Effect of cation size variance on spin and orbital order in Eu$_{1-x}$(La$_{0.254}$Y$_{0.746}$)$_x$VO$_3$

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(Dated: February 18, 2022)

We have investigated the R-ion ($R =$ rare earth or $Y$) size variance effect on spin/orbital order in Eu$_{1-x}$(La$_{0.254}$Y$_{0.746}$)$_x$VO$_3$. The size variance disturbs one-dimensional orbital correlation in C-type spin/G-type orbital ordered states and suppresses this spin/orbital order. In contrast, it stabilizes the other spin/orbital order. The results of neutron and resonant X-ray scattering denote that in the other ordered phase, the spin/orbital patterns are $G$-type/$C$-type, respectively.

Perovskite-type transition-metal oxides $R$MO$_3$ ($R =$ rare earth elements or $Y$, $M =$ transition metal ones) and the electron- and hole-doped systems show a lot of attractive physical properties related with $d$ electrons and have been investigated extensively$^1$. In $R$MO$_3$, electronic and magnetic states can be changed by controlling the $M$-$O$-$M$ bond angle, doping carrier, applying magnetic and electric fields, and so on.$^2$ Among these, the $M$-$O$-$M$ bond angle is systematically dependent on the $R$-site ionic radius.$^3$. On the other hand, the structural disorder caused by the size mismatch of the $R$-site cations is also used as the controllable parameters$^2$$^4$$^5$.$^6$. We describe this disorder as the “size variance (SV)”, expressed by $(r_i^2)$ - $(r_i')^2$ ($r_i$ is the $R$-site ionic radius). In general, the SV suppresses the long-range spin, charge, and orbital order, and consequently the critical temperature ($T$) decreases with increasing the SV$^2$$^4$$^5$.$^6$. In nearly half doped manganites, the SV effect induces the suppression of long range charge/orbital order (CO/OO) and ferromagnetic one. As a result, the manganites undergo the phase transition from the long range CO/OO insulator or ferromagnetic metal to spin glass insulator$^5$. In this paper, we report on the findings that the SV induces instability of one spin/orbital ordered state but stabilizes the other one in RVO$_3$. This system consequently shows the novel spin/orbital phase transition from one long range order to the other long range order by changing SV. The phase transition between the two types of spin/orbital long range orders in RVO$_3$ induced by SV is new phenomena, and quite different from those in the manganites, where the phase transition from long range spin/charge/orbital ordered states to short range ordered ones occurs by the increase of SV.

RVO$_3$ is one of the prototypical systems with spin and orbital degrees of freedom of $t_{2g}$ electrons. There are two electrons in the $3d$ orbitals of $V^{3+}$. One electron always occupies $d_{xy}$ orbital due to the symmetry-lowered crystal field by the orthorhombic distortion, which is coupled ferromagnetically to the other electron in either $d_{yz}$ or $d_{zx}$ orbital through Hund’s rule coupling. RVO$_3$ shows two types of the spin/orbital order concomitantly with the structural phase transition, i.e. $C$-type spin order ($C$-SO)/$G$-type orbital order ($G$-OO) with $P21/b$ monoclinic structure, and $G$-SO/C-OO with $Pbnm$ orthorhombic one$^8$$^9$$^{10}$.$^{11}$. In $C$-OO the electronic configurations of $d_{xy}$$d_{xz}$$d_{yz}$$d_{zy}$ are alternately arranged in ab plane and identical along $c$ axis (Fig. 2(a)), while in G-OO, those are alternately arranged in all three directions (Fig. 2(b)). $C$-type/$G$-type SO patterns are shown in the same manner as the OO as presented in Figs. 2(a) and (b). The transition $T$ of each SO/OO show systematic dependence on the $r_i$$^{12}$. On the other hand, Yan and co-workers investigated the SV effect on the SO/OO order in RVO$_3$$^{14}$. They melt-grew Y$_{1-x}$(La$_{0.2337}$Lu$_{0.7663}$)$_x$VO$_3$ polycrystals, where the average $r_i$ is fixed to be the same as that of $Y^{3+}$. In this system, the change of the V-O-V bond angle is vanishingly small, while the variance linearly increases with $x$. With increasing $x$, the transition $T$ of $G$-SO/$C$-OO is enhanced while those of $C$-SO/$G$-OO are suppressed. Their results have also suggested that in large variance region, there is only one magnetically ordered state. But there are few information about this state.

In RVO$_3$, the SV of $R$-ions seems not only to destabilize one long-range SO/GO, but also to stabilize the other order. To clarify the SV effect in this $t_{2g}$ orbital system, we have investigated the SO/OO in Eu$_{1-x}$(La$_{0.254}$Y$_{0.746}$)$_x$VO$_3$ single crystal. The pure material ($x = 0$) EuVO$_3$ undergoes one pattern of SO/GO order, i.e. a structural phase transition from orthorhombic to monoclinic lattices accompanied with G-OO at 204 K and also a magnetic transition from paramagnetic to C-OO at 131 K, as $T$ is lowered$^{15}$$^{16}$. This compound is located near the phase boundary between two SO/GO states. So we expected that if the large SV actually stabilizes the $G$-SO/$C$-OO, the $G$-SO/$C$-OO would appear in Eu$_{1-x}$(La$_{0.254}$Y$_{0.746}$)$_x$VO$_3$. In these compounds, the average ionic radius of (La$_{0.254}$Y$_{0.746}$)$^{3+}$ is the same as that of Eu$^{3+}$, and the variance linearly in-
In this study, we have measured the magnetization ($M(\text{emu/mol})$) of EuVO$_3$ with changing the SV. Except for $x = 1.0$, the $M$ except for $x = 1.0$ shows a significant jump at 132 K which we assigned as the transition of C-SO ($T_{SO1}$) [15, 16]. The same magnetic transition has been observed below $x \approx 0.8$. In addition, a new anomaly in $T$-dependent $M$, which we defined as $T_{SO2}$, appears in the samples with $x \approx 0.4$, and $T_{SO2}$ increases with $x$. At $T_{SO2}$, the antiferromagnetic spin pattern is changed from C-type to the other one, as described later. With increasing $x$, the magnitude of $M$ at low $T$ decreases, which may be related with the decrease of magnetic Eu$^{3+}$.

Figure 2 presents the spin/orbital phase diagram of Eu$_{1-x}$(La$_{0.25}$Y$_{0.746}$)$_x$VO$_3$ determined by the results in Figs. (c) and (d). $T_{SO1}$ and $T_{SO2}$ decrease with increasing $x$ and vanish above $x \approx 0.8$. As described later, the new anomaly in Fig. (d) accompanies not only the G-SO but also the C-OO, and this transition $T$ ($T_{SO2} = T_{OO2}$) appears above $x \approx 0.4$ and is gradually enhanced with $x$. This suggests that the G-SO/C-OO is stabilized by the SV. With further increasing $x$, only G-SO/C-OO exists near $x = 1.0$.

Figure 3 shows the $T$ dependence of lattice constants $a$, $b$, $c$ as well as $M$ and $C$ for $x = 0$, 0.4, and 1.0 samples [22]. At $T_{OO1}$, $T$ dependence of lattice constants have kinks, and the $C$ has a peak, indicating the structural phase transition from the orthorhombic $Pbnm$ to monoclinic $P2_1/b$ lattices concomitantly with the G-OO as decreasing $T$ (Figs. (a), (b), (d)-(f), and (h)). On the other hand, the anomaly of $M$ and peak of $C$ at $T_{SO1}$ indicate the magnetic transition to C-SO (Figs. (c), (d), (g), and (h)). As shown in Figs. (e)-(l), lattice constants, $M$, and $C$ have anomalies at $T_{SO2} = T_{OO2}$ for

FIG. 1. (Color online) Schematic views of spin (arrows) and orbital order: (a) G-SO/C-OO and (b) C-SO/G-OO. (c) $T$-dependent $M$ for Eu$_{1-x}$(La$_{0.25}$Y$_{0.746}$)$_x$VO$_3$ with applied 1 kOe in zero-field cooling (ZFC) and field cooling (FC) processes. The open green, closed blue, and double red triangles indicate $T_{SO1}$, $T_{SO1}$, and $T_{SO2}$, respectively. (d) $1/M$ as a function of $T$ for these compounds. Except for $x = 1.0$, the dashed lines represent the Curie-Weiss fitting between $T_{SO1}$ and $T_{OO1}$, and solid lines above $T_{OO1}$.
x = 0.4 and 1.0 samples. These results reveal that the magnetic and structural phase transitions occur together at $T_{SO2}$. The changes of lattice constants are very similar to the orbital phase transition to C-OO\textsuperscript{23}. These behaviours suggest the existence of the lower-T orthorhombic phase with the C-OO (and coupled to G-SO).

To confirm the pattern of SO/OO at the ground state above $x = 0.35$, we performed the RXS and ND measurements for the $x = 1.0$ sample. Fig. 4 (a) shows the X-ray absorption spectrum at 300 K for $x = 1.0$. The rising of the absorption spectrum near 5.48 keV is due to the $V K$ main edge. Fig. 4 (b) shows the energy dependence of the intensity of (1 0 0) orbital reflection at various $T$. This reflection does not obey the extinction rule but corresponds to the propagation vectors for C-OO. The symmetry of the degenerated orbital states at each $V^{3+}$ site can be investigated through azimuthal angle dependence of orbital reflections. As shown in Fig. 4 (c), the (1 0 0) reflection normalized by the (2 0 0) fundamental one at the main edge is maximum with the electric vector of incident beam $E_i \parallel b$ configuration and nearly vanishes with $E_i \parallel c$. Model calculations for $\pi'$ and $\sigma'$ components in C-OO are also shown in Fig. 4 (c). (In a simple G-OO model, $\pi'$ and $\sigma'$ components are equal to zero.) In our calculations, the atomic scattering tensor of each $V^{3+}$ ion is the same as that in Ref. [11] and the structural distortion, estimated by the Rietveld analysis for $x = 1.0$, is considered. The good agreement between the experimental and calculated data of each component, shown in Fig. 4 (c), indicates the existence of C-OO.

Figure 4 (d) displays the $T$ dependence of the normalized intensity of the (1 0 0) orbital reflection with the $E_i \parallel b$ configuration at the main edge in a warming run. Figure 4 (e) demonstrates a comparison between $T$ dependences of the integrated intensity of (0 1 1) and (0 1 0) magnetic Bragg reflections measured by ND in a warming run. The (0 1 1) reflection is caused by the G-SO, and the (0 1 0) by the C-SO\textsuperscript{3}. The intensity of the (1 0 0) orbital reflection and (0 1 1) magnetic Bragg reflection are suddenly reduced around $T_{SO2} = T_{OO2}$ as $T$ is increased. These results indicate that the G-SO/C-OO occurs below $T_{SO2} = T_{OO2}$ in the $x = 1.0$ sample. The intensity of (1 0 0) orbital reflection remains finite even above $T_{SO2} = T_{OO2}$, which is caused by the C-OO fluctuation and perhaps the RXS component from local crystal symmetry of space group Pbnm.

The SV generally suppresses the long range order of spin, orbital, and charge. The gradual decrease of $T_{OO1}$ and $T_{SO1}$ with the variance reveals that the SV destabilizes C-SO/G-SO in Eu\textsubscript{1−x}(La\textsubscript{0.254}Y\textsubscript{0.746})\textsubscript{x}VO\textsubscript{3}. However, the appearance of G-SO/C-OO and the increase of $T_{SO2} = T_{OO2}$ with increasing the SV cannot be explained by the general scenario. To account for this anomalous behavior of G-SO/C-OO, one may remember the $R$-site covalency effect\textsuperscript{23, 22}. In Eu\textsubscript{1−x}(La\textsubscript{0.254}Y\textsubscript{0.746})\textsubscript{x}VO\textsubscript{3}, however, the $R$-site covalency is almost constant, because the average ionic radius of $R$-site is unchanged.

On the other point of view, the competition of two SO/OO states in RVO\textsubscript{3} is emphasized\textsuperscript{22}. Among these states, the C-SO/G-OO includes the quasi-one-dimensional (quasi-1D) orbital chain along c-axis, which is described by quasi-1D model for orbital pseudospin ($T = 1/2$). This quasi-1D antiferroic orbital chain strongly
enhanced the quantum orbital fluctuation, and causes 1D optical response and the orbital excitation\cite{11,12,26–30}. When the SV increases, the 1D orbital chain is easily derailed, and 1D orbital correlation (orbital order and fluctuation) is suppressed. As a result, the C-SO/G-OO is destabilized but the competing SO/OO, G-SO/C-OO, is relatively stabilized. Therefore, in the present systems the ground state is changed from C-SO/G-OO to G-SO/C-OO and $T_{\text{SO2}} = T_{\text{OO2}}$ is gradually enhanced with $x$. The G-SO/C-OO phase only exists around $x = 1.0$ in this system, while the SV-free $RVO_3$ always has the C-SO/G-OO at low $T$\cite{13}. This difference between the present system and $RVO_3$ without $R$-ion SV indicates that the destruction of 1D orbital chain by SV of $R$-ions plays an important role of the disappearance of C-SO/G-OO.

We have clarified the spin/orbital phase diagram for $\text{Eu}_{1-x}(\text{La}_{0.254}\text{Y}_{0.746})_x\text{VO}_3$ with controllable cation SV by changing $x$. By increasing SV, G-OO and C-SO tend to be destabilized, while the other ordered phase is stabilized. We confirmed that this spin/orbital ordered state is the G-type/C-type by using ND and RXS measurements, respectively. The SV disturbs 1D orbital chain in the state. The suppression of 1D orbital correlation causes the phase transition from C-SO/G-OO to G-SO/C-OO states.

This study has been approved by the PF Program Advisory Committee (No. 2009S2-008). The ND measurement was performed under the User program conducted by ISSP, Univ. of Tokyo (No. 10402)).

\begin{figure}[h]
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\includegraphics[width=\textwidth]{figure4.png}
\caption{(Color online) Diffraction results for $x = 1.0$ sample of $\text{Eu}_{1-x}(\text{La}_{0.254}\text{Y}_{0.746})_x\text{VO}_3$. (a) X-ray absorption spectrum at 300 K. (b) Photon-energy spectra of the $\sigma^+ + \pi'$ component of (1 0 0) orbital reflection at various $T$. The incident beam has $\sigma$ polarization and $E_i$ is parallel to the $b$ axis. (c) Closed and open circles indicate the intensity of the $\pi'$ and $\sigma'$ components of (1 0 0) reflection normalized by (2 0 0) fundamental one as a function of azimuthal angle. Red solid and dashed lines are model calculations for C-OO of the $\pi'$ and $\sigma'$ components. (d) $T$ dependence of intensity of the $\sigma^+ + \pi'$ component of the normalized (1 0 0) reflection at 5.48 keV. Vertical lines indicate $T_{\text{SO2}} = T_{\text{OO2}}$. (e) $T$ dependence of intensity of (0 1 1) and (0 1 0) magnetic Bragg reflections, indicated by closed and open circles, respectively. $k_i = 2.66\,\text{Å}^{-1}$ is the momentum of incident neutrons.}
\end{figure}

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