Elastic softening in HoFe$_2$Al$_{10}$

S. Kamikawa$^{1*}$, I. Ishii$^1$, Y. Noguchi$^1$, H. Goto$^1$, T.K. Fujita$^1$, F. Nakagawa$^1$,
H. Tanida$^1$, M. Sera$^1$, and T. Suzuki$^1$

$^1$Hiroshima University, Higashihiroshima, Japan
d140235@hiroshima-u.ac.jp, ish@hiroshima-u.ac.jp, tsuzuki@hiroshima-u.ac.jp

Abstract
To investigate the $4f$-electronic states under the crystal electric field (CEF) in HoFe$_2$Al$_{10}$, we carried out ultrasonic and specific heat measurements on single-crystalline samples. We found elastic softening of the transverse elastic modulus $C_{55}$ below 20 K and two Schottky peaks at 2 and 20 K in the magnetic specific heat. By theoretical analyses of the modulus and the magnetic specific heat based on the CEF theory, we reproduced the elastic softening and the two Schottky peaks, and obtained the CEF parameters.

Keywords: HoFe$_2$Al$_{10}$, crystal electric field, elastic modulus, specific heat, elastic softening

1 Introduction
A series of ternary compounds $LnM_2$Al$_{10}$ ($Ln$ = rare earth, $M$ = Fe, Ru, Os) crystallizes into the orthorhombic YbFe$_2$Al$_{10}$-type structure with the space group $Cmcm$. At the early researches, Thiede et al. reported the magnetism of polycrystalline $Ln$Fe$_2$Al$_{10}$. Recently, $Ln$M$_2$Al$_{10}$ was studied extensively not only for $M$ = Fe but also for $M$ = Ru and Os by using single crystals. The magnetic properties of $Ln$M$_2$Al$_{10}$ are usually considered to originate from the $4f$-electrons of $Ln$ ion. This is because the $d$-electrons of $M$ ion are in the closed-shell condition. The band calculation for isomorphic compound LaRu$_2$Al$_{10}$ revealed that the $4d$-electron bands of the Ru ion are at about 0.2 Ry below the Fermi level and there is little contribution of the $d$-electron near Fermi level. It is believed that the similar situation commonly exists in $Ln$M$_2$Al$_{10}$. In fact, the effective magnetic moments of most of $Ln$M$_2$Al$_{10}$ are close to the value expected for the $4f$-electron contribution of the free $Ln^{3+}$ ions. Most of $Ln$M$_2$Al$_{10}$ compounds show the antiferromagnetic ordering of localized $4f$-electron at low temperatures. However, CeM$_2$Al$_{10}$ exhibits a Kondo semiconducting behavior, indicating the $4f$-electrons are itinerant. Therefore, $Ln$M$_2$Al$_{10}$ has rich variety of the $4f$-electronic properties from the localized magnetism to the strongly correlated electronic property.

To investigate the $4f$-electronic states in $Ln$M$_2$Al$_{10}$, we have performed ultrasonic measurements on $Ln$M$_2$Al$_{10}$, systematically. In this work, we focus on HoFe$_2$Al$_{10}$. The magnetic susceptibility of polycrystalline HoFe$_2$Al$_{10}$ shows a Curie-Weiss behavior above 50 K. The effective magnetic
moment estimated in the experiment is 10.6(1) μB. The value is the same as the theoretically expected moment 10.60 μB of the free Ho\(^{3+}\) ion with the total angular momentum \(J = 8\). This result indicates that the 4\(f\)-electrons in the Ho\(^{3+}\) ion are almost localized. The specific heat divided by temperature of HoFe\(_2\)Al\(_{10}\) exhibits the Schottky peak at 1.5 K, suggesting that the energy gap between the ground and first excited state is estimated to be within 3 K.\(^6\) Here, the degeneracy of total angular momentum of the 4\(f\)-electrons in the free Ho\(^{3+}\) ion is lifted by the orthorhombic CEF.

2 Experimental

We adopted the Al self-flux method to grow single-crystalline HoFe\(_2\)Al\(_{10}\) and non-magnetic reference compound LuRu\(_2\)Al\(_{10}\). The lattice parameters of HoFe\(_2\)Al\(_{10}\) are \(a = 8.953\) Å, \(b = 10.137\) Å, and \(c = 8.997\) Å, respectively. The specific heat was measured by the thermal relaxation method using the commercial PPMS system (Quantum Design) between 2 and 40 K. The elastic modulus \(C_{55}\) was measured from 2 to 150 K by using the phase comparison-type pulse echo method.\(^7\) The \(C_{55}\) is the transverse mode propagating along the \(c\)-axis with the polarization direction along the \(a\)-axis. The absolute value of elastic modulus \(C_{ii}\) is calculated using an equation \(C_{ii} = \rho v^2\) with room temperature mass density \(\rho = 4.445\) g/cm\(^3\), where \(v\) is the sound velocity in a sample.

3 Results and Discussion

Fig. 1 shows temperature (\(T\)) dependence of the magnetic specific heat \(c_{4f}\) in HoFe\(_2\)Al\(_{10}\). Here, we calculated \(c_{4f}\) by subtracting the experimentally measured specific heat of LuRu\(_2\)Al\(_{10}\) from that of HoFe\(_2\)Al\(_{10}\). \(c_{4f}\) exhibits two Schottky peaks centered at 2 and 20 K. The temperature of the peak at 2 K is corresponding to that of the Schottky peak reported by Reehuis \textit{et al.}.\(^7\)

![Figure 1](image)

**Figure 1:** The \(T\) dependence of the magnetic specific heat \(c_{4f}\) in HoFe\(_2\)Al\(_{10}\). The black open circle and red solid curve are the experimental data and the calculation result by using the CEF effect, respectively.
The $T$ dependence of $C_{55}$ is shown in Fig. 2. $C_{55}$ increases monotonically with decreasing $T$ below 150 K and exhibits elastic softening below 20 K. The softening continues down to 2 K. In order to examine the origin of the characteristic elastic softening in $C_{55}$, we assume the CEF effect in $HoFe_2Al_{10}$. The CEF Hamiltonian under the orthorhombic symmetry consists of nine terms up to the sixth-order term.8) To simplify the analysis, we only take account up to the fourth-order term as shown below. We performed the theoretical analysis of $C_{55}$ by assuming the CEF effect with the strain-quadrupole interaction and quadrupole-quadrupole interaction, respectively. The effective Hamiltonian $H_{\text{eff}}$ for the $C_{55}$ is as follows:

$$H_{\text{eff}} = H_{\text{CEF}} - gO_{zx}^{\prime}\varepsilon_{zx} - g^{\prime}\langle O_{zx} \rangle_0\varepsilon_{zx},$$

(1)

$$H_{\text{CEF}} = B_2^0O_2^0 + B_2^2O_2^2 + B_4^0O_4^0 + B_4^2O_4^2 + B_4^4O_4^4,$$

(2)

where $B_m^n$ (the azimuthal quantum number: $n = 0, 2, 4$, and the magnetic quantum number: $m = 2, 4$), $O_m^n$, $g$, and $g^{\prime}$ are a CEF parameter, a Stevens operator, a strain-quadrupole coupling constant, and a quadrupole-quadrupole coupling constant, respectively.9-11) The modulus $C_{55}$ is the linear response to the strain $\varepsilon_{zx}$ corresponding to the quadrupole $O_{zx}$, $\langle O_{zx} \rangle_0$ represents the thermal average of the quadrupole operator $O_{zx}$. The $T$ dependence of the elastic modulus $C_{55}(T)$ is given by the equation:

$$C_{55}(T) = C_0(T) - \frac{N_0g^{\prime}\chi_{s}(T)}{1 - g^{\prime}\chi(T)},$$

(3)

| $B_2^0$  | $B_2^2$  | $B_4^0$  | $B_4^2$  | $B_4^4$  | $|g|$   | $g^{\prime}$ | $a^{\prime}$ | $b^{\prime}$ | $c^{\prime}$ |
|----------|----------|----------|----------|----------|--------|-----------|-----------|-----------|-----------|
| -0.21    | 0.17     | 0.29×10^-2 | -0.01 | -0.76×10^-2 | 7.23   | -0.001   | 61.26     | -2.96    | -2.37     |

Table 1: Fitting parameters of the elastic modulus $C_{55}$: $B_m^n$ (K), $|g|$ (K), $g^{\prime}$ (K), $a^{\prime}$ (GPa), $b^{\prime}$ ($\times10^{-5}$ GPa/K$^2$), and $c^{\prime}$ ($\times10^{-10}$ GPa/K$^4$).

Figure 2: The $T$ dependence of the transverse elastic modulus $C_{55}$ in $HoFe_2Al_{10}$. The black open circle, red solid curve, and blue broken curve are the experimental data, the fitting result, and the background stiffness, respectively.

The $T$ dependence of $C_{55}$ is shown in Fig. 2. $C_{55}$ increases monotonically with decreasing $T$ below 150 K and exhibits elastic softening below 20 K. The softening continues down to 2 K. In order to examine the origin of the characteristic elastic softening in $C_{55}$, we assume the CEF effect in $HoFe_2Al_{10}$. The CEF Hamiltonian under the orthorhombic symmetry consists of nine terms up to the sixth-order term. To simplify the analysis, we only take account up to the fourth-order term as shown below. We performed the theoretical analysis of $C_{55}$ by assuming the CEF effect with the strain-quadrupole interaction and quadrupole-quadrupole interaction, respectively. The effective Hamiltonian $H_{\text{eff}}$ for the $C_{55}$ is as follows:
where $\chi_s(T)$ is the so-called strain susceptibility and $N_0 = 4.89 \times 10^{27} \text{ m}^{-3}$ is the number density of Ho ions per unit volume at room temperature.$^{11,12}$ $\chi_s(T)$ on the basis of the CEF model can be written as follows:

$$
\chi_s(T) = \frac{1}{Z} \sum_k \exp \left( \frac{-E_k}{k_B T} \right) \left( \frac{1}{k_B T} \right) |\langle k | O_{zz} | k \rangle|^2 - 2 \sum_i \frac{|\langle k | O_{zz} | i \rangle|^2}{E_k - E_i},
$$
(4)

$$
Z = \sum_k \exp \left( \frac{-E_k}{k_B T} \right).
$$
(5)

Here, $|k\rangle$, $E_k$, $Z$, and $k_B$ are an eigenfunction of the CEF level, the eigenvalue of $|k\rangle$, the partition function, and the Boltzmann constant, respectively.$^{11}$ We assumed the background stiffness as $C_0(T) = a' + b'T^2 + c'T^4$. The Schottky specific heat $C_{sch}(T)$ based on the CEF model is given by the following expression:

$$
C_{sch}(T) = R \left[ \frac{2k_B^2 \exp \left( \frac{-E_k}{k_B T} \right)}{T^2 Z} \right],
$$
(6)

where $R$ is the gas constant.$^{14}$

As shown in Fig. 2, the elastic softening of $C_{55}$ is reproduced very well by using the parameters listed in Table 1. This result suggests that the softening originates from the CEF effect. To our knowledge, this is the first report on the CEF effect determined by the ultrasonic measurement in $\text{LnM}_2\text{Al}_{10}$. The calculated result of the Schottky specific heat with the CEF parameters in Table I is shown in Fig. 1. The two Schottky peaks at around 2 and 20 K are reproduced by the theoretical curve. This result supports the validity of the CEF parameter in Table 1. However, the absolute value of the calculated peak at 2 K and the temperature of the calculated peak around 25 K differ from the data slightly. The difference might arise from the neglect of the sixth-order term in the CFE parameter. To determine the CEF parameters more precisely, measurements of other modes ($C_{11}$, $C_{22}$, $C_{33}$, $C_{44}$, and $C_{66}$), the magnetic susceptibility, and the magnetization under applied magnetic fields along the three crystal axes are in progress.

### 4 Conclusion

We grew the single crystalline HoFe$_2$Al$_{10}$, and performed the elastic stiffness and specific heat measurements on HoFe$_2$Al$_{10}$. We found the elastic softening of $C_{55}$ below 20 K and two Schottky peaks at 2 and 20 K. In the theoretical fitting with the CEF parameters under the orthorhombic symmetry up to fourth-order term, the softening of $C_{55}$ is reproduced. We clarified the CEF parameters in HoFe$_2$Al$_{10}$ for the first time. The CEF parameters we proposed explain the two Schottky peaks in the magnetic specific heat as the result from the CEF effect.

### Acknowledgments

This work was supported by JSPS KAKENHI Grant Numbers 262870830A, 26800189, 24540376, 26800188, and 2624706001 from the Ministry of Education, Culture, Sports, Science, and Technology of Japan.
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