Raman scattering study in iridium pyrochlore oxides

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Abstract. Raman scattering spectra of iridium pyrochlore oxides R$_2$Ir$_2$O$_7$ (R=Nd, Sm, and Eu) have been measured. These three compounds undergo metal-insulator transition. Below the transition temperature $T_{MI}$, new peaks appear for R = Sm and Eu, but no remarkable change for R = Nd. Therefore, Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$ accompany structural change with the transition, but not the case for Nd. Even if Nd$_2$Ir$_2$O$_7$ deforms, the distortion is different from that of Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$, because the spectra of Nd are clearly different from those of Sm and Eu below $T_{MI}$.

1. Introduction

Pyrochlore iridium oxides R$_2$Ir$_2$O$_7$ with rare-earth ion R show metal-insulator transition. Yanagishima and Maeno[1] have reported resistivity data of R$_2$Ir$_2$O$_7$ for wide variety of rare-earth atoms. They have shown that the pyrochlore iridium oxides are metallic for large R and become nonmetallic for smaller R. The metal-insulator transition has been found between Eu and Gd. On the other hand, Taira et al.[2] have reported magnetic transition around 120 K for R=Y, Sm, Eu and Lu. The magnetic transition is similar to spin-glass transition, since small frozen magnetic moment appears below the transition temperature under field-cooled measurement and the magnetic susceptibility is different from that under zero-field-cooled measurement. Since this transition is found for Y and Lu without magnetic moments, the origin of the transition is expected to be an order of magnetic moment of Ir. Recently, Matsuhira et al.[3] have reported resistivity of Pr, Nd, Sm and Eu compounds. They found that the resistivity of R = Sm and Eu shows upward turn below the transition temperature and also that Nd$_2$Ir$_2$O$_7$ shows similar upturn in resistivity. Therefore, the magnetic transition of R = Sm and Eu accompanies metal-insulator transition. The metal-insulator transition temperatures $T_{MI}$ are 36, 117 and 120 K for R = Nd, Sm and Eu, respectively. For Pr, the resistivity shows no kink structure but a minimum around 40 K[4] like the Kondo effect. The metal-nonmetal boundary will locate between Pr and Nd, though the electronic transport property is quite complicated in the iridium pyrochlore oxides.

The metal-insulator transition of R = Sm accompanies magnetic transition. If this magnetic transition occurs on Ir, this electronic state change at $T_{MI}$ will give us a possibility of structural deformation, because it affects largely chemical bonding between Ir and O. Thus, the study of
the structural deformation will shed light on mechanism of the transition. In this paper, we have measured temperature dependences of Raman spectra for R = Nd, Sm and Eu to investigate whether they undergo structural deformation below $T_{MI}$ or not.

2. Experimental procedure

Single crystal of Nd$_2$Ir$_2$O$_7$ and sintered samples of powder of Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$ was used in this study. The single crystal fo Nd$_2$Ir$_2$O$_7$ is prepared by KF-flux method previously reported in ref. [5]. Preparation method of these sintered samples has been described previous report[3], where the sample #2 of Sm$_2$Ir$_2$O$_7$ has been employed in this present paper. The single crystal of Nd$_2$Ir$_2$O$_7$ has a clear triangle (111) surface. Raman spectra were measured on the (111) surfaces for Nd$_2$Ir$_2$O$_7$.

Raman scattering spectra were measured using a triple-monochromator (JASCO NR-1800) with a liquid-N$_2$ cooled CCD detector (Princeton Instruments Inc. LN/CCD-1100PB). Excitation light was 514.5nm line of an Ar$^+$ laser and its power was 10 mW before a sample surface. For the measurements at low temperatures, a cryostat cooled by a GM cryocooler (SHI SRDK-205) was used. The samples were set in He atmosphere.

3. Result and Discussion

Space group of undeformed pyrochlore structure is Fd3m, and its irreducible representations of Raman active phonons are $A_{1g} + E_g + 4T_{2g}$. To determine the irreducible representation of observed peaks, we have measured polarization dependences of the Nd$_2$Ir$_2$O$_7$ single crystal on the (111) surface. On the (111) surface, Raman spectra does not depend on polarization of incident light, but depends only on angle of polarization of scattered light from that of incident light. Therefore, there are two independent spectra for parallel and perpendicular polarizations. We can assign the irreducible representations from intensity ratio of two spectra.

Figure 1 shows these two spectra of Nd$_2$Ir$_2$O$_7$ at room temperature together with assignment of peaks. In this figure, ‘pol’ and ‘depol’ mean parallel and perpendicular polarization spectra, respectively. A peak at 506 cm$^{-1}$ is assigned to $A_{1g}$ mode because of strong suppression of intensity in ‘depol’ spectra. Three peaks at 303, 342, and 618 cm$^{-1}$ have the same intensity ratio, and a very weak peak at 549 cm$^{-1}$ also has the same intensity ratio in an experimental accuracy. Then, they could be assigned to four $T_{2g}$ modes. However, as we will see later, the peak at 342 cm$^{-1}$ vanishes at low temperatures for R = Sm and Eu. Therefore, the peak at
342 cm$^{-1}$ does not correspond to a simple phonon excitation, and is labeled as P1. The other three peaks are assigned to T$_{2g}$. The remaining peaks at 392 cm$^{-1}$ and 657 cm$^{-1}$ show intensity ratios that don’t agree with the ratio of any single irreducible representation, and are labeled as P2 and P3, respectively. The peak P3 has often been reported as second order scattering for pyrochlore oxides (e.g. refs. [6, 7]), though its origin has still been unclear. The peak P2 may be remaining E$_g$ or T$_{2g}$ overlapped by broad excitation P1. In summary, we assign four modes, A$_{1g}$+3T$_{2g}$, and observe three other peaks that are unassigned at this stage. Figure 2 shows ‘pol’ spectra at room temperature for R = Nd, Sm and Eu. These spectral shapes are quite similar to each other. Then, we apply the assignments of R = Nd to those for R = Sm and Eu.

Figure 3 shows ‘pol’ spectra at 4 K for R = Nd, Sm and Eu. The spectrum of R = Nd is not changed from the spectrum at room temperature qualitatively. However, in the spectra of R = Sm and Eu, at least three new peaks (N1, N2 and N3) appear (N1 is doublet for R = Eu). Therefore, we can conclude that the symmetry of the structure is lowered at low temperature in R = Sm and Eu. Although these new peaks have not been found below T$_{MI}$ in R = Nd, there is a possibility that strong low-energy peak obscures the weak peaks. Thus, structural change in R = Nd cannot be evaluated from these new peaks. In addition, the P1 peak is not found at 4 K for R = Sm and Eu. This result leads the conclusion that P1 is not a simple excitation, as mentioned above. On the other hand, invariance of the spectral shapes of R = Nd suggests that structural change of R = Nd is absent or very small beyond the experimental accuracy. Since small increase of energy has been found below T$_{MI}$ for R = Nd, very small structural change may be present. We can conclude that structure of R = Nd below T$_{MI}$ is at least different from that of R = Sm and Eu, because temperature dependence of P1 is quite different. The temperature dependence of the spectra for R = Eu are shown in Fig. 4. We can see that the intensity of P1 becomes weak at low temperatures. P1 vanishes around T$_{MI}$, 120 K. Below T$_{MI}$, energies of P2 and A$_{1g}$ shift clearly, and new peaks appear. These behaviors have been also observed for R = Sm.

The intensity of N1 and the energies of P2 and A$_{1g}$ at various temperatures are shown in Fig. 5 and Fig. 6, respectively. These temperature dependences are complicated. The intensity of N1 is very small above 100 K and increases rapidly below 100 K. The energy of A$_{1g}$ gradually decreases below T$_{MI}$ and remarkably decreases below 100 K. The energy of P2 suddenly diminishes around 120 K, and takes minimum. Then, the energy of P2 increases at low temperatures. From these temperature dependences, we can see that the structural distortion occurs largely below 100 K in addition to small distortion below 120 K. Since the phase transition has been found only at 120 K, these complex variations will be caused by anomalous development of an order parameter.
Figure 5. Temperature dependence of intensity of N1 mode in Eu$_2$Ir$_2$O$_7$.

Figure 6. Temperature dependence of energies of $A_{1g}$ (top) and $P_2$ (bottom) in Eu$_2$Ir$_2$O$_7$.

or peculiar coupling mechanism between these phonons and the order parameter.

Now, we discuss the structure below $T_{MI}$ for R = Sm and Eu. The subgroups of Fd3m with the highest symmetry are F̅43m, Fd3 and F4$_1$32. Among them, only F̅43m is achieved by structural distortion in the pyrochlore structure. For F̅43m, Raman active phonons become 4$A_1$+4$E$+11$T_2$. Thus, 13 additional peaks should appear. The present result is not sufficient to discuss the subgroup symmetry, since we have found three or four peaks below $T_{MI}$.

4. conclusion

Raman spectra of Nd$_2$Ir$_2$O$_7$, Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$ have been studied from 4 K to 300 K to investigate their structures below metal-insulator transition temperature, $T_{MI}$. At least three peaks have appeared below $T_{MI}$ for Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$. Therefore, these two compounds undergo structural change losing some symmetry under the transition. On the other hand, Raman spectra of Nd$_2$Ir$_2$O$_7$ have not shown any qualitative change. This suggests that Nd$_2$Ir$_2$O$_7$ has no or very small structural distortion below $T_{MI}$. Even if Nd$_2$Ir$_2$O$_7$ deforms below $T_{MI}$, the distortion is different from that of Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$, because the peak P1, which vanishes around $T_{MI}$ for Sm$_2$Ir$_2$O$_7$ and Eu$_2$Ir$_2$O$_7$, is clearly found even at 4 K for Nd$_2$Ir$_2$O$_7$.

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