Itinerant-electron metamagnetism of magnetocaloric material ErCo$_2$ and their borides

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Abstract. The itinerant-electron metamagnetic transition of ErCo$_2$ has been investigated as a function of a lattice constant. In order to control a lattice constant of ErCo$_2$, we prepared several kinds of compounds including boron, ErCo$_2$B$_x$. A considerable lattice expansion is observed, though the crystal structure of cubic C15 Laves phase is kept after increasing the concentration of boron up to $x=0.1$. In addition, the typical change of the Curie temperature is enhanced from 35 to 65 K due to the volume expansion of ErCo$_2$B$_x$. This result implies that the magnetic coupling is exclusively determined by the volume of the compound.

1. Introduction
Materials having large magnetocaloric effects (MCE’s) are utilized as magnetic refrigerants because of their energy efficiency and environmental safety. Recently, a large MCE was discovered in first-order metamagnetic transition materials. For example, La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds exhibit large values of the isothermal entropy change $\Delta S$ around the Curie temperature $T_C$ in the concentration range $0.81 \leq x \leq 0.89$[1]. Such large MCE’s are explained by a large magnetization change at $T_C$ and a strong temperature dependence of the critical field for the itinerant-electron metamagnetic transition. In addition, by hydrogen absorption into La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds, the lattice constant is not only increased without a change in the NaZn$_{13}$-type structure, but $T_C$ is also increased. These behaviors come from the volume expansion of the La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds through magnetovolume effects. Therefore, the large MCE’s are obtained for the La(Fe$_{0.88}$Si$_{0.12}$)$_{13}$H$_y$ compounds in the wide temperature range between $T_C=195$ K for $y=0$ and $T_C=323$ K for $y=1.5$, keeping the large $\Delta S$ around $T_C$[2].

On the other hand, the rare earth elements also exhibit large MCE’s. In RX$_2$ (R= rare earth which has a local moment, X= transition metal) compounds which crystallise in the Laves phase structure, magnetic investigations revealed that an induced moment arises in the magnetically ordered state due to 4$f$-3$d$ exchange interactions[3, 4, 5]. For example, the metamagnetic properties of RCo$_2$ system play a decisive role in determining the order of the magnetic transition. In the magnetic field change from 0 to 4 T, the large $\Delta S$ of ErCo$_2$ has been obtained to be 38 J/kgK[6], which is much larger than that of La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds[2].

RCo$_2$ is promising magnetic refrigerants working only at low temperature range below 100 K because $T_C$ of RCo$_2$ is much smaller than that of La(Fe$_x$Si$_{1-x}$)$_{13}$ compounds. However, RCo$_2$
compounds exhibit the large magnetovolume effects[7] in the same way as La(Fe$_{x}$Si$_{1-x}$)$_{13}$, and so it is expected that $T_C$ of RCo$_2$ may be increased by increasing the lattice constant. In the present study, the itinerant-electron metamagnetic transition of ErCo$_2$ has been investigated as a function of a lattice constant.

2. Experimental
The polycrystalline samples were prepared as starting materials by arc-melting the constituent 99.9%-pure Er, 99.9%-pure Co and 99%-pure B under high purity argon atmosphere. In order to control a lattice constant of ErCo$_2$, we prepared several kinds of compounds including boron, ErCo$_2$B$_{x}$ ($0 \leq x \leq 0.2$). To improve homogenity, the ingot was turned over and remelted several times. The samples were checked by conventional x-ray powder diffraction experiments using Cu-K$_\alpha$ radiation. The dc magnetic susceptibility was measured in the temperature range $2.0 \leq T \leq 300$ K using a Quantum Design MPMS-5 superconducting quantum interference device magnetometer.

3. Results and discussion
Figure 1 shows X-ray powder diffraction patterns of ErCo$_2$. The results confirmed that the main phase is the cubic C-15 Laves structure over the whole composition range of $0 \leq x \leq 0.2$. 

![X-ray powder diffraction patterns of ErCo$_2$B$_x$.](image-url)
At \( x=0 \), the lattice constant is estimated to be \( a=7.124 \text{Å} \). As increasing the concentration of boron up to \( x=0.07 \), a considerable lattice expansion is observed as signified by the low angle shift of XRD peaks, though the crystal structure remains unchanged. On the other hand, some of unknown peaks are detected in the compounds of \( x=0.1 \) and 0.2 indicating some of impurity phase.

Figure 2 shows the temperature dependence of dc magnetic susceptibility \( \chi \) under a field of 1 kOe. The curves of all compounds exhibit a characteristic ferromagnetic behavior. At \( x=0 \), \( \chi \) shows a distinct decrease with increasing temperature, which is consistent with the previous reports[6, 7]. On the other hand, it demonstrates the strong effects of doping boron on magnetic behaviors. At \( x=0.04 \) and 0.07, \( \chi \) exhibits a two step increase, one of which can be attributed to the impurities. In order to detect \( T_C \) of the main phase of ErCo\(_2\), we show the temperature derivative of dc-magnetic susceptibility \( d\chi/dT \) of several samples in Figure 3. Here \( T_C \) is defined as the temperatures showing minimum of \( d\chi/dT \). \( T_C \) is obtained to be 45 K at \( x=0 \), and increases as increasing the concentration of boron up to \( x=0.07 \). Above \( x=0.1 \), \( T_C \) decreases again and a sharp anomaly of \( d\chi/dT \) is observed around \( T_C = 34 \text{K} \) at \( x=0.2 \).

**Figure 2.** The temperature dependence of dc magnetic susceptibility under a field of 1 kOe.

**Figure 3.** The temperature derivative of dc-magnetic susceptibility \( d\chi/dT \). The arrows indicate the Curie temperature \( T_C \).

Figure 4 shows \( T_C \) and lattice constant \( a \) as a function of the concentration range \( x \). It is found that \( a \) shows maximum around \( x=0.1 \). It is reasonable to assume that the volume of C15 Laves phase of ErCo\(_2\) expands by increasing the concentration of boron element up to \( x=0.07 \). Indeed, the volume expansion of La(Fe\(_{0.88}\)Si\(_{0.12}\))\(_{13}\) are also caused by hydrogen absorption, keeping the cubic NaZn\(_{13}\)-type structure[2]. On the other hand, the suppression of \( a \) above \( x \sim 0.1 \) may be related to the appearance of the impurity phase, which is observed in the X-ray diffraction pattern in Figure 1. Since the volume magnetostriction causes the change of the magnetic interaction, \( T_C \) shows maximum around \( x=0.1 \).

In Figure 5, \( T_C \) is plotted as a function of lattice constant \( a \). It is found that the magnetic interaction of ErCo\(_2\) system can be controlled by the volume of the compound between \( T_C = 35 \) and 65 K, and that \( T_C \) show a maximum at \( a \sim 7.14 \text{Å} \), where \( x=0.04 \sim 0.07 \).
4. Summary

By doping boron into ErCo$_2$, the lattice constant is increased though crystal structure remains unchanged. Curie temperature $T_C$ increases significantly due to the volume expansion of ErCo$_2$B$_x$ compounds through magnetovolume effect. Therefore, ErCo$_2$B$_x$ may be one of the most promising magnetic refrigerants working in wide temperature range between 35 and 65 K.

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