Ultrasonic Study on the Hexagonal Antiferromagnet Dy$_3$Ru$_4$Al$_{12}$

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Abstract. In the distorted kagome lattice antiferromagnet Dy$_3$Ru$_4$Al$_{12}$ with $T_N$ = 7 K, a crystal electric field (CEF) effect is expected at high temperatures. To investigate the CEF effect and the phase transition at $T_N$, we performed ultrasonic measurements on a single-crystalline sample. At high temperatures, both the longitudinal elastic modulus $C_{11}$ and the transverse modulus $C_{44}$ increase monotonically with decreasing temperature. Below 60 K a characteristic elastic softening is observed in $C_{44}$ in contrast to $C_{11}$ with monotonic hardening down to $T_N$. We analyzed $C_{44}$ using the Curie-Weiss-type equation and obtained a negative parameter: $\Theta$ which is proportional to a quadrupole-quadrupole coupling constant under the hexagonal CEF. With further decreasing temperature, both moduli exhibit abrupt elastic hardening at $T_N$ due to a magnetostriction.

1. Introduction

Many compounds of which magnetic ions form a kagome lattice have attracted considerable interest for their fascinating magnetic properties originating from geometrical frustration of spins [1, 2, 3, 4]. The ternary rare-earth compounds $R_3$Ru$_4$Al$_{12}$ ($R$: rare-earth) crystallize in the hexagonal Gd$_3$Ru$_4$Al$_{12}$-type structure (space group $P6_3/mmc$) [5, 6, 7, 8, 9]. In this hexagonal structure, constituent atoms are stacked in layers perpendicular to the $c$-axis with $R$-Al and Ru-Al layers alternately, and $R$ atoms form a distorted kagome net.

In the Dy-based compound Dy$_3$Ru$_4$Al$_{12}$, the electrical resistivity shows a metallic behavior [8]. The specific heat exhibits a clear peak at $T_N = 7$ K indicating the phase transition. The transition is of first-order and is not accompanied by a structural transformation [9]. A cusp-type anomaly is observed at $T_N$ in the magnetic susceptibility along the magnetically easy $c$-axis. Magnetization experiments manifested that there are one and two meta-magnetic phase transitions in the magnetic field along the $a$- and $c$-axes, respectively, suggesting rather complicated magnetic structure. The phase transition at $T_N$ is reported as an...
antiferromagnetic ordering with two possible noncollinear magnetic structures by neutron diffraction experiments [8].

At high temperatures, the magnetic susceptibility obeys the Curie-Weiss law above 100 K along the \(a\)-axis and above 170 K along the \(c\)-axis, suggesting an almost localized character of 4f-electrons. The estimated effective magnetic moments (10.1 \(\mu_B\) for both axes) are close to the value of the free Dy\(^{3+}\) ion (10.6 \(\mu_B\)) [8]. A crystal electric field (CEF) effect is expected in Dy\(_3\)Ru\(_4\)Al\(_{12}\) and magnetic anisotropy can be attributed to the CEF effect. Here, the sixteen-fold multiplet of the Dy\(^{3+}\) ion splits into eight Kramers doublets in the hexagonal CEF, where the total angular momentum \(J\) is equal to 15/2. In the present work, we carried out ultrasonic measurements on Dy\(_3\)Ru\(_4\)Al\(_{12}\) in order to study the CEF effect on the elastic moduli and the phase transition at \(T_N\).

2. Experimental

A single crystal of Dy\(_3\)Ru\(_4\)Al\(_{12}\) was grown by a modified Czochralski method [8]. The elastic moduli \(C_{11}\) and \(C_{44}\) were measured as a function of the temperature \(T\) from 4.2 to 150 K using the phase comparison-type pulse echo method [10]. The modulus \(C_{11}\) is the longitudinal mode propagating along the \(a\)-axis, and \(C_{44}\) is the transverse mode propagating along the \(a\)-axis with the polarization direction along the \(c\)-axis. We used LiNbO\(_3\) transducers with the fundamental resonance frequency of about 30 MHz. The modulus \(C_{ii}\) was calculated using the relation

\[
C_{ii} = \rho v^2
\]

with a room-temperature mass density \(\rho = 6.30\ \text{g/cm}^3\), where \(v\) is the sound velocity in a sample. The absolute value of \(v\) is estimated at 4.2 K by using the sample length and a time interval between pulse echoes.

3. Results and discussion

Figure 1 shows the \(T\) dependence of the longitudinal elastic modulus \(C_{11}\) in Dy\(_3\)Ru\(_4\)Al\(_{12}\). The modulus \(C_{11}\) increases monotonically with decreasing \(T\) down to \(T_N\). An abrupt elastic hardening is detected at \(T_N\), as shown in the inset of Fig. 1.

![Figure 1](image-url)

**Figure 1.** Temperature dependence of the longitudinal elastic modulus \(C_{11}\). The inset represents the same data in an expanded scale below 15 K.

The \(T\) dependence of the transverse modulus \(C_{44}\) is shown in Fig. 2. At high temperatures, monotonic hardening is observed above 60 K. The modulus \(C_{44}\) turns into soften below 60 K. The elastic softening stops at \(T_N\), and then \(C_{44}\) exhibits abrupt hardening at \(T_N\), as shown in the inset of Fig. 2. Further elastic softening appears below 6 K.

The softening between \(T_N\) and 60 K in \(C_{44}\) is a characteristic behavior originating from a quadrupole interaction under the CEF. To simplify the analysis, we performed the theoretical
fitting based on the Curie-Weiss-type formula for the co-operative Jahn-Teller effect [11].

\[ C(T) = C_0 \frac{T - T_c}{T - \Theta}, \]

where \( \Theta \) is proportional to a quadrupole-quadrupole coupling constant and \( T_c - \Theta \) is a measure of Jahn-Teller energy including a strain-quadrupole coupling constant. We assumed the background stiffness \( C_0 \) as

\[ C_0 = a + bT^2 + cT^4, \]

where \( a, b, \) and \( c \) are constants.

![Figure 2](image2.png)

**Figure 2.** Temperature dependence of the transverse elastic modulus \( C_{44} \). The inset represents the same data in an expanded scale below 15 K.

![Figure 3](image3.png)

**Figure 3.** Temperature dependence of \( C_{44} \). The red solid and blue broken curves demonstrate the fitting result and the background stiffness, respectively.

The softening of \( C_{44} \) is well reproduced above \( T_N \) with fitting parameters listed in Table 1, as shown in Fig. 3. This analysis reveals that the softening of \( C_{44} \) arises from the quadrupole interaction. Furthermore, the negative value of \( \Theta \) suggests that the interaction is of antiferroquadrupolar-type. Under the hexagonal CEF with the Dy\(^{3+}\) ion \((J = 15/2)\), no elastic...
softening is expected by only the ground doublet, since the Kramers doublet has no quadrupole degeneracy. The softening is caused by an indirect quadrupole interaction between the ground doublet and the excited doublets, such as our earlier results of YbIrGe and YbPtGe [12, 13]. Consequently, we obtained information of the quadrupole interaction due to 4f-electronic states of the Dy\(^{3+}\) ion under the hexagonal CEF from the \(T\) dependence of \(C_{44}\). In the future works, we are planning to measure the elastic moduli of other modes (\(C_{33}\) and \(C_{66}\)) and perform the theoretical fitting using the hexagonal CEF to reproduce the elastic moduli and the magnetic susceptibility.

As for the phase transition at \(T_N\), antiferromagnetic ordering is reported by neutron diffraction experiments [8]. In thermal expansion measurements, anisotropic step-wise lattice contraction due to a magneto-elastic coupling is detected at \(T_N\) [9]. Both moduli \(C_{11}\) and \(C_{44}\) show the abrupt elastic hardening at \(T_N\). Our results also indicate that a strain strongly couples to a magnetic order parameter. These hardening might originate from the magnetostriction and can be explained by the thermodynamic theory of elastic modulus with the Landau theory [14].

### Table 1. Fitting parameters of \(C_{44}\): \(\Theta\) (K), \(T_c - \Theta\) (K), \(a\) (GPa), \(b\) (\(\times 10^{-4}\) GPa/K\(^2\)), and \(c\) (\(\times 10^{-9}\) GPa/K\(^4\)).

| \(\Theta\) | \(T_c - \Theta\) | \(a\) | \(b\) | \(c\) |
|------------|------------------|------|------|------|
| -25.3      | 4.36             | 70.9 | -3.37| 1.32 |

4. Conclusion
The elastic moduli \(C_{11}\) and \(C_{44}\) were measured in the distorted kagome lattice antiferromagnet Dy\(_3\)Ru\(_4\)Al\(_{12}\). We found characteristic elastic softening due to the quadrupole interaction below 60 K in the transverse modulus \(C_{44}\) in contrast to the longitudinal modulus \(C_{11}\) without the softening. The negative \(\Theta\) obtained by the Curie-Weiss-type fitting suggests that there is the antiferroquadrupolar interaction. The indirect quadrupole interaction between the ground doublet and the excited doublets under the hexagonal CEF plays a central role for the softening. The abrupt elastic hardening, owing to the strong coupling between the strain and the magnetic order parameter, is observed at \(T_N\) in both modes.

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References
[1] Ramírez A P 1994 Annu. Rev. Mater. Sci. 24 453
[2] Moessner R and Chalker J T 1998 Phys. Rev. B 58 12049
[3] Okamoto Y, Yoshida H and Hiroi Z 2009 J. Phys. Soc. Jpn. 78 033701
[4] Sengupta K, Forthaus M K, Kubo H, Katoh K, Umeo K, Takabatake T and Abd-Elmeguid M M 2010 Phys. Rev. B 81 125129
[5] Niermann J and Jeitschko W 2002 Z. Anorg. Allg. Chem. 628 2549
[6] Ge W, Ohta H, Michioka C and Yoshimura K 2012 J. Phys.: Conf. Ser. 344 012023
[7] Nakamura S, Toyoshima S, Kabeya N, Katoh K, Nojima T and Ochiai A 2014 J. Phys. Soc. Conf. Proc. 3 014004
[8] Gorbunov D I, Henriques M S, Andreev A V, Gukasov A, Petriček V, Baranov N V, Skourski Y, Eigner V, Paukov M, Prokleška J and Gonçalves A P 2014 Phys. Rev. B 90 094405
[9] Henriques M S, Gorbunov D I, Kriegner D, Valiska M, Andreev A V and Matěj Z 2016 J. Magn. Magn. Mater. 400 125
[10] Lüthi B, Bruls G, Thalmeier P, Wolf B, Finsterbusch D and Kouroudis I 1994 J. Low Temp. Phys. 95 257
[11] Lüthi B 2005 Physical Acoustics in the Solid State (Verlag Berlin Heidelberg: Springer) p 121
[12] Ishii I, Noguchi Y, Kamikawa S, Goto H, Fujita T K, Katoh K and Suzuki T 2014 J. Phys. Soc. Jpn. 83 043601
[13] Xi X, Ishii I, Noguchi Y, Goto H, Kamikawa S, Araki K, Katoh K and Suzuki T 2015 J. Phys. Soc. Jpn. 84 124602
[14] Rehwald W 1973 Adv. Phys. 22 721