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# Raman scattering spectra of LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>

K Nagano<sup>1</sup>, T Hasegawa<sup>1</sup>, N Ogita<sup>1</sup>, M Udagawa<sup>1, 2</sup>, H Tanida<sup>3</sup>, D Tanaka<sup>3</sup>, M Sera<sup>3</sup>, T Nishioka<sup>4</sup> and M Matsumura<sup>4</sup>

<sup>1</sup> Graduate School of Integrated Arts and Sciences, Hiroshima University, Higashi-Hiroshima 739-8521, Japan

<sup>2</sup> Institute for Advanced Material Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

<sup>3</sup> Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

<sup>4</sup> Graduate School of Integrated Arts and Sciences, Kouchi University, Kochi 780-8520, Japan

E-mail: m114128@hiroshima-u.ac.jp

**Abstract**. Phonon spectra of LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub> have been studied by Raman scattering from 3.4K to 300K. Polarization dependence at room temperature gives the precise mode assignment for the sake of first principles calculation results. The measured Raman spectra are well explained by the space group Cmcm and there is no remarkable difference between LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>. Since we observed no anomaly at T<sub>0</sub> = 27K in CeRu<sub>2</sub>Al<sub>10</sub>, the lattice distortion due to the structural transition has not been detected. From the temperature dependence of the vibrational frequency of Ce and La, their vibrational amplitude is not large in CeRu<sub>2</sub>Al<sub>10</sub> and LaRu<sub>2</sub>Al<sub>10</sub>, that is, close to harmonic case.

#### 1. Introduction

CeRu<sub>2</sub>Al<sub>10</sub> has the orthorhombic YbFe<sub>2</sub>Al<sub>10</sub>-type structure with space group Cmcm [1]. CeRu<sub>2</sub>Al<sub>10</sub> shows the transition at  $T_0 = 27K$  [2-4], while LaRu<sub>2</sub>Al<sub>10</sub> shows no anomaly. It is reported that this transition is the antiferromagnetic order [5, 6], but the Ce moments appear along c-axis determined by neutron diffraction [5], in spite of the magnetic easy axis along the a-axis. This discrepancy and the origin of this magnetic order are not well understood, and the transition temperature is too high for the RKKY interaction. On the other hand, spin-Peierls transition was suggested to explain the peculiar temperature dependence of resistivity [7]. In this case, the lattice distortion should follow [8].

To clarify whether the lattice distortion exists or not below  $T_0$ , the phonon Raman scattering spectra have been measured for LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>. Since the lattice distortion accompanies with new peaks in Raman scattering spectra, the additional peaks judge the existence of the distortion. In addition, CeRu<sub>2</sub>Al<sub>10</sub> was suggested as a cage compound [9]. In the large cage with a small guest atom, the vibration of the guest atom becomes anharmonic and this anharmonicity is experimentally determined by the energy decrease of the vibrational frequency with decreasing temperature [10, 11]. To clarify the characteristic feature of CeRu<sub>2</sub>Al<sub>10</sub>, LaRu<sub>2</sub>Al<sub>10</sub> was employed as the reference, where LaRu<sub>2</sub>Al<sub>10</sub> does not show the phase transition.

#### 2. Experimental

We employed single crystals of LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>. They were grown by the Al selfflux method. Three different surfaces with (100), (010), and (001) planes were polished by alumina powder with 0.05  $\mu$  m in diameter to reduce the diffuse scattering of the incident light. Raman scattering spectra were analyzed by the triple-monochromator (JASCO NR-1800) and detected by the liquid-N<sub>2</sub> cooled charge coupled device (CCD) detector (Princeton Instruments Inc. LN/CCD-1100PB). For excitation light, the 514.5nm line of the Ar<sup>+</sup> laser (Spetra Physics Stabilite 2017 Ion Laser) was employed and the natural emission lines of the Ar<sup>+</sup> laser were excluded by the premonochromator. For the measurements at low temperatures, the cryostat cooled by the GM cryocooler (SHI SRDK-205) was used. The energy of the measured spectra was calibrated using natural emission lines of a He-Ne laser.

YbFe<sub>2</sub>Al<sub>10</sub> type structure gives the Raman active modes as  $10A_g + 9B_{1g} + 6B_{2g} + 8B_{3g}$ . These modes can be separately observed in the six polarization geometries. The polarization geometry is denoted by (I,S), where I and S are the polarization directions of the incident and scattered light, respectively. In this study x, y, z were [1,0,0], [0,1,0], and [0,0,1], respectively. In (x,x), (y,y), and (z,z) polarization geometries  $A_g$  modes can be observed, and  $B_{1g}$ ,  $B_{2g}$ , and  $B_{3g}$  mode are observed in (x,y), (z,x), and (y,z), respectively. Since there are two rare-earth atoms in the primitive cell, their degree of freedom is decomposed as  $A_g + B_{1g} + B_{3g} + B_{1u} + B_{2u} + B_{3u}$  and the Raman active modes are  $A_{g}$ ,  $B_{1g}$  and  $B_{3g}$  among them. Other Raman active modes are the vibrations of Al.

#### 3. Results and discussion

Polarization dependence at room temperature is shown in Fig.1, where solid triangles denote the phonon peaks in each symmetry and cross marks denote the natural emission peaks of  $Ar^+$  laser. The open square marks observed in (y,y) polarization are  $B_{3g}$  modes, because the polarization direction of the incident laser was slightly inclined from the b-axis. The observed lattice vibrations are  $10A_g + 8B_{1g} + 6B_{2g} + 8B_{3g}$ , which are close to  $10A_g + 9B_{1g} + 6B_{2g} + 8B_{3g}$  predicted by group theory.



Fig.1: Polarization dependence of Raman spectra of  $LaRu_2Al_{10}$  and  $CeRu_2Al_{10}$  at room temperature. The triangle marks denote the assigned modes and cross marks show the natural emission peaks of the incident laser. The open square marks observed in (y,y) polarization are  $B_{3g}$  modes.

No.		1	2	3	4	5	6	7	8	9	10
Ag	La	107.4	133.5	180.1	197.8	246.5	281.4	320.4	336.3	363.2	388.6
	Ce	106.1	129.8	174.7	197.3	245.3	285.9	315.9	330.6	364.8	386.8
B <sub>1g</sub>	La	99.4	171.0	193.5	217.4	-	288.5	319.2	334.9	378.2	
_	Ce	96.6	166.7	192.6	215.9	-	288.2	322.6	336.5	384.9	
B <sub>2g</sub>	La	165.5	234.9	273.6	288.2	311.7	435.0				
_	Ce	165.7	241.0	278.7	294.4	314.6	443.5				
B <sub>3g</sub>	La	106.1	156.8	187.5	210.1	242.8	313.4	349.6	376.6		
_	Ce	102.2	154.7	189.3	216.4	244.6	315.3	354.0	369.3		

Table1: Phonon energies of LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub> and their assignment. Energy unit is cm<sup>-1</sup>.

Thus, the present result is consistent with the crystal structure with space group Cmcm, though one  $B_{1g}$  mode is missing due to its weak intensity. Remarkable difference between LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub> has not been found.

The observed frequencies and their assignments are summarized in Table1. The vibrational frequencies of the rare-earth ions are about  $105 \text{cm}^{-1}$  and  $130 \text{cm}^{-1}$  in  $A_g$  modes,  $100 \text{cm}^{-1}$  in  $B_{1g}$  mode, and  $105 \text{cm}^{-1}$  in  $B_{3g}$ . These were determined by the comparison with the first principle calculation result [12]. The rare-earth vibration in  $A_g$  mode becomes two vibrations due to the hybridization between the rare-earth and Al modes.

We discuss the phonon frequency difference between La and Ce from the structural point of view. The lattice parameter of  $LaRu_2Al_{10}$  is larger by a = 0.041 Å, b = 0.028 Å, and c = 0.031 Å than those of  $CeRu_2Al_{10}$  [1]. The ionic diameter of  $La^{3+}$  is larger by 0.054 Å than that of  $Ce^{3+}$  [13]. Therefore, the change of ionic diameter is larger than that of the lattice parameters. Thus, the force constants between La and Al should be stronger than those between Ce and Al. While the force constants between Al and Al for  $LaRu_2Al_{10}$  are weaker than those for  $CeRu_2Al_{10}$ , because of the lattice parameter increase. Therefore, the frequency of the Ce vibration will be lower than that of La, and the frequencies of the Al vibrations in  $CeRu_2Al_{10}$  may be higher than those of  $LaRu_2Al_{10}$ . The La/Ce vibration satisfies this tendency. However, some modes of the Al vibrations violate this tendency. In table1, the corresponding modes with larger energy-decrease than  $4cm^{-1}$  are shown by square. This anomaly can be explained by a difference of charge distribution between  $LaRu_2Al_{10}$  and  $CeRu_2Al_{10}$ .



Fig.2: Raman spectra of  $CeRu_2Al_{10}$  at 3.4K and 300K. The triangle marks denote the assigned modes in table1. The cross marks are the natural emissions of the incident laser. The square marks observed in (y,y) polarization are  $B_{1g}$  modes, because the polarization direction of the incident laser was slightly inclined from the b-axis.

Temperature dependence of Raman spectra has been measured from 3.4K to 300K for LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>. Raman spectra of CeRu<sub>2</sub>Al<sub>10</sub> at 3.4K and 300K are shown in Fig.2. If the lattice deforms, new peaks should appear in Raman spectra. However we have not found any new peak between 3.4K and 300K in LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub> in the present experimental accuracy. Therefore, the lattice distortion does not occur below  $T_0 = 27K$  in CeRu<sub>2</sub>Al<sub>10</sub>. The vibration of La/Ce is harmonic, since the remarkable energy decrease has not been observed.

### 4. Conclusions

We have investigate the phonon Raman spectra of single crystalline LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>. We have successfully assigned the observed 32 peaks as  $10A_g + 8B_{1g} + 6B_{2g} + 8B_{3g}$  by the polarization dependence. The observed Raman spectra are well explained by the space group Cmcm. The lattice distortion has not been observed below  $T_0 = 27K$  in CeRu<sub>2</sub>Al<sub>10</sub>, judging from no additional peaks at 3.4K. We have found the possibility of the electronic state difference by the phonon energy difference between LaRu<sub>2</sub>Al<sub>10</sub> and CeRu<sub>2</sub>Al<sub>10</sub>.

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# References

- [1] Thieda V M T, Ebel T, and Jeitxchko W 1998 J. Mater. Chem. 8 125.
- [2] Strydom A M 2009 *Physica* B **404** 2981
- [3] Nishioka T, Kawamura Y, Takesaka T, Kobayashi R, Kato H, Matsumura M, Kodama K, Matsubayashi K, and Uwatoko Y 2009 *J. Phys. Soc. Jpn.* **78** 123705
- [4] Muro Y, Motoya K, Saiga Y, and Takabatake T 2010 J. Phys.: Conf. Series 200 012136
- [5] Khayavin D D, Adroja D T, Strydom A M, Manuel P, Chapon L C, Peratheepan P, Knight K, Deen P, Ritter C, Muro Y, and Takabatake T 2010 *Phys. Rev.* B **82** 100405(R)
- [6] Robert J, Mignot J M, Andre G, Nishioka T, Kobayashi R, Matsumura M, Tanida H, Tanaka D, and Sera M 2010 *Phys. Rev.* B **82** 100404(R)
- [7] Hanzawa K 2010 J. Phys. Soc. Jpn. 79 043710
- [8] Hanzawa K 2010 J. Phys. Soc. Jpn. 79 084704
- [9] Tanida H, Tanaka D, Sera M, Tanimoto S, Nishioka T, Matsumura M, Ogawa M, Moriyoshi C, Kuroiwa Y, Kim J E, Tsuji N and Takata M 2011 Phsy. Rev. B 84 115128
- [10] Udagawa M, Hasegawa T, Takasu Y, Ogita N, Suekuni K, Avila M A, Takavatake T, Ishikawa Y, Takeda N, Nemoto Y, Goto T, Sugawara H, Kikuchi D, Sato H, Sekine C, Shirotani I, Yamaura J, Nagao Y and Hiroi Z 2008 J. Phys. Soc. Jpn. 77 Suppl. A 142
- [11] Takasu Y, Hasegawa T, Ogita N, Udagawa M, Avila M A, Suekuni K, Ishii I, Suzuki T and Takabatake T 2006 Phys. Rev. B 74 174303
- [12] Hasegawa unpublished.
- [13] Templeton D H, and Dauben C H 1961 *The rare earth*, ed F I Spedding and A H Daane (New York, John Wiley) p 20