Magnetic Phase Transitions and Lattice Changes in Rare Earth Metals Studied by X-ray Diffraction under a Magnetic Field

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The lattice change of the rare earth metals Dy, Ho and Er has been studied by x-ray diffraction under a magnetic field in the *c*-plane of a hexagonal crystal. Continuous and discontinuous changes of the *c*-lattice parameter accompanying magnetic phase transitions have been observed in these metals, and satellite reflections caused by the lattice modulation have been found in the distorted helix and helifan phases of Ho and the distorted helix phase of Dy. In Er, the 2nd- and 4th-order satellites appeared below 4.5 T at 35 K, and the 6th-order satellite has been observed above 4.5 T in addition to the 2nd- and 4th-order satellites. These results can be explained with the magnetoelastic effect and the magnetic structure calculated by the self-consistent mean field method, except for the result for Er above 4.5 T at 35 K, where a strongly distorted fan magnetic structure should be assumed to explain the presence of the 6th-order satellite of the lattice modulation.

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1. Introduction

Heavy rare earth metals have a variety of magnetic structures below the ordering temperatures.¹⁾ Helical magnetic structures which are confined in the *c*-plane of the hexagonal close packing crystal appear in Dy and Ho below the Néel temperature T_N . In Er, the magnetic moment oscillates along the *c*-axis below T_N and it transforms to an *a*-*c* cycloidal magnetic structure which is realized in a plane containing the *a*- and *c*-axes. An application of magnetic field on these rare earth metals induces the magnetic phase transitions, which has been studied both experimentally and theoretically in many years. For a proper helix structure²⁾ as in Dy and Ho, a helix transforms to a fan magnetic structure and reaches a ferromagnet when the magnetic field is applied in the *c*-plane. In Ho, however, an unknown magnetic phase was found³⁾ in a narrow range between the helix and fan phases, and this unknown phase has been really identified later as a "helifan"⁴⁾ which has been suggested by a self-consistent mean field calculation. In a magnetic field along the *a*-axis for Er,⁵⁾ magnetic phase transitions exhibit more complicated behaviors, and in the *a*-*c* cycloidal phase, the experimental and calculated results suggest that the cycloid structure transforms to a cone structure in the plane containing the *b*- and *c*-axes, and becomes a fan structure in a plane containing the *a*- and *c*-axes above the magnetic field of 4 T. However, the magnetic structure at high magnetic field region is still not clear.

The crystal lattice of rare earth metals is strongly affected by the magnetic structure through the magnetoelastic effect⁶⁾ and the change of the lattice caused by the magnetic phase transition can be observed not only as the elongation or contraction of the lattice but also as the modulation⁷⁾ of the crystal lattice. In this work, a magnetic phase has been trans-

formed by the application of a magnetic field, and the change of the lattice accompanying the magnetic phase transition has been studied for Dy,⁸⁾ Ho^{9,10)} and Er¹¹⁾ by means of x-ray diffraction technique. Various magnetic structures induced by magnetic field have been determined by self-consistent mean field calculations in order to explain the results of the lattice change, but the determination of the magnetic structure from the observation of the lattice modulation has been also demonstrated for Er.

2. Experimental Results

Experiments on the lattice change under magnetic field have been performed with an x-ray triple-axis diffractometer installed at a conventional rotating copper anode x-ray source of 18 kW. The (002) reflection of a vertically bent pyrolytic graphite monochromator is used before the sample position so as to focus an x-ray beam on the sample. A split-pair type superconducting magnet which produces a maximum magnetic field of 8 T perpendicular to the scattering plane has been installed on a large goniometer head. After the sample, a flat germanium (111) or pyrolytic graphite (002) reflection is used as an analyser crystal so as to reduce the background noise. When we use the germanium (111) as an analyser, the reflection from $K\alpha_2$ incident beam can be adjusted to eliminate.

2.1 Ho and Dy

The (006) reflection of Dy and Ho single crystals has been observed at various temperatures in the helix phase as a function of a magnetic field along the easy direction of magnetization, the *a*-axis for Dy and the *b*-axis for Ho. The magnetic field dependence of the diffraction pattern along the *c** direction of Ho at 80 K has been measured with the use of a germanium (111) analyser and the results are illustrated in Fig. 1. The line profile for a single phase is well reproduced by a Gaussian function and the profiles were analysed by fitting with sums of Gaussians. Solid lines are the results of

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Fig. 1 Diffraction patterns of the (006) reflection of Ho at 80 K in various magnetic fields. Measurements were made with an increasing magnetic field.

fitting and dotted straight lines correspond to the positions of the Bragg reflections for various magnetic phases having different c lattice parameters. Two successive first order phase transitions accompanied by the discontinuous changes in the c lattice parameter have been observed in a narrow region of the magnetic field around 2 T, and a second order transition occurs around 4 T. As shown later, the discontinuous changes correspond a helix to helifan and a helifan to fan transitions, and the continuous change corresponds to a fan to ferromagnetic transition. The magnetic field dependence of the c lattice parameter in Ho obtained from the (006) reflection is illustrated in Fig. 2, together with the results for 40 and 60 K. Solid lines in the figure are the result of calculation at 80 K as described below. In the helix and the helifan phase in Ho, satellite reflections have been observed around the (00 k) reflection along the c^* direction where k is an even integer. The magnetic field dependence of the (0, 0, $6 - 2q_{\text{mag}}$) satellite in the helifan phase at 80 K is illustrated in Fig. 3, where q_{mag} is the fundamental wave number of the magnetic modulation. The pairs of sharp peaks correspond to $K\alpha_1$ and $K\alpha_2$ incident x-ray beams. The solid lines represent the results of fitting with the squared Lorentzian functions. As shown in Fig. 3(a), two broad satellites having different wave numbers seem to exist at 2.0 T with increasing magnetic field. One of the two wave numbers is the twice the value of the fundamental wave number q_{mag} for the helifan (3/2) which was reproduced by the calculation. The satellite disappeared above 2.2 T and no satellite is detected in the higher magnetic field region. With decreasing magnetic field, a sharp satellite appeared in

Fig. 2 Magnetic field dependence of the c lattice parameter of Ho at 40, 60 and 80 K. The solid thick and thin lines indicate calculated results. (See text)

Fig. 3 Satellite reflections along the c^* direction around the (006) of Ho at 80 K under various magnetic fields in the helifan phase. Measurements were made with (a) increasing and (b) decreasing the magnetic fields.

a range between 2.1 and 1.8 T, as shown in Fig. 3(b), which makes contrast with the increasing process. The intensity is approximately 10^{-4} of the (006) Bragg reflection and these satellites caused by the helifan structure have been detected in the temperature range between 35 and 110 K within a narrow range of magnetic field of 0.4 T. Positions for detecting satellite in the B-T magnetic phase diagram is shown in Fig. 4 by (+) and (×) symbols which indicate the detection of satellite with increasing and decreasing magnetic field processes respectively. The range of appearance for the helifan

Fig. 4 B-T magnetic phase diagram of Ho for a magnetic field along the b -axis. The detection of the satellite reflection from the helifan phase with increasing and decreasing processes are represented as (+) and (x) symbols respectively.

structure observed by detecting the satellite is in agreement with that determined by the change of the c lattice parameter shown in Fig. 2. In the helix phase, the satellite reflection has been found at the $(0, 0, 6 - q_{\text{mag}})$ position which is the same position as the magnetic modulation of the helix structure. The intensity increases with increasing magnetic field, and at 80 K, it disappeared abruptly around 2 T where the helix to helifan phase transition occurs. The amplitude of the lattice modulation can be calculated from the satellite intensity and the magnetic field dependence of the amplitude $u(nq_{\text{mag}})$ in helix and helifan phase is illustrated for Ho in Fig. 5.

The magnetic field dependence of the c lattice parameter in Dy also exhibits the discontinuous or continuous change accompanying the transition from the helical to fan or ferromagnetic structures. Satellite reflections have been observed at 120, 150 and 173 K in the helix phase at the $(0, 0, 6 - q_{\text{mag}})$ position. Search for the helifan structure as in Ho has been carefully made but neither the extra Bragg reflection as shown in Fig. 1 nor satellite reflection caused by the helifan structure could be detected. The satellite observed in the helix phase of Dy shows also the same characteristic behavior as in Ho.

In a phase of the fan magnetic structure both in Ho and Dy, the satellite reflection at $2q_{\text{mag}}$ position is also expected to observe, but no appreciable satellite intensity could be detected.

2.2 Er

In magnetic phases below the Néel temperature, the satellites caused by the lattice modulation were observed under various magnetic fields along the a -axis. In contrast with Dy and Ho, the lattice modulation in Er exhibits a complicated behavior and the higher order satellites have been detected. Figure 6 shows the magnetic field dependence of the satellite reflections around (004) and (006) reflections at 35 K in the a - c cycloidal magnetic phase. $2q_{\text{mag}}$ and $4q_{\text{mag}}$ components, where q_{mag} is the wave number of the cycloidal magnetic structure, are observed below 4.4 T. The result is the

Fig. 5 The magnetic field dependence of the amplitude of the lattice modulation in Ho at a distorted helix and helifan phases. Solid lines are the best fitting result of calculations taking into account the result for the change of the c -lattice parameter shown in Fig. 2. (See text)

same as the previous work with zero magnetic field⁷⁾ in the a - c cycloidal phase. At about 4.5 T, the q_{mag} obtained by the satellite measurement changes discontinuously from $4/15$ to $2/7$, which has been also observed for the wave number of the magnetic modulations by neutron diffraction.⁴⁾ $6q_{\text{mag}}$ component of satellites suddenly appears above 4.5 T, and the c lattice parameter changes discontinuously at the same magnetic field. These discontinuous lattice changes correspond to the magnetic phase transition from a cycloidal to fan structure in the plane containing the a and c axes (a - c fan structure) which was suggested by the neutron diffraction study.⁴⁾ At 5 T, $6q_{\text{mag}}$ component has been observed in a temperature range between 25 K and 45 K, and the value of q_{mag} was found to change discontinuously from $2/7$ to an incommensurate value above 37 K. $2q_{\text{mag}}$ component persists up to the Néel temperature of 84 K but $4q_{\text{mag}}$ was not detected above 37 K. The transition to the incommensurate state is also observed for $2q_{\text{mag}}$ satellite. Figures 7(a) and (b) are the magnetic field and temperature dependences of the n -th order Fourier component of the lattice modulation amplitude $u(nq_{\text{mag}})$ obtained from the results mentioned above. As shown in Fig. 7(a), $u(nq_{\text{mag}})$ is almost independent of magnetic field at 35 K except the sudden appearance of $u(6q_{\text{mag}})$ amplitude. In the temperature dependence of $u(nq_{\text{mag}})$ in Fig. 7(b), it is noted that, below 30 K, $u(6q_{\text{mag}})$ at 5 T is the largest among $u(nq_{\text{mag}})$. The result indicates that the magnetic structure of Er is complicated especially in a region of low temperature and high magnetic field along the a -axis, which will be discussed later.

In the cone spiral magnetic phase below the Curie temperature of 18.5 K, a satellite reflection was observed at q_{mag} . The value of q_{mag} changes discontinuously above 2 T from $5/21$ to $6/26$ and an additional weak $2q_{\text{mag}}$ reflection appears. The c lattice parameter also changes discontinuously at 2 T, and the results correspond to the first order magnetic phase transition from the cone to fan structure in the a - b plane, which was also observed by neutron diffraction.⁵⁾

Er 35K

Fig. 6 Magnetic field dependence of the 2nd-, 4th- and 6th-order satellites along the c^* direction at 35 K in Er. The value of q_{mag} in reduced unit obtained from the position of the satellite is indicated by arrows.

Fig. 7 The dependence of $u(nq_{\text{mag}})$ on magnetic field at a temperature of 35 K (a), and on temperature at a magnetic field of 5 T (b) in Er.

3. Discussions

A change of the lattice parameter and the lattice modulation can be analysed by a magnetoelastic effect, and the determination of the magnetic structures under various magnetic fields is essential to describe the behavior of the lattice. Detailed calculations for determining magnetic structures have been performed with a self-consistent mean field method.¹⁾ The Hamiltonian for the magnetic moment in the m -th layer can be written as

$$H_m^{MF} = H_{\text{cryst}} - \sum_l J_l S_m \langle S_m \rangle - \frac{1}{2} \sum_l J_l \langle S_m \rangle \langle S_{m+l} \rangle - g \mu_B S_m H \quad (1)$$

where the first term is the crystal field, the second and third terms are the exchange interaction energy with mean field approximation and the fourth term is a Zeeman energy. Using eq. (1), the stable magnetic structure of rare earth metals in a magnetic field can be well determined by calculating the free energy for various magnetic structures. A change of the atomic spacing $\varepsilon_{m,m+l}$ between the m -th and $m+l$ th layers along the c -direction caused by the magnetic structure can be obtained by minimizing E

$$E = \sum_{m,l} \left\{ \frac{1}{2} \phi_l \varepsilon_{m,m+l}^2 - \left(\frac{\partial J_l}{\partial r} \right) \varepsilon_{m,m+l} S_m \cdot S_{m+l} \right\} \quad (2)$$

where ϕ_l is the elastic constant between m and $m+l$ th layers. We neglect a symbol $\langle \rangle$ for the thermal averaged magnetic moment. The first term is the elastic energy between atoms and the second term is the magnetoelastic energy arising from the distance dependence of the exchange constant. $\varepsilon_{m,m+l}$ is expressed as

$$\varepsilon_{m,m+l} = \frac{l\Delta c}{2} + u_{m+l} - u_m \quad (3)$$

where Δc is the change of the c lattice parameter caused by the magnetic order and u_m is the displacement from the average position of the m -th layer. Note that a twice of the distance between nearest neighbor layers corresponds to the c lattice parameter, which gives a factor 1/2 in eq. (3). Assuming the elastic interaction acts only between the nearest neighbor layers and the lattice modulation is expressed by the Fourier series

$$u_m = \sum_n u(nq) \sin(nqm\pi), \quad (4)$$

we obtain the relation between the lattice change and the magnetic structure from eq. (2),

$$\begin{aligned} & -4 \sum_n u(nq) \sin(nqm\pi) \sin^2(nq\pi/2) \\ & = \sum_l \frac{1}{\phi_1} \left(\frac{\partial J_l}{\partial r} \right) (S_{m+l} \cdot S_m - S_m \cdot S_{m-l}) \end{aligned} \quad (5)$$

and

$$\Delta c = \sum_l \frac{2l}{\phi_1} \left(\frac{\partial J_l}{\partial r} \right) \langle S_m \cdot S_{m+l} \rangle_{av}, \quad (6)$$

where $\langle \rangle_{av}$ in eq. (6) indicates the average value in a magnetic unit cell. The value of the scalar products of the magnetic moments in eq. (5) depends on the layer in the distorted helix, helifan and fan structures. The magnetic structure affects the lattice not only the lattice parameter given by eq. (6), but also producing the lattice modulation which is described by eq. (5). Most of experimental results shown in the preceding section have been analysed with eqs. (5) and (6). In Ho, the stable magnetic structure at a given magnetic field has been determined by eq. (1) as that having the lowest free energy among various magnetic structures. The c lattice parameter and the amplitude of the lattice modulation have been calculated and the results for 80 K are shown by solid lines in Figs. 2 and 5. In the calculation for the lattice, a derivative of the second order crystal field parameter has been also taken into account in eq. (2), in addition to the derivatives of the exchange interaction up to the third neighbors. These parameters have been determined so as to obtain the best fitting results. The agreement between calculations and experimental results is fairly good. A role of the crystal field in the change of the lattice, however, seems to be small at least in high temperature region, and most of the behaviors in lattice can be explained by the distant dependence of the exchange interactions. A relation in wave number between the lattice modulation and magnetic structure can be also understood by this model. The helifan structure is calculated to be stable in a very narrow range of magnetic field and the effect of this structure for the lattice is shown around 2 T in Figs. 2 and

5. The amplitude of the lattice modulation in fan magnetic phase has been calculated to be very small, which agrees with the difficulty in detecting the satellite. Details for the analysis on Ho will be described in a separate paper.¹²⁾ The same analysis as in Ho has been also performed on Dy and the lattice changes in a distorted helix phase have been well reproduced by the calculations.

As has shown in Figs. 6 and 7, the lattice modulation in Er behaves more complicated than that in Ho, and higher order satellite intensities are found to be comparable with that of the fundamental satellite. The analysis has been made by taking into account up to the 2nd neighbor exchange interactions ($l = 2$) in eq. (5). The magnetic moment at m -th site is expressed as

$$\begin{aligned} S_{m,x} &= \sum_n s_x(n) \sin(nqm\pi) \\ S_{m,y} &= \sum_n s_y(n) \sin(nqm\pi) \\ S_{m,z} &= \sum_n s_z(n) \cos(nqm\pi), \end{aligned} \quad (7)$$

where x , y and z coordinates correspond to a , b and c axes in the hexagonal system respectively. Using the experimental results by x-ray and neutron¹⁴⁾ diffraction at 35 K without magnetic field, two parameters $(\partial J_1/\partial r)/\phi_1$ and $(\partial J_2/\partial r)/\phi_1$ have been determined by comparing the lattice modulation (left hand side in eq. (5)) with the magnetic structure (right hand side). From the observation for satellite intensities of lattice and magnetic modulations,¹⁴⁾ $u(2q_{mag})$, $u(4q_{mag})$ and $s_x(n)$, $s_z(n)$ are obtained. $s_y(n)$ is always zero because the magnetic structure in this temperature range is an a - c cycloid and the magnetic moment is in an a - c plane. The amplitude of the lattice modulation has been determined so as to $u(2q_{mag}) > 0$ and $u(4q_{mag}) < 0$,⁷⁾ and the sign of $s_x(n)$ and $s_z(n)$ are assumed to change alternatively by changing n , in order to describe the "squared up structure" of Er.¹⁴⁾ Using eq. (6), two parameters thus obtained reproduced the value of Δc at 35 K estimated by the extrapolation from high temperature paramagnetic state.¹³⁾ A b - c irregular cone magnetic structure which is realized above 2 T at 35 K is reproduced by the self-consistent mean field method by Jehan *et al.*⁵⁾ The calculated lattice modulation using this magnetic structure and the parameters obtained at zero magnetic field can well reproduce the observed lattice modulation. However, as shown in Fig. 8, the experimental results at 6 T cannot be well reproduced by the calculation using the a - c fan magnetic structure obtained by the self consistent mean field method.⁵⁾ The reason for the disagreement is due to the appearance of a large $6q_{mag}$ component satellite above 4.5 T. In order to explain the behavior of the lattice modulation shown by the solid line in Fig. 8,⁸⁾ the a - c fan magnetic structure should be distorted substantially from the simple fan structure. The distorted fan magnetic structure has been determined to reproduce the lattice modulation using eqs. (6) and (7) with the same parameters at 0 T. Two assumptions have been made: $S_{m,z}$ calculated by the self-consistent mean field method is used in eq. (7), and $S_{m,x}$ is expressed by even number components of Fourier series. $s_x(0)$ obtained from the magnetization

Fig. 8 Lattice modulation in Er at 35 K and 6 T. The solid line denotes the reproduced result obtained by observation of satellites and the dotted line denotes the calculated result. (See text)

Fig. 9 Distorted a - c fan structure at 35 K and 6 T in Er obtained by the observation of the lattice modulation. The number at a top of each magnetic moment indicates the sequence of layers.

measurement at 35 K is $4.5\mu_B$. The calculated result of the fan structure is illustrated in Fig. 9. A phase factor is adjusted so as to make symmetric structure along the c axis. The value of magnetic moments in Fig. 9 depend on site, and especially at 0 or 7-th layer, the magnetic moment is very small and has no $S_{m,z}$ component. This distorted fan magnetic structure makes possible to explain the appearance of the $6q_{\text{mag}}$ component of satellite for the lattice modulation. The result by neutron

diffraction⁴⁾ also suggested the presence of the “(303) type” structure in high magnetic field region, and this is consistent with the distorted fan structure in Fig. 9.

4. Conclusions

An x-ray diffraction experiment under magnetic field revealed the effects of various magnetic structures on the crystal lattice in rare earth metals of Dy, Ho and Er. In Ho, the c lattice parameter which is modified by the helifan magnetic structure was found in a narrow range of magnetic field. The lattice modulation was observed also in helifan and distorted helix phases. From these results, the range of the helifan structure in a magnetic phase diagram for Ho has been determined. In Er, the lattice modulation was found to be complicated, which is reflected from complicated magnetic structures. These lattice changes can be well explained by a magnetoelastic effect assuming the magnetic structure determined by a self-consistent mean field method, except the high magnetic field region in Er. In high magnetic field region at low temperatures above the Curie temperature, a new distorted fan magnetic structure is proposed in order to describe the behavior of the lattice modulation. The observation of the lattice modulation of Er below the Curie temperature of 18.5 K indicates that the c -axis component of the magnetic moment of the cone structure oscillates along the c -axis.

REFERENCES

- 1) J. Jensen and A. R. Mackintosh: *Rare Earth Magnetism*, Clarendon Press, Oxford, (1991), pp. 1–403.
- 2) Y. Kitano and T. Nagamiya: *Prog. Theor. Phys.*, **31** (1964), 1–43.
- 3) W. C. Koehler, J. W. Cable, H. R. Child, M. K. Wilkinson and E. O. Wollan: *Phys. Rev.*, **158** (1967), 450–461.
- 4) J. Jensen and A. R. Mackintosh: *Phys. Rev. Lett.*, **64** (1990), 2699–2701.
- 5) D. A. Jehan, D. F. McMorrow, J. A. Simpson, R. A. Cowley, P. P. Swaddling and K. N. Clausen: *Phys. Rev.*, **B50** (1994), 3085–3091.
- 6) E. W. Lee: *Proc. Phys. Soc.*, **84** (1964), 693–707.
- 7) K. Iwasa, N. Wakabayashi, T. Takabatake, H. Fujii and T. Shigeoka: *J. Phys. Soc. Jpn.*, **63** (1994), 127–134.
- 8) Y. Kida, K. Tajima, Y. Shinoda, K. Hayashi and H. Ohsumi: *J. Phys. Soc. Jpn.*, **68** (1999), 650–654.
- 9) H. Ohsumi, K. Tajima, N. Wakabayashi, Y. Shinoda, K. Kamishima and T. Goto: *J. Phys. Soc. Jpn.*, **66** (1997), 1896–1899.
- 10) H. Ohsumi and K. Tajima: *J. Phys. Soc. Jpn.*, **67** (1998), 1883–1885.
- 11) G. Masada and K. Tajima: *J. Phys. Soc. Jpn.*, **68** (1999), 2414–2419.
- 12) H. Ohsumi: *J. Phys. Soc. Jpn.*, to be published.
- 13) F. Darnell: *Phys. Rev.*, **132** (1963), 1098–1100.
- 14) M. Habenschuss, C. Stassis, S. K. Sinha, H. W. Deckman and F. H. Spedding: *Phys. Rev.*, **B10** (1974), 1020–1026.