PHYSICAL REVIEW B **69**, 100102(R) (2004)

Interplay between structural instability and lattice dynamics in $\mathrm{EuRh_2(P_xAs_{1-x})_2}$

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(Received 30 October 2003; published 22 March 2004)

The interplay between the crystallographic structure, valence state, and lattice dynamics of the series $\mathrm{EuRh_2(P_xAs_{1-x})_2}$ ($x=0$, 0.5, and 1) has been investigated using x-ray diffraction, the ^{151}Eu Mössbauer effect, and the ^{151}Eu nuclear inelastic scattering of synchrotron radiation, respectively. We show that the first-order, isostructural phase transition (α phase→β phase), which occurs at $x_c \approx 0.85$, is not connected with a change of the $\mathrm{Eu^{2+}}$ valence state but is associated with a significant modification of the Eu partial phonon density of states (PDOS). Lattice dynamical calculations on $\mathrm{EuRh_2(P_xAs_{1-x})_2}$ show that the observed change in the PDOS can be attributed to the structural change at the phase transition.

DOI: 10.1103/PhysRevB.69.100102 PACS number(s): 71.27.+a, 63.20.−e, 76.80.+y

In recent years there has been a continuous interest in investiging the ground-state properties of systems in which lattice and electronic degrees of freedom are intimately connected. Known examples are $3d$ and $4d$ transition-metal oxide systems such as $\mathrm{La_{1-x}Sr_xMnO_3}$ (Ref. 1) and $\mathrm{Ca_{2-x}Sr_xRuO_4}$ (Ref. 2). Another interesting class of systems which reveals strong electronic correlation effects is the class of rare-earth (R) transition-metal (T) phosphides $RT_2\mathrm{P}_2$ which crystallize in the tetragonal $\mathrm{ThCr_2Si_2}$-type structure. In these compounds structural phase transitions of first and second order with extremely anisotropic changes of the lattice parameters can be easily induced by changing the composition ($\mathrm{EuRh_{2-x}Co_xP_2}$, Ref. 3), temperature ($\mathrm{EuRh_2P_2}$, Ref. 4), or applying external pressure ($\mathrm{EuCo_2P_2}$, Refs. 5,6). Such a structural instability is due to the existence of two extremely different P-P distances along the c axis which result in two isostructural phases: the α phase for a large P-P distance ($d_{\text{P-P}} \approx 2.8$ Å) with a nonbonding P-P state and the β phase for a short distance ($d_{\text{P-P}} \approx 2.3$ Å), forming a P-P single bond state. The interplay between such structural phase transitions and electronic and magnetic phase transitions has been recently demonstrated by high pressure experiments on $\mathrm{Eu}T_2\mathrm{P}_2$ ($T=\mathrm{Fe,Co}$):[6,7] the pressure-induced $\alpha \to \beta$ structural transition is associated with a valence change from magnetic $\mathrm{Eu^{2+}}$ to nonmagnetic $\mathrm{Eu^{3+}}$ and the disappearance of the Eu ($4f$) sublattice magnetism is accompanied by a simultaneous appearance of Co ($3d$) sublattice magnetism. Also band-structure calculations on $RT_2\mathrm{P}_2$ compounds reveal that the $\alpha \to \beta$ structural phase transition strongly affects the electronic structure of these systems.[8,9]

In this respect, a central issue which has to be addressed is whether and to what extent the $\alpha \to \beta$ structural phase transition is related to a corresponding change of the dynamical properties of the lattice. To provide an answer to this fundamental question, we have investigated the structural, electronic, and lattice dynamical properties of the series $\mathrm{EuRh_2(P_xAs_{1-x})_2}$, $0 \leq x \leq 1$, which crystallizes in the $\mathrm{ThCr_2Si_2}$-type structure in the whole concentration range. This system is an excellent candidate for such a study, since it undergoes an isostructural phase transition by increasing the P concentration (i.e., decreasing the unit-cell volume) above a critical concentration $x_c \approx 0.85$ (Ref. 10). This phase transition is associated with a sharp decrease of the volume of about 9%, which suggests a composition-induced structural phase transition from a nonbonding P-P state (α phase for $x<0.85$) to a single P-P bond state in $\mathrm{EuRh_2P_2}$ (β phase for $x>0.85$).

In this work, using x-ray diffraction, the ^{151}Eu Mössbauer effect (ME), and the ^{151}Eu nuclear inelastic scattering (NIS) of synchrotron radiation, we were able to investigate the interplay between such a structural instability, the valence state of Eu, and the lattice dynamics in $\mathrm{EuRh_2(P_xAs_{1-x})_2}$. We show that the first-order, isostructural phase transition at $x_c \approx 0.85$ is not connected with a change of the $\mathrm{Eu^{2+}}$ valence state, but it is associated with a significant modification of the Eu partial phonon density of states (PDOS). We further show from lattice dynamical calculations on $\mathrm{EuRh_2(P_xAs_{1-x})_2}$ that such a change of PDOS of Eu can be explained by the structural change at the phase transition.

High quality samples of $\mathrm{EuRh_2(P_xAs_{1-x})_2}$, $0 \leq x \leq 1$, were prepared as described in Ref. 3. X-ray diffraction measurements were performed at 300 K using Cu $K\alpha$ radiation with a Siemens D5000 diffractometer in Bragg-Brentano geometry. The analysis of the room-temperature x-ray diffraction data shows that all samples are single phase of the body-centered tetragonal $\mathrm{ThCr_2Si_2}$-type structure (space group $I4/mmm$). ^{151}Eu ME measurements as a function of concentration and temperature were performed using a 100 mCi $^{151}\mathrm{SmF_3}$ source which was kept during the measurements at the same temperature as the absorbers. The setup for the NIS experiment at the undulator beamline ID22N of the ESRF, Grenoble, consisted of a high heat-load monochromator that reduced the energy bandwidth of the 21.542 keV radiation to $\Delta E \approx 3.5$ eV and delivered an x-ray beam with an intensity

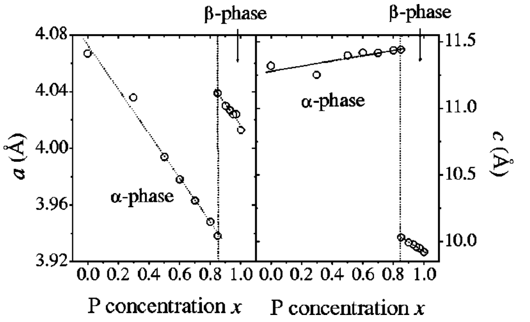

FIG. 1. Lattice parameters a and c of $EuRh_2(P_xAs_{1-x})_2$ at $T=300$ K plotted against the phosphorous concentration x. The dashed lines are guides to the eye.

of $\sim 10^{12}$ photons/s. The beam was further monochromatized to $\Delta E \approx 1.3$ meV by a nested high-resolution monochromator (HRM) using an asymmetric Si(4 4 0) and a symmetric Si(12 8 8) reflection, combined with a collimating Be compound refractive lens.[11–13] The resultant intensity of the beam at the sample was $\sim 6\times 10^7$ photons/s at a storage ring current $I_{SR}=90$ mA. The samples were mounted on a cold finger of a He-flow cryostat. The delayed photons of the nuclear deexcitation were detected by an avalanche photodiode (APD) detector.[14] In order to cover a large solid angle, the APD was placed directly under the sample, outside of the cryostat.

The concentration dependence of the lattice constants a and c of the series $EuRh_2(P_xAs_{1-x})_2$ is plotted in Fig. 1. Starting from $EuRh_2As_2$ (α phase, $x=0$), one observes upon increasing of the P concentration (x) a smooth decrease of a and a slight increase of c. At a critical concentration $x_c \approx 0.85$ one finds an abrupt, slight increase of a ($\Delta a/a \sim 2.5\%$) and a very large decrease of c ($\Delta c/c \sim 12.5\%$). Above x_c the lattice constants a and c decrease smoothly with increasing P concentration up to $x=1$ ($EuRh_2P_2$, β phase). Such a strong anisotropic change of the lattice constants at x_c indicates that the transition from the α to the β phase is associated with a change from the nonbonding state for $0 \leqslant x \leqslant 0.85$ (for $EuRh_2As_2$, $d_{\text{As-As}}=2.97$ Å) to a single bond state for $0.85 \leqslant x \leqslant 1$ with $d_{\text{P-P}}=2.30$ Å for $EuRh_2P_2$.

In order to find out whether the isostructural $\alpha \rightarrow \beta$ phase transition in $EuRh_2(P_xAs_{1-x})_2$ is connected with a change of the valence state of Eu (e.g., $Eu^{2+} \rightarrow Eu^{3+}$ or an intermediate valence state), we have performed systematic ^{151}Eu ME measurements on several samples with $0 \leqslant x \leqslant 1$ at temperatures between 300 K and 4.2 K. In Fig. 2 we show some typical ME spectra in the α phase ($x=0$ and 0.5) and the β phase ($x=1$) collected at 300 K and 4.2 K. At 300 K all samples show a single absorption line with a small asymmetrical broadening due to an unresolved electric quadrupole splitting (ΔE_Q). The position of the absorption line for samples in the α phase ($x=0$ and 0.5) corresponds to an isomer shift $S=-11.3(1)$ mm/s, typical for a Eu^{2+} state, and is shifted towards more positive velocities [$S=-7.6(1)$ mm/s] for the sample in the β phase ($EuRh_2P_2$, $x=1$). This indicates a lower s electron density at the Eu nucleus in the α phase compared to that in the β phase. At 4.2 K the ME spectra (for all samples) show a magnetic hyperfine splitting due to the ordering of the Eu $4f$ moments at low temperatures. This is not surprising since both $EuRh_2As_2$ and $EuRh_2P_2$ display antiferromagnetic order below $T_N \approx 50$ K (Ref. 15). However, the magnitude of the hyperfine splitting, i.e., of the effective hyperfine field B_{eff}, at the Eu nuclei for $EuRh_2P_2$ (β phase) is clearly larger than that for samples in the α phase ($x=0$ and 0.5).

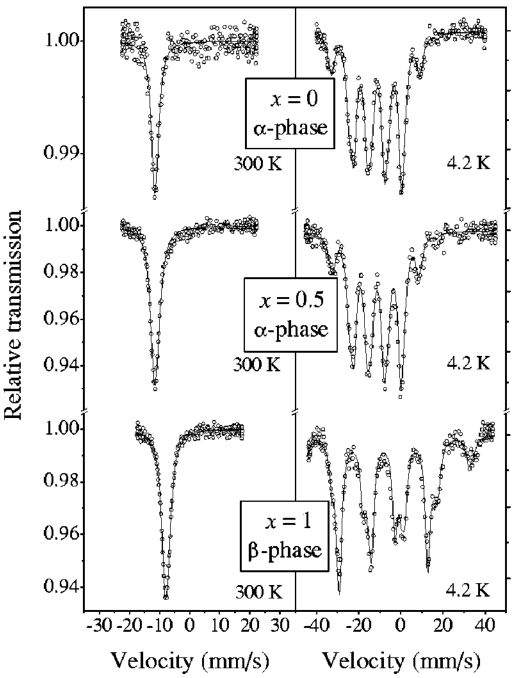

FIG. 2. Mössbauer spectra of $EuRh_2(P_xAs_{1-x})_2$ for $x=0$, 0.5, and 1, at room temperature and 4.2 K. The circles represent experimental data points, while the lines are the fits.

In Figs. 3(a)–3(c) we show the variation of all ME parameters (S, ΔE_Q, and B_{eff}) at $T=4.2$ K as a function of the P concentration. As evident from the figure, all ME parameters show an abrupt change at the critical concentration $x_c \approx 0.85$ for the $\alpha \rightarrow \beta$ structural phase transition. A detailed quantitative analysis of the concentration dependence of the ME parameters will be published elsewhere.[16] Here, we only discuss the stability of the valence state of Eu at the $\alpha \rightarrow \beta$ phase transition. As we mentioned above [see also Fig. 3(a)], there is a large increase of the isomer shift at $x_c \approx 0.85$. We attribute such an increase of S [from $-11.3(1)$ mm/s for $x=0$ to $-7.6(1)$ mm/s for $x=1$] to the volume collapse at the $\alpha \rightarrow \beta$ phase transition. A change of the valence state from Eu^{2+} to a Eu^{3+} (nonmagnetic) state at the $\alpha \rightarrow \beta$ phase transition is ruled out by the observation of long range magnetic order in all samples in the β phase. Also an intermediate valence state of Eu in the β phase ($EuRh_2P_2$) can be excluded by the following argument: the temperature-induced change of the isomer shift between 4.2 and 300 K is found to be of *negative* sign and very weak ($\partial S/\partial T \approx -6\times 10^{-4}$ mm/s/K for $EuRh_2P_2$). Such a negative sign clearly indicates that the electron density at the Eu nucleus decreases with increasing temperature and this is caused by the thermal lattice expansion rather than by a thermal admixture of the Eu^{3+} configuration into the Eu^{2+} ground state. In the latter

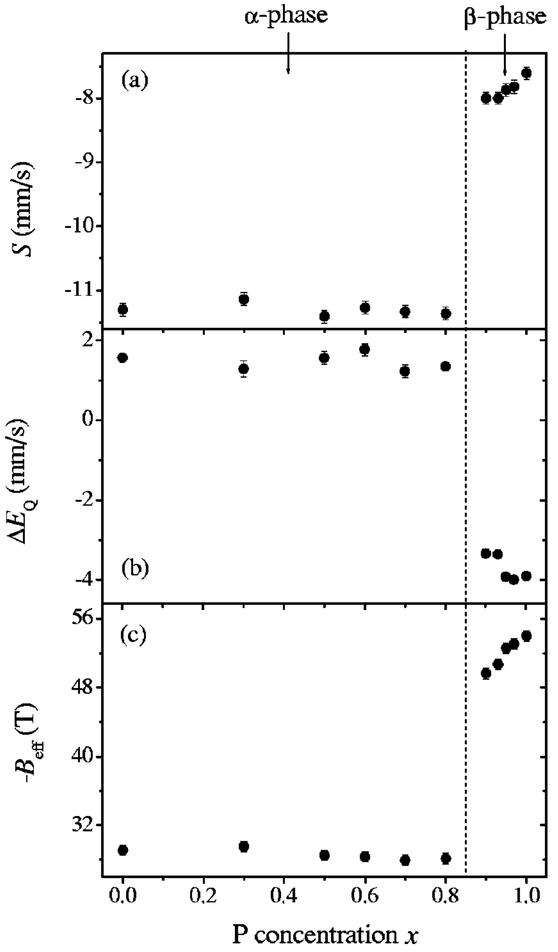

FIG. 3. Variation of the hyperfine parameters of ^{151}Eu in $EuRh_2(P_xAs_{1-x})_2$ at $T=4.2$ K as a function of the phosphorous concentration x as results from the ME measurements: (a) isomer shift S; (b) quadrupole splitting ΔE_Q; (c) hyperfine magnetic field B_{eff}.

case one finds a *positive* and large $\partial S/\partial T$ (Ref. 17). Furthermore, we find that the Néel temperature of $EuRh_2P_2$ increases with increasing pressure up to about 4 GPa ($\partial T_N/\partial p=2$ K/GPa, Ref. 15), suggesting local moment behavior as expected for a stable Eu^{2+} state.[18] These experimental findings clearly show that the isostructural $\alpha\rightarrow\beta$ phase transition in $EuRh_2(P_xAs_{1-x})_2$ is not connected with a change of the Eu^{2+} valence state.

To gain a deeper insight into the nature of the lattice dynamics at the $\alpha\rightarrow\beta$ phase transition we have performed ^{151}Eu NIS measurements on the three compounds with $x=0$, 0.5 (α phase), and 1 (β phase). The NIS technique is a powerful tool to directly determine the partial phonon density of states of Mössbauer nuclei in a given system, which is particularly useful at phase transitions.[19] In our case we can experimentally determine the Eu PDOS and therefore directly relate the structural changes at the $\alpha\rightarrow\beta$ phase transition with the phonon frequencies of Eu atoms in these lattices. The measured spectra are shown in the insets of Fig. 4. In order to sufficiently suppress multiphonon scattering, the measurements have been performed at low temperature $T=100$ K in the paramagnetic phase. Measurements performed on $EuRh_2P_2$ at $T=4.2$ K in the magnetically ordered phase do not show any difference with respect to the 100 K measurements. This indicates that the partial DOS of Eu is not affected by the ordering of the Eu^{2+} magnetic moments. The phonon DOS can be obtained from the measured spectra by a simple iterative procedure as described in Ref. 20. Figure 4 shows the Eu PDOS for the three compounds under study, as extracted from the NIS spectra measured at $T=100$ K. The PDOS of $EuRh_2As_2$ (α phase) shows a dominant peak at an energy of 10.5 meV. The substitution of 50% As by P induces a small decrease of the unit-cell volume ($\sim 2.5\%$), as can be deduced from Fig. 1. However, no change can be observed within the experimental accuracy in the position of the peak in the Eu PDOS of $EuRh_2(P_{0.5}As_{0.5})_2$ as compared to $EuRh_2As_2$, but only a slight broadening of the peak at 10.5 meV. On the other hand, following the $\alpha\rightarrow\beta$ phase transition, the PDOS changes significantly. The main phonon peak of $EuRh_2P_2$ (β phase) is shifted to higher energies (13.5 meV) and a pronounced shoulder appears at even higher energies (~ 16 meV).

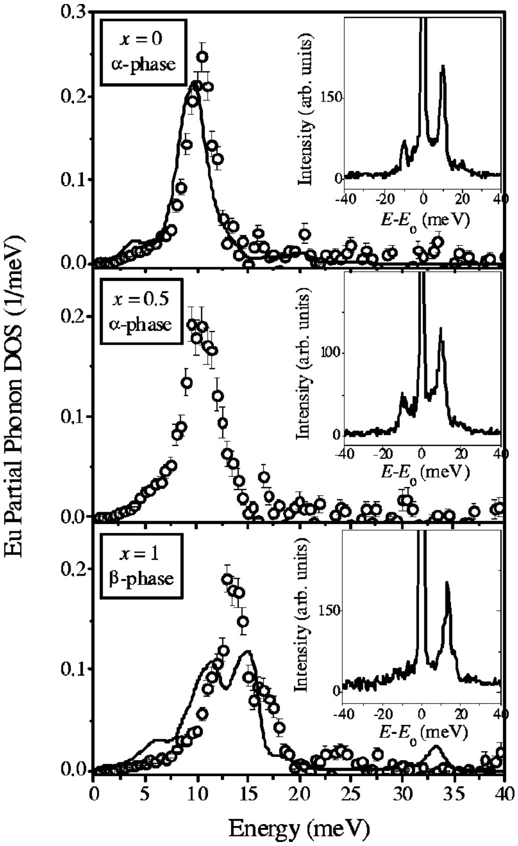

FIG. 4. Eu partial phonon density of states for $EuRh_2(P_xAs_{1-x})_2$ ($x=0$, 0.5, and 1) at $T=100$ K. The circles represent the PDOS as obtained from the measured NIS spectra (shown in the inset of each graph, where $E_0=21.542$ keV is the energy of the^{151}Eu resonance). The lines are calculations as described in the text.

The experimental PDOS can be analyzed within harmonic lattice dynamics. Since the phonon data are restricted to the Eu PDOS, it is not possible to refine a lattice dynamical model. Instead, force constants and potential parameters were estimated from the comparison with structurally related borocarbides[21] and with LaNi and CeNi.[22] A simple model with two force constants per atom pair (radial and transverse) was developed. For all shells with Eu Born-Mayer potentials $[V(r)=Ae^{-r/r_0}]$ were used to determine the force constants. This allows us to simulate the effect of the structural change on the Eu-phonon modes. However, the model should be considered as extremely poor concerning any Rh or P/As contribution. Using the structural parameters as determined by the x-ray diffraction measurements one can get a satisfactory description of the Eu PDOS of $EuRh_2As_2$ (see Fig. 4). With the same Eu potential we calculate the Eu PDOS for $EuRh_2P_2$ just by changing the structural parameters. This $EuRh_2P_2$ model is in reasonable agreement with the experimental PDOS of Eu although the difference to $EuRh_2As_2$ is rather strong. In particular, the strong hardening of the Eu phonon spectrum and the large asymmetrical broadening of the single peak at the $\alpha \rightarrow \beta$ phase transition are well reproduced by this model. These phenomena can therefore be completely attributed to the structural effect: the shorter bond distances between Eu and its neighbors in the β phase yield stronger forces.

In conclusion, the interplay between the structural instability, the valence state of Eu, and lattice dynamics in $EuRh_2(P_xAs_{1-x})_2$ have been investigated using x-ray diffraction, the ^{151}Eu Mössbauer effect, and the ^{151}Eu nuclear inelastic scattering of synchrotron radiation. It is shown that the first order, structural phase transition (α phase $\rightarrow \beta$ phase) at $x_c \approx 0.85$ is not accompanied by a change of the Eu^{2+} valence state but is associated with a significant modification of the Eu partial phonon density of states. Theoretical calculations on samples in the α phase $(x=0)$ and β phase $(x=1)$ reveal that such a large change of the PDOS can be completely explained by the structural change at the phase transition.

This work was financially supported by the Deutsche Forschungsgemeinschaft (SFB 608).

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