Broken symmetry of cage surrounding magnetic dopant Cr ion in cubic GaN

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Abstract. The X-ray absorption spectra around the Cr K-edge are observed to reveal the strange behaviour on the magnetism of the dilute magnetic semiconductor GaCrN with a cubic structure ( \( \text{Ft}3m = \text{Td} \)). The radial distribution function analyzed in the part of the X-ray absorption fine structure shows the splitting in the first and the second nearest neighbours into two peaks, indicating that the Cr ion substitutes the Ga ion but shifts from just the lattice site of the Ga ion. This local lattice instability breaking the symmetry is explained by pseudo-Jahn – Teller effect. In the relation to the local lattice instability, the electronic ground state of the Cr ion in the cubic GaN is discussed.

1. Introduction

Marvellous development of today’s electronics and information technology is supported by the charge and the spin of electrons. The two degrees of freedom of electron, charge and spin, have been utilized separately. Adding the spin degree of freedom to conventional semiconductor charge-based electronics will add substantially more capability and performance to electronic devices. Recently, the new technology called spintronics has emerged, where the charge and spin of electrons are simultaneously utilized in one system [1]. Diluted ferromagnetic semiconductors (DMS) have been of much interest due to their potential use in spintronics applications. We have reported room temperature ferromagnetism in GaN-based diluted magnetic semiconductors, such as GaCrN [2-6], which is studied here, and GaGdN [7].

GaN crystallizes either in a stable hexagonal (wurtzite type, abbreviated hereafter as h-GaN) structure or a metastable cubic (zinc-blend type, abbreviated hereafter as c-GaN) one depending on substrates and growth conditions. We found that GaCrN-grown layers sometimes exhibit metastable cubic poly-type in spite of the growth on sapphire (0001) substrates with the same hexagonal structure [8]. The cubic GaN has some advantages with respect to the hexagonal one such as higher carrier mobility, direct band gap, and easy cleavage. Many reports have appeared on the epitaxial growth of high-quality c-GaN on GaAs [9], Si [10] and 3C-SiC [11] substrates. As regards the substrate, GaAs substrate is well developed and large-area conductive substrates are commercially available. Also, it is easily cleavable and its thermal expansion coefficient is near to that of GaN. Hence, we have grown cubic GaCrN on GaAs (001) substrates, intentionally.

In this proceeding, we report on the local structural change around Cr atoms in c-GaCrN on GaAs substrate and to survey the origin of the magnetism in the dilute magnetic semiconductors, GaCrN, the lattice instability breaking the symmetry and the electronic state of the Cr ion in c-GaN is discussed.

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2. Experiments

The sample layers were grown on a GaAs (001) substrate by the gas source electron-cyclotron-resonance (ECR) plasma-assisted molecular-beam epitaxy (MBE) techniques. Several monolayers of GaAs were grown at rather low substrate temperature (560°C) on a thermally cleaned GaAs substrate. Here, the Ga flux and the As flow rate were set at 1.2×10^{-7} Torr and 1 sccm, respectively. The GaN buffer layers were grown for 10min at T_{sub}=600°C on the GaAs buffer layers in order to make the high quality sample layers. The GaCrN sample layers were successively grown while keeping the substrate temperature at T_{sub}=600°C for 105 min. The GaN cap layers were grown for 5min to terminate the growth layers. The Ga flux and N₂ flow rate were set at 5.6×10^{-8} Torr and 0.8 sccm for the growth of GaN buffer layers, GaCrN, and the cap layers, respectively. The thickness of the layer is estimated to be approximately 300 nm. We prepared two samples with different concentrations (1 atomic % and 0.9 atomic%) of the Cr ions.

The excitation spectra showing the X-ray absorption fine structure (XAFS) around the Cr K-edge have been observed at the bending magnet beam-line BL9A in the Photon Factory (PF, Tsukuba, KEK), and to make sure the results obtained, also partially observed at the bending magnet beam-line BL01B1 in SPring-8 (Harima). The X-rays incident to the specimens were collimated by a preposition mirror, monochromatized by Si (111) double-crystals, and focused on the specimen by a postposition mirror with about 1 × 1 mm² of the beam size. The X-ray energy was calibrated at the pre-edge of the Cu foil (12.7185 degrees). All the spectra were detected by means of a solid-state detector =SSD (Ge: Li) with 19 elements, because the specimens studied here are dilute (~1 atomic % or less) and very thin, as described above, (corresponding to a few monolayers when converted into CrN). The energy window of a multi-channel analyzer is limited just to count X-ray photons of Cr Kα lines. An aluminium pipe was placed just in front of the specimen to break elastic scattering by air in the X-ray path to the specimen. The incident angles to the specimens were chosen as 5 ~ 7 degree. The recording time is typically 2 hours per specimen. All spectra were measured at room temperature. The spectra observed were analyzed using REX2000 code (Rigaku Co. ltd.).

3. Results

The XAFS excitation spectra are recorded with a fluorescence mode in the wide energy range up to 17.0 Å⁻¹ despite the fact that this is so dilute system. The absolute number of the Cr ions in the area exposed to the X-ray beams is about 2 – 5×10^{13} atoms.

![Figure 1. k^3-weighted XAFS oscillations of the two samples with different concentration of the Cr ions. A: 1.0 % of Cr concentration, B: 0.9 % of Cr concentration.](image-url)
Figure 1 shows the XAFS oscillation parts extracted from the excitation spectra of the two samples containing the Cr atom concentrations of a 1-atomic % (A) and a 0.9-atomic % (B). The excitation spectra presented here are measured at PF. The explicit XAFS oscillation can be seen up to 16 Å⁻¹ for both samples. The oscillation forms of both the samples are similar. Figure 2 presents the magnitude of the radial distribution function (RDF) Fourier-transformed from the \( k^3 \)-weighted XAFS oscillation of the figure 1. To achieve the high resolution in the bond length, the range of the Fourier-transformation is taken widely from 2 Å⁻¹ to 16.1 Å⁻¹ despite of the sample dilution. The splitting of the peaks around 1 – 2 Å and 2 – 3 Å corresponding to the Cr – N bond and the Cr – Ga bond respectively are found. The distances of each peak are nearly same. The dopant Cr ion should be surrounded by four N ions in c-GaN, whose site symmetry is Td, when the Cr ion is placed just on the lattice point of the Ga ion. However, the observed splitting of the peaks indicates that the Cr ion deviates from the lattice point.

The refinement of the RDFs is carried out by a code REX 2000 under the base of the Mac Kale databases. The results for the sample A are given in Table I. Almost same values are drawn for the sample B. It should be noticed that the reliability factors are low despite the complicate case. The coordination numbers of each group are same ratio, 2.2 : 2.1, and 6.0 : 5.9. The bond distances of the first group are close to that of CrN and that of GaN. However, the second distances are considerably short, suggesting the large-deformity surroundings around the Cr ion. By the way, the bond distances of c-GaN and CrN (\( \text{Fm\text{3}m, NaCl structure} \)) are 1.949 Å and 2.070 Å for the first nearest neighbours, and 3.183 Å and 2.921 Å for the second neighbours, respectively.

Table I. The values obtained by the refinement for the sample A using a code REX 2000.

| Shell   | coordination number | Distance (Å) | Debye-Waller factor | R-factor (%) |
|---------|---------------------|--------------|---------------------|-------------|
| Cr – N  | 2.2                 | 1.96±0.02    | 0.062               | 7.8         |
| Cr – N  | 2.1                 | 2.08±0.02    | 0.017               |             |
| Cr – Ga | 6.0                 | 2.75±0.02    | 0.087               | 4.0         |
| Cr – Ga | 5.9                 | 2.89±0.03    | 0.060               | 5.6         |
Figure 3 shows the degree of the curve fitting for a Cr – Ga (2.89Å±0.03) peak of sample A as one of the demonstration. The agreement between the measured values (solid line) and the fitted points (white circles) is good, reflecting the value (5.6%) of the R-factor.

4. Discussion
At first, we are devoted to discuss the electronic ground state of the Cr ion in c-GaN, where the Cr atom is forced to take a triply ionized state and the electron configuration of the outermost shell is (3d)\(^6\). As well known, the five-fold \(d\) orbital branches off to a two-fold \(e\) state and a three-fold \(t_2\) state under Td symmetry. Based on a balance of ligand field strength and electron repulsion force, the ground state of such trivalent \(Cr^{3+}\) ion is considered to take one of the two types of electronic configurations, that is, a high spin state in which electron configuration is \((e)^3(t_2)^1\) or a low spin state in which it is \((e)^1\). For the high-spin electron configuration, the multiplets are reduced to \(e \otimes e \otimes t_2 = 2T_1 + 2T_2\) while the ground state is \(T_1\). The multiplets in the low-spin state are \(e \otimes e \otimes e = E\), and the ground state is \(2^E\) \([12]\).

The matrix elements of electron–lattice (Jahn – Teller) interaction are expressed as

\[
M_{\Gamma' \Gamma} = \langle q(\Gamma' \gamma') | (\partial V(r, \mathbf{Q})/\partial \mathbf{Q}_{\Gamma}) | \mathbf{Q}_{\Gamma'} | q(\Gamma \gamma) \rangle.
\]

where \(\mathbf{Q}_{\Gamma'}\) is normal coordination belonging to irreducible representation \(\Gamma\) and its component \(\gamma\). To examine the equation (1), the normal modes at the local Cr configuration should be taken into account, and these are reduced into \(\alpha, e,\) and \(2t_2\) modes. The basis vectors of one of the \(t_2\) modes are \((x, y, z)\), which mean the self-shift of the central ion. The XAFS analysis given in table I direct our point of view to this normal mode relevant. Assuming it, let us examine equation (1). It is found that the electronic state \(2T_1\) of the ground state of the high spin configuration gives non-zero values for equation (1), because \(T_1 \otimes T_1 = A_1 + E + T_1 + T_2\), and these reduced representations include the same irreducible representation \(t_2\) as the normal mode. In contrast, the low spin state, which has ground state \(2^E\), gives zero values because the direct product \(E \otimes E = A_1 + A_2 + E\) does not give \(T_2\). Thus, the electronic configuration of the \(Cr^{3+}\) ion is assigned to the high spin state \(2T_1\).

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References
[1] Wolf S. A, Awschalom D. D, Buhrman R. A, Daughton J. M, von Molnár S, Roukes M. L, Chtchelkanova A. Y and Treger D. M, 2001 Science 294 1488.
[2] Hashimoto M, Zhou Y. K, Kanamura M and Asahi H, 2002 Solid State Commun., 122 37.
[3] Hashimoto M, Zhou Y. K, Kanamura M, Katayama-Yoshida H and Asahi H, 2003 J. Cryst. Growth 251 327.
[4] Hashimoto M, Tanaka H, Asano R, Hasegawa S and Asahi H, 2004 Appl. Phys. Lett. 84 4191.
[5] Hashimoto M, Tanaka H, Emura S, Kim M. S, Honma T, Umesaki N, Zhou Y. K, Hasegawa S and Asahi H, 2004 J. Cryst. Growth 273 149.
[6] Kim M.S, Zhou Y. K, Kimura S, Emura S, Hasegawa S and Asahi H, 2005 J. Cryst. Growth 278 675.
[7] Choi S. W, Emura S, Kimura S, Kim M. S, Zhou Y. K, Teraguchi N, Suzuki A, Yanase A and Asahi H, 2006 J. Alloys and Compounds 408-412 717.
[8] Shanthi S, Hashimoto M, Zhou Y. K, Kimura S, Emura S, Hasegawa S, Hasuieke N, Harima H and Asahi H, 2005 Appl. Phys. Lett. 86 092102.
[9] Sung L. W, Lin H. H and Chia, C. T, 2002 J. Cryst. Growth 241 320.
[10] Wang D, Hiroyama Y, Tanaka M, Ichikawa M and Yoshida S, 2000 J. Cryst. Growth 216 44.
[11] Wu J, Yamaguchi H, Nagasawa H, Yamaguchi Y and Onabe K, 1998 J. Cryst. Growth 189-190 420.
[12] Kamimura H, Sugano S, and Tanabe Y, “Ligand Field Theory and Its Application” Syokabo (1988) Tokyo (in Japanese).