学位論文要約

Magnetic, Superconducting, and Phononic Properties in Caged Compounds RT_2Zn_{20} (R: rare-earth, T=Ru, Rh, Os, Ir)

(カゴ状化合物 RT_2Zn_{20} (R: 希土類, T=Ru, Rh, Os, Ir) の磁性, 超伝導およびフォノン物性)

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Rare-earth intermetallic compounds with caged structures have been extensively studied because they show various interesting phenomena such as heavy-fermion states, unconventional superconductivity, and multipole ordering. Recently, such phenomena have been reported in a family of RT_2Zn_{20} (R: rare-earth, T: transition metal). $YbCo_2Zn_{20}$ has the largest electronic specific heat coefficient of 8 J/(K^2 mol) among the intermetallic rare-earth compounds. PrT_2Zn_{20} (T=Rh, Ir) with non-Kramers doublet ground states show superconducting transitions in the presence of antiferroquadrupole orders. On the other hand, since they have a cage-like structure, it is expected that low-energy vibrations of guest ions in the atomic cages may play a role in the physical properties. RRu_2Zn_{20} (R=La, Pr) and $LaIr_2Zn_{20}$ exhibit structural transitions at T_s=150, 138, and 200 K, respectively. The first principles calculation of LaT_2Zn_{20} (T=Ru, Ir) pointed out that the Zn atom at the 16c site in the R_2Zn_{12} cage vibrates at low frequencies, and the vibration would be related to the structural transition.

In the present work, to detect the low-energy vibration of the Zn(16c) atom and reveal the interplay between the vibration of the Zn atom and the structural transition, specific heat, inelastic x-ray scattering, and Raman scattering measurements for RT_2Zn_{20} (R=La, Pr, Y, T=Ru, Rh, Os, Ir) have been performed. In addition, to investigate systematically the magnetic, transport, and structural properties of RT_2Zn_{20}, we have focused on new isostructural compounds ROs_2Zn_{20} (R=La, Ce, Pr, Nd). In the caged compounds, the vibrational energy of the guest atoms could be lowered by expanding the cage. Since the lattice constants of the compounds with T=Os are the largest among RT_2Zn_{20} (T=Ru, Rh, Os, Ir), the low-energy vibration of Zn(16c) could contribute to the physical properties. Thereby, the electrical resistivity, ac and dc magnetic susceptibilities, and specific heat of ROs_2Zn_{20} have been measured in the temperature range from 0.04 to 300 K.

(1) Low-energy Zn vibration in RT_2Zn$_{20}$ (R=Y, La, Ce, Pr, Nd, T=Ru, Ir)

For the $LaRu_2Zn_{20}$, the temperature dependence of the lattice specific heat divided by temperature cubed, $C_{\rm lat}/T^3$, exhibits a peak at around 15 K. The analysis of $C_{\rm lat}/T^3$ using the Debye and Einstein models indicates the presence of two Einstein modes with characteristic temperatures of 35 and 82 K, respectively. The IXS measurements of $R\mathrm{Ru_2Zn_{20}}$ (R=La, Pr) revealed the phonon dispersion relation of the transverse modes along the [110] direction and the longitudinal ones along the [111] direction. Along the [111] and [110] directions, weakly dispersive phonon excitations were found, respectively, at around 3 and 7 meV, whose energy values agree with the Einstein temperatures. The 3 meV phonon mode in $PrRu_2Zn_{20}$ is also observed by the Raman scattering measurement. The first principles calculation allows us to identify the optical phonon mode at 3 meV as the low-energy vibration of Zn (16c). On the other hand, in $PrIr_2Zn_{20}$ with no structural transition, the corresponding optical phonon mode was not found at 3 meV. The smaller-size cage surrounding Zn(16c) in $PrIr_2Zn_{20}$ probably shifts the optical phonon modes to higher energy of 7 meV, which would hinder the structural transition.

(2) Magnetic and transport properties of $R\mathrm{Os_2Zn_{20}}$ (R=La, Ce, Pr, and Nd)

The specific heat and electrical resistivity measurements of $R\mathrm{Os_2Zn_{20}}$ revealed that all the compounds exhibit structural transitions. The lattice specific heat analysis of $LaOs_2Zn_{20}$ shows the existence of optical phonon modes with Einstein temperatures of 34 K and 76 K. It is probably attributed to the low-energy vibration of Zn (16c), because the value is almost the same as those of $LaRu_2Zn_{20}$. The transition temperature $T_{\rm s}$ is decreased by following the lanthanoid contraction. This fact implies that the high temperature phase is stabilized by the increase of the vibration energy of the guest atom due to the shrinkage of the cage.

Concerning the magnetic properties, the magnetic susceptibility of $CeOs_2Zn_{20}$ is order of 10^{-3} emu/mol and the Sommerfeld coefficient is approximately ten times larger than that of $LaOs_2Zn_{20}$, indicating that the Ce ions are in valence fluctuating states. For $NdOs_2Zn_{20}$, a ferromagnetic transition was observed at 0.6 K. The CEF ground state was determined to be a Kramers doublet by the mean field calculation. $PrOs_2Zn_{20}$ displays a peak at around 14 K in the magnetic specific heat, and the peak is reproduced by a

two-level model with a doublet ground state and a triplet excited state separated by an energy of Δ=35 K. However, the doubly degenerated ground sate is probably lifted at $T < T_{\rm s}$ by the symmetry lowering of the Pr site. Thereby, no magnetic or quadrupole order manifests itself down to 0.04 K. On the other hand, $PrOs_2Zn_{20}$ undergoes a superconducting transition at $T_{\rm SC}$=0.06 K. The superconducting transition was also observed in La counterpart $LaOs_2Zn_{20}$ at $T_{\rm SC}$=0.07 K. The initial slope of the upper critical field of $PrOs_2Zn_{20}$ is about three times larger than that of $LaOs_2Zn_{20}$, suggesting a larger value of effective mass of $PrOs_2Zn_{20}$.

In summary, we have studied the phononic properties of RT_2Zn_{20} (R=Y, La, Ce, Pr, Nd, T=Ru, Ir). The low-energy phonon modes of Zn(16c) in $R Ru_2Zn_{20}$ (R=La, Pr) are observed at 3 meV, although those of $PrIr_2Zn_{20}$ showing no structural transition shift to higher energy of 7 meV. This fact implies that the 3 meV mode induces the structural transition in $R Ru_2Zn_{20}$ (R=La, Pr). In new isostructural compounds $R Os_2Zn_{20}$ (R=La, Ce, Pr, Nd), structural transitions are observed. The transition temperature decreases with shrinking the cage size, suggesting that the cage size is a decisive parameter for the occurrence of the structural transition. $CeOs_2Zn_{20}$ and $NdOs_2Zn_{20}$ exhibit valence fluctuations and ferromagnetic transition, respectively. Since the CEF ground state of $PrOs_2Zn_{20}$ is probably a non-magnetic singlet, there appears no magnetic or quadrupole order. In $LaOs_2Zn_{20}$ and $PrOs_2Zn_{20}$, superconducting transitions were found at $T_{\rm SC}$=0.07 K and 0.06 K, respectively.