial role in a large variety of interesting physical properties. We have recently reported multiple temperature induced magnetization reversals and orbital ordering induced structural phase transitions in YVO<sub>3</sub> single crystals.<sup>1-3</sup> In cooling of a YVO<sub>3</sub> single crystal in a field of less than 4 kOe, the magnetization first increases just below the Néel temperature  $T_N=116$  K and then decreases after reaching a maximum, crossing zero at 95 K and becomes negative. The magnetization always suddenly switches its sign on crossing the first order phase transition temperature at  $T_s=77$  K in a moderate magnetic field. This compound is an insulator with V<sup>3+</sup> *3d* magnetic ions of spin  $S=1$ . The observed net magnetization results from the canted antiferromagnetic moments. Our theoretical model,<sup>2</sup> which involves a competition between the single-ion magnetic anisotropy and

the antisymmetric Dzyaloshisky-Moriya interaction, can count for all the features of the peculiar magnetic behavior between the Néel temperature  $T_N$  and the first order phase transition  $T_s$ . The phase transition at  $T_s$  is associated with an abrupt change of both spin and orbital ordering states, accompanied by a magnetization reversal.<sup>2,3</sup> It is found that below  $T_s$  the magnetic structure is of *G* type, in which the magnetic coupling is antiferromagnetic (AF) both in the *ab* plane and between two adjacent planes, while above  $T_s$  the ordered spin configuration has a *C*-type phase with an AF coupling in the *ab* plane and a ferromagnetic (FM) coupling between two adjacent planes.<sup>4</sup> According to the Goodenough-Kanamori rules<sup>5</sup> the *G*- and *C*-type spin configurations will lead to *C*- and *G*-type orbital orderings, respectively. The two different orbital orderings in YVO<sub>3</sub> are supported by band structure calculations,<sup>6</sup> Hartree-Fock calculations,<sup>7</sup> resonant x-ray scattering studies,<sup>8,9</sup> and detailed structure investigations.<sup>10</sup> We have found that the *G*-type orbital ordering onset temperature in YVO<sub>3</sub> is  $T_0$

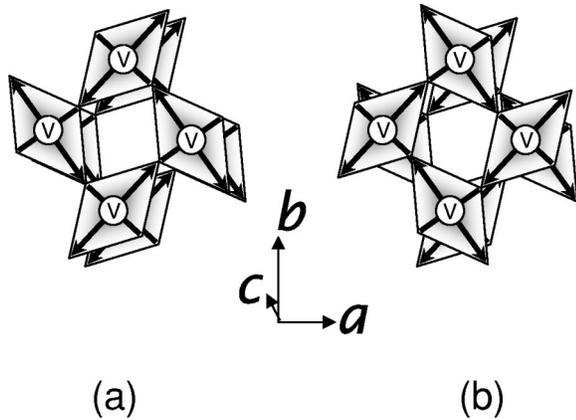


FIG. 1. Schematic presentation of the cooperative JT distortion in the  $ab$  plane below the orbital ordering temperature. V ions are sitting at the centers and oxygen (omitted for clarity) are at the corners of the  $\text{VO}_6$  octahedra. The octahedra are elongated with the long and short V-O bond distances alternating along the  $[110]$  and  $[1, -1, 0]$ , respectively. (a) In the C-type orbital ordering state the arrangement is the same in all the  $ab$  planes (“in phase”) and (b) in the G-type orbital ordering state the arrangement of the alternating V-O bonds is rotated about  $90^\circ$  along the  $c$  axis in the adjacent planes.

$=200$  K, well above the Néel temperature  $T_N=116$  K.<sup>1-3</sup> From the crystal structure point of view, the cooperative Jahn-Teller distortion of the  $\text{VO}_6$  octahedra due to the orbital ordering will be evidenced by changes of crystal symmetry and local arrangement of bond distances and bond angles. It is found in  $\text{YVO}_3$  that the long and short V-O bond distances of the distorted  $\text{VO}_6$  octahedra alternate along the  $[110]$  and  $[1\bar{1}0]$  directions in the  $ab$  plane. For the C-type orbital ordering this bonding arrangement is “in phase” with the same alternating pattern in all planes, while for the G type the arrangement is “out of phase” with the octahedra rotated about  $90^\circ$  around the  $c$  axis in the adjacent planes (Fig. 1).

The anomalous negative magnetization has also been reported by several groups in the  $\text{LaVO}_3$  polycrystalline samples.<sup>11-14</sup> It is found that, if a  $\text{LaVO}_3$  sample is cooled in a magnetic field of 1 kOe, its magnetization is oriented opposite to the applied field direction below a temperature  $T_t=138$  K  $< T_N=144$  K. Goodenough *et al.*<sup>13</sup> proposed that this anomalous “diamagnetism” is caused by a reversal of the ferromagnetic component of a canted antiferromagnet on cooling through a cooperative, first order magnetostrictive distortion at  $T_t$ , below which the orbital angular momentum is maximized. They argued that the response of the orbital moment to the forces generated at the first order phase transition can reverse the Dzyaloshinsky vector of the antisymmetric interaction so as to create a canted spin component in a direction opposite to the applied field, given that  $T_t$  is close to  $T_N$ . The crystal structure of  $\text{LaVO}_3$  has been extensively studied before. It was reported that it is cubic at room temperature and undergoes a phase transformation to a tetragonal symmetry at 137 K,<sup>15</sup> or to an orthorhombic symmetry at around 130 K.<sup>11</sup> It was later found by Bordet *et al.* that  $\text{LaVO}_3$  undergoes a crystallographic-antiferromagnetic tran-

sition at about 140 K from orthorhombic with space group  $Pbnm$  to monoclinic with space group  $P2_1/b11$ .<sup>16</sup> In the orthorhombic structure all V sites are equivalent, while two independent V sites exist in the monoclinic structure. These two V sites form alternate layers along the  $c$  axis. Above the transition all the  $\text{VO}_6$  octahedra are tilted around the three crystallographic axes and are elongated along the  $[110]$  direction. The elongation increases below the transition and occurs in different directions,  $90^\circ$  apart, in the two V sites in the monoclinic structure. This observed arrangement of the elongated  $\text{VO}_6$  octahedra at low temperature strongly supports the existence of the G-type orbital ordering below the transition. A neutron diffraction study by Zubkov *et al.* indicates a C-type antiferromagnetic structure below the Néel temperature in  $\text{LaVO}_3$ ,<sup>17</sup> corresponding to the G-type orbital ordering according to the Goodenough-Kanamori rules. However, the first order magnetostrictive transition at  $T_t$  is a few degrees below the Néel temperature, and the crystallographic and magnetic structures between these two temperatures have never been carefully studied. Furthermore, the nature of the transition at  $T_t$  is not yet fully understood.

In order to understand the underlying physics of the peculiar negative magnetization in  $\text{LaVO}_3$ , Nguyen and Goodenough have also investigated the magnetic properties of  $\text{CeVO}_3$  compounds<sup>18,19</sup>. They do not find any negative magnetization if  $\text{CeVO}_3$  samples are field-cooled (FC). They reported that  $\text{CeVO}_3$  has an orthorhombic perovskite structure at room temperature, is a canted antiferromagnet below a Néel temperature  $T_N=136$  K and also exhibits a first-order magnetostrictive distortion at a  $T_t=124$  K  $< T_N$ , similar to that in  $\text{LaVO}_3$ . Zubkov *et al.* have reported that both  $\text{LaVO}_3$  and  $\text{CeVO}_3$  have the same C-type antiferromagnetic structure below  $T_N$  and a sudden change of the lattice distortion at  $T_N$ .<sup>17</sup>

In this paper we report a detailed study of the low temperature structural transformation in  $\text{LaVO}_3$  and  $\text{CeVO}_3$  with high resolution high energy synchrotron x-ray diffraction.  $\text{LaVO}_3$  undergoes a gradual lattice distortion below  $T_N=143$  K without change of crystal symmetry and a first order phase transition at  $T_t=141$  K with a symmetry lowering to monoclinic  $P2_1/b11$ .  $\text{CeVO}_3$  exhibits a second order phase transition at  $T_0=154$  K from orthorhombic  $Pbnm$  to monoclinic  $P2_1/b11$  and an isostructural first order phase transition at  $T_N=134$  K. These phase transitions are discussed in term of spin and orbital ordering.

## II. EXPERIMENTAL

High quality powder samples used in this experiment were obtained by pulverizing single crystals of  $\text{LaVO}_3$  and  $\text{CeVO}_3$ . The single crystals were grown with the travelling solvent floating zone mirror furnace. Initial polycrystalline  $\text{LaVO}_3$  and  $\text{CeVO}_3$  materials for the single crystal growth were prepared by the chemical reduction of  $\text{LaVO}_4$  and  $\text{CeVO}_4$ , respectively, in a flow of hydrogen at  $1000^\circ\text{C}$ . The  $\text{LaVO}_4$  and  $\text{CeVO}_4$  powders were made with high temperature solid state reaction using predried  $\text{La}_2\text{O}_3$  (99.999 %),  $\text{Ce}_2\text{O}_3$  (99.999 %), and  $\text{V}_2\text{O}_5$  (99.993 %, metals basis).

Synchrotron x-ray powder diffraction was performed on a

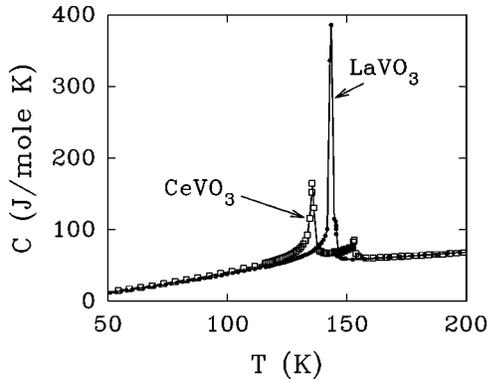


FIG. 2. The specific heat as a function of temperature for  $\text{LaVO}_3$  (filled circles) and for  $\text{CeVO}_3$  (open squares).

triple-axis high energy diffractometer at beamline 11ID-C, Basic Energy Science Synchrotron Radiation Center, Advanced Photon Source, Argonne National Laboratory. The diffractometer is operated in the vertical scattering plane with a monochromatic beam of high energy photons, which can be tuned to three available values 60, 98, and 115 keV, obtained from three monochromators Si(111), Si(220) and Si(311) single crystals, respectively. A Si(220) single crystal was used as an analyzer. The angular resolution is  $0.002^\circ$ , and the  $\Delta d/d$  resolution is better than  $2 \times 10^{-3}$ . Low temperatures were obtained by the use of a displax cryostat with a temperature stability better than 0.1 K. The  $2\theta$  zero offset was calibrated with a standard Si(220) single crystal. The Bragg peak profile can be simply described by a Lorentzian function, which is used to determine the peak positions in the data analysis.

The specific heat measurements were performed on single crystals of  $\text{LaVO}_3$  and  $\text{CeVO}_3$  using a semiadiabatic heat pulse technique, with a Quantum Design PPMS system. Figure 2 shows the specific heat as a function of temperature. Two phase transitions in  $\text{CeVO}_3$  occur at  $\sim 155$  and  $\sim 135$  K, respectively, while in  $\text{LaVO}_3$  the two phase transition temperatures at about 143 K are very close with a difference of  $\sim 2$  K.

### III. RESULTS AND DISCUSSIONS

The temperature dependence of the structural lattice distortion has been monitored by scanning some characteristic Bragg peaks through the phase transitions. Figure 3 shows a powder pattern containing reflections (110) and (002) of  $\text{LaVO}_3$  from 137 to 145 K. A first order phase transition at  $T_t = 141$  K can clearly be seen, where two phases are co-existing. It is apparent that a gradual shift to a higher scattering angle of reflection (002) starts from the Néel temperature  $T_N = 143$  K. Positions of the reflections are obtained by a multiple peak fitting process and plotted in Fig. 4 which shows the variation of the peak position as a function of temperature for reflections (110), (002),  $(02\bar{2})$ , (022), and (202). Below  $T_t$ , a splitting of reflections  $(02\bar{2})$  and (022) and the fact that reflections (110) and (202) remain in single peaks indicate the crystal symmetry is lowered to monoclinic

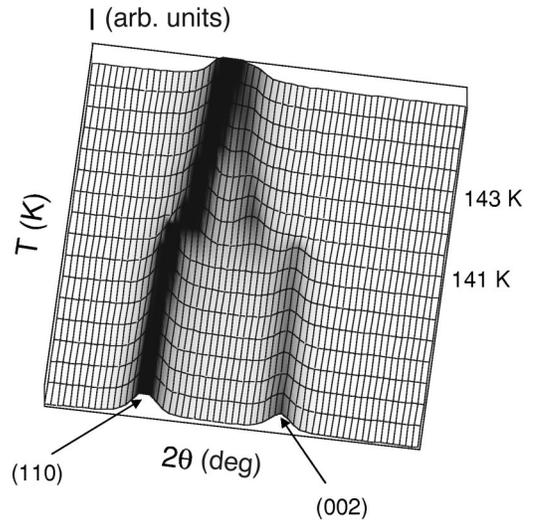


FIG. 3. Surface plot of the diffraction pattern for reflections (110) and (002) in  $\text{LaVO}_3$  as a function of temperature.

structure with  $\alpha \neq 90^\circ$ , in support of the space group  $P2_1/b11$  as found by Bordet *et al.*<sup>16</sup>

The lattice parameters were calculated from the peak positions. The monoclinic angle  $\alpha$  in the low-temperature phase was obtained from the following equation

$$\frac{1}{d_{02\bar{2}}^2} - \frac{1}{d_{022}^2} = 4 \cos \alpha \frac{1}{d_{020}} \frac{1}{d_{002}},$$

where  $1/d_{hkl} = 2 \sin(\theta)/\lambda$  with Bragg angle  $\theta$  and x-ray wavelength  $\lambda$ . The lattice parameters are plotted in Fig. 5 for  $\text{LaVO}_3$ . The monoclinic angle  $\alpha = 90.121(4)^\circ$  is very close to the value of  $90.125^\circ$  obtained by Bordet *et al.*<sup>16</sup> From both Figs. 4 and 5 it is apparent that in addition to the abrupt switch of the crystal structure at  $T_t$ , the temperature dependence of the lattice parameters between  $T_N = 143$  K and  $T_t$  is

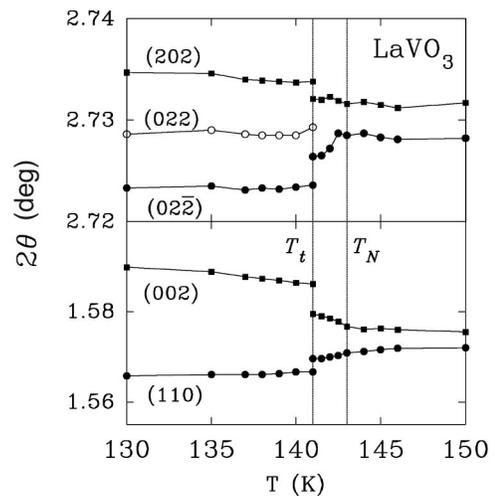


FIG. 4. Peak position as a function of temperature for reflections (110) and (002) (lower panel) and  $(0,2,-2)$ , (022), and (202) (upper panel) for  $\text{LaVO}_3$ . The standard error bars are much smaller than the symbols (also for Figs. 5, 7, and 8).

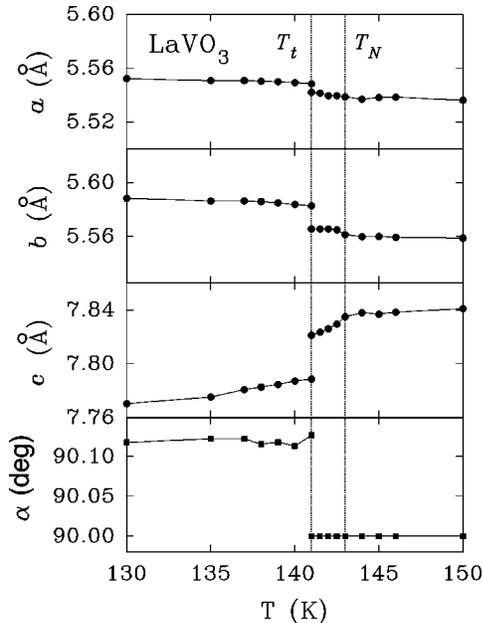


FIG. 5. Temperature dependence of the lattice parameters for  $\text{LaVO}_3$ .

quite different from that above  $T_N$ . A second order phase transition at  $T_N$ , associated with the antiferromagnetic ordering, is indicated.

It is difficult to understand the microscopic origin of the C-type antiferromagnetic phase in  $\text{LaVO}_3$  in which both antiferromagnetic and ferromagnetic interactions coexist because the crystal structure above the Néel temperature is almost cubic with almost equal V-V bonds, and thus magnetically equivalent. Khaliullin *et al.* have suggested in their theoretical study that quantum fluctuations among the  $\text{V}^{3+} t_{2g}$  orbitals play an important role in this case.<sup>20</sup> They argued that local fluctuations among the orbitals trigger FM interactions along the  $c$  axis to form the C-type magnetic phase, which could be stable only at low temperature when a coherent spin state breaking the cubic symmetry is formed. Their theory is based on a simplified cubic structure without any local distortion. However, neither the magnetic structure nor the crystal structure between  $T_N$  and  $T_t$  has ever been carefully studied before, probably owing to the very small temperature interval and a lack of high quality samples. Recent Hartree-Fock calculations have shown that the C- and G-type phases are energetically very close.<sup>7</sup> Based on the fact that the crystal structure between  $T_N$  and  $T_t$  differs significantly from that above  $T_N$ , the magnetization reverses at  $T_t$ , and compared with the finding in  $\text{YVO}_3$ , we argue that the magnetic structure in  $\text{LaVO}_3$  between  $T_N$  and  $T_t$  has the G-type phase, accompanied by a gradually ordered orbital occupation of the C type, lifting the orbital degeneracy which causes lattice distortion from the almost pseudocubic matrix symmetry. Both these spin and orbital orderings are compatible with the  $Pbnm$  symmetry and are consistent with the Goodenough-Kanamori rules. This idea is further supported by the observation of the magnetization reversal at  $T_t$ , which is very similar to the magnetic behavior at  $T_s$  in  $\text{YVO}_3$ , where the magnetization reversal is associated with a

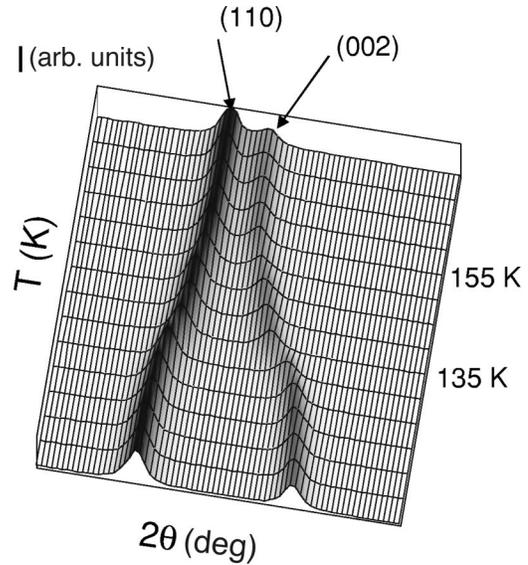


FIG. 6. Surface plot of the diffraction pattern for reflections (110) and (002) in  $\text{CeVO}_3$  as a function of temperature.

sudden change of both the magnetic and orbital ordering from one type to the other. A detailed study of the magnetic structure and local distortion as well as the magnetic properties of high quality  $\text{LaVO}_3$  samples between the two temperatures  $T_N$  and  $T_t$  is in progress.

It is found that  $\text{CeVO}_3$  has an orthorhombic perovskite structure with space group  $Pbnm$  at room temperature. The structural transformation in  $\text{CeVO}_3$  is illustrated in Fig. 6, where two reflections (110) and (002) are plotted as a function of temperature. One can see that two phase transitions occur at about 154 and 134 K, respectively. It is found that with decreasing temperature on crossing  $T_0 = 154$  K the reflection (022) gradually splits into two peaks ( $02\bar{2}$ ) and (022), while no splitting for reflections (110) and (202) occurs. This indicates the crystal structure symmetry is lowered from the orthorhombic  $Pbnm$  to the monoclinic  $P2_1/b11$  at  $T_0$ . Figure 7 shows the temperature dependent peak positions for several reflections (110), (002), ( $02\bar{2}$ ), (022), and (202). The lattice parameters are plotted in Fig. 8 as a function of temperature. The monoclinic angle  $\alpha$  gradually increases with decreasing temperature, with an enhancement at 134 K, and reaches a value of  $90.10^\circ$  at lower temperature, smaller than that in  $\text{LaVO}_3$ , as expected.

The phase transition at  $T_0 = 154$  K in  $\text{CeVO}_3$  is very similar to the orbital ordering induced phase transition at  $T_0 = 200$  K in  $\text{YVO}_3$ . A preliminary Rietveld refinement of a low temperature diffraction pattern gives a similar local  $\text{VO}_6$  distortion and V-O bonding arrangement as in the low temperature phase in  $\text{LaVO}_3$ . This indicates the phase transition at  $T_0$  originates from the G-type orbital ordering. However, due to the presence of heavy Ce atoms in the compound, the x-ray diffraction is less sensitive to the oxygen atoms. On the other hand, the displacements of the oxygen atoms are rather small owing to the relatively weak JT coupling for the  $t_{2g}$  orbitals, compared to the  $e_g$  orbitals. A detailed neutron diffraction study on this orbital ordering induced phase transition in  $\text{CeVO}_3$  is in progress.

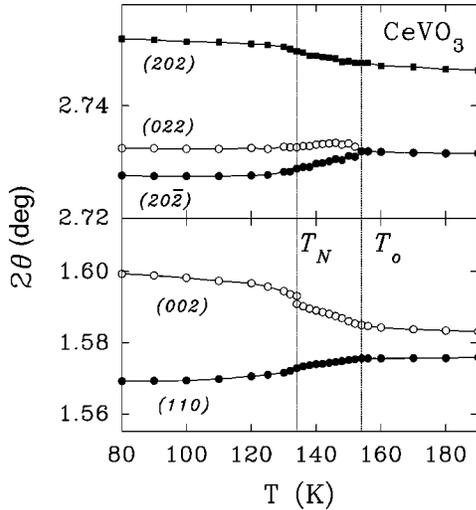


FIG. 7. Peak position as a function of temperature for reflections (110) and (002) (lower panel) and (0,2,-2), (022), and (202) (upper panel) for  $\text{CeVO}_3$ .

The phase transition at  $T_N = 134$  K is apparently related to the antiferromagnetic ordering. At  $T = T_N$  the width of reflection (002) is almost double the width at temperatures away from  $T_N$  if a single peak is used in the fitting, indicating the phase transition at  $T_N$  is of the first order and two phases coexist at the transition temperature. Since a specific heat measurement of  $\text{CeVO}_3$  consists of only two peaks at about 155 and 135 K, respectively, we believe the structural phase transition  $T_N$  is coincident with the Néel temperature. There is no crystal structural evidence for a magnetostrictive distortion below  $T_N$  as reported by Nguyen *et al.*<sup>18</sup> The microscopic origin of this phase transition can be ascribed to an orbital ordering enhanced magnetostrictive distortion, resulting from the spin-orbital interaction.

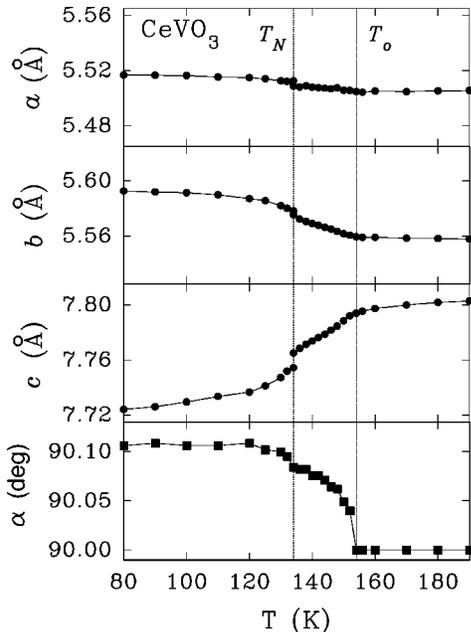


FIG. 8. Temperature dependence of the lattice parameters for  $\text{CeVO}_3$ .

The onset temperature  $T_0$  for the  $G$ -type orbital ordering is well above the Néel temperature in both  $\text{YVO}_3$  and  $\text{CeVO}_3$ , and it induces a second order structure transition. In  $\text{LaVO}_3$  it occurs at  $T_t$  a few degrees below  $T_N$ , associated with a sudden lattice distortion resulting from a first order phase transition. It is known that at room temperature the perovskite structure of these orthovanadates  $\text{LnVO}_3$  are all distorted from cubic symmetry due to a mismatch between the equilibrium bond lengths of  $\text{Ln-O}$  and  $\text{V-O}$ . The mismatch is described by the tolerance factor  $t$ . It is found that with decreasing  $t$  the Néel temperature  $T_N$  decreases, while the onset temperature for the  $G$ -type orbital ordering increases. Obviously, there is a crossover of these two temperatures between  $\text{LaVO}_3$  and  $\text{CeVO}_3$ . This can be understood because for a smaller  $t$ , one has a larger structure distortion from cubic, and thus the buckling of the  $\text{VO}_6$  octahedra will become larger, which will make the  $\text{V-O-V}$  bond angle further away from  $180^\circ$ . Thus, the superexchange interaction between two neighbor V ions, mediated by a bridge oxygen atom, will be reduced. On the other hand, a strong orthorhombic distortion will help lifting the orbital degeneracy, and thus will enhance the cooperative Jahn-Teller distortion. We are performing a detailed study of the relation between the orbital ordering transition temperature and the structure distortion in order to gain a better understanding of the correlation between the orbital, spin, and lattice distortion.

#### IV. CONCLUSIONS

In summary we have studied the structural phase transition in  $\text{LaVO}_3$  and  $\text{CeVO}_3$  with high energy synchrotron x-ray diffraction. Both compounds have an orthorhombic perovskite structure with space group  $Pbnm$  at room temperature. With decreasing temperature  $\text{CeVO}_3$  undergoes a second order phase transition at  $T_0 = 154$  K with crystal symmetry lowered to monoclinic  $P2_1/b11$ , induced by  $G$ -type orbital ordering, and a first order phase transition at the Néel temperature  $T_N$ , accompanied by a sudden lattice change. In the latter case the  $C$ -type antiferromagnetic ordering enhances the cooperative JT distortion, resulting in a spontaneous change in the crystal structure.  $\text{LaVO}_3$  retains the pseudocubic structure down to the Néel temperature  $T_N = 143$  K. Below  $T_N$  the lattice parameters change gradually with increasing  $a$  and  $b$  and decreasing  $c$ , while the symmetry remains orthorhombic  $Pbnm$ . It is apparent that the antiferromagnetic ordering is accompanied by a gradual structural distortion. At  $T_t = 141$  K the structure suddenly transforms to a monoclinic symmetry with space group  $P2_1/b11$ , associated with a  $G$ -type orbital ordering. In comparison with the transition of magnetic and orbital ordering in  $\text{YVO}_3$  and in consideration of the magnetization reversals observed in both  $\text{LaVO}_3$  and  $\text{YVO}_3$ , we suggest that the phase transition should be associated with a change of both spin and orbital ordering configurations, namely from a high-temperature phase of  $G$ -type magnetic and  $C$ -type orbital ordered state to a low temperature phase of  $C$ -type magnetic and  $G$ -type orbital ordered state. Such a change will induce a magnetization reversal similar to the magnetization switch-

ing at the transition temperature  $T_s=77$  K in  $YVO_3$ .<sup>1</sup> However, the high temperature phase above  $T_s$  in  $YVO_3$  will be the low temperature phase in  $LaVO_3$ . It is found that the onset temperature for the orbital ordering increases while the Néel temperature decreases monotonically with decreasing lanthanide ionic radii.

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