



# Hydration of the HCl and NH<sub>3</sub> molecules adsorbed on amorphous water–ice surface

M. Kondo<sup>a,b</sup>, H. Kawanowa<sup>a,b</sup>, Y. Gotoh<sup>b</sup>, R. Souda<sup>a,b,\*</sup>

<sup>a</sup>Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan

<sup>b</sup>Department of Materials Science and Technology, Science University of Tokyo, Noda, Chiba 278-8510, Japan

Available online 27 August 2004

## Abstract

The interactions between HCl and NH<sub>3</sub> molecules adsorbed on amorphous solid water (ASW) have been investigated by temperature-programmed time-of-flight secondary ion mass spectrometry (TP-TOF-SIMS). The NH<sub>4</sub><sup>+</sup> ion is sputtered predominantly from codeposited HCl and NH<sub>3</sub> molecules on ASW due to collision-induced proton transfer reactions. The NH<sub>4</sub><sup>+</sup> yield is enhanced above 60 K as a consequence of the formation of the NH<sub>4</sub>Cl molecule. The NH<sub>4</sub><sup>+</sup> yield steeply decays above 100 K due to the hydration of the NH<sub>4</sub>Cl molecules, and the almost complete hydration occurs above 140 K. The H/D exchange is induced rapidly between D<sub>2</sub>O and NH<sub>4</sub>Cl molecules above 120 K. These behaviors strongly suggest that mobile water molecules exist on the surface above 100–120 K.

© 2004 Elsevier B.V. All rights reserved.

PACS: 79.20.Rf; 34.70.+e; 34.50.Dy

Keywords: Water; Ammonia; Hydrogen chloride; Ammonium chloride; Solvation; H/D exchange; Secondary ion mass spectrometry

## 1. Introduction

The nature of water–ice is very important in astrophysical environment, because it is believed to be a major component of comets, planetary rings, and interstellar clouds. Recently, Antarctic ozone depletion is very serious problem. It is likely that Antarctic stratospheric clouds (PSCs) play the key role in inducing this phenomenon [1,2]. It is believed that PSCs mainly consist of water–ice [1], and Cl<sup>−</sup> ion has a lot to do with Antarctic ozone depletion. HCl is the simplest molecule that include Cl atom and plays

an important role in chemistry of PSCs. Hynes and co-workers insist that the HCl is ionized thermodynamically at the water–ice surface and that the formation of quasi-liquid surface layer is not necessary to induce ionization [1]. So far, Fourier transform infrared spectroscopy (FT-IR) [3–7], thermal desorption spectroscopy (TDS) [8,9], and ultraviolet photoelectron spectroscopy (UPS) [10,11] have been utilized to understand molecular reactions on the water–ice surface. SIMS may have a potentiality for characterization of molecules on the surface due to its extremely high surface sensitivity. The yield of sputtered ion depends much on chemical environment, which is called ‘matrix effect’. The hydrogen-bond matters are of interest in this respect. Rabalais and coworkers [12] revealed that the most abundant ions sputtered

\* Corresponding author. Tel.: +81-29-860-4429;

fax: +81-29-851-6280.

E-mail address: [souda.ryutarou@nims.go.jp](mailto:souda.ryutarou@nims.go.jp) (R. Souda).

from pure water–ice films are protonated water cluster ions. Kang and collaborators [2,13] discussed interactions of  $\text{NH}_3$  and  $\text{HCl}$  molecules adsorbed on water–ice films. They claimed that  $\text{NH}_4^+$  and  $\text{H}_3\text{O}^+$  ions, created as a consequence of acid–base reactions, can be sputtered. More recently, Souda et al. [14,15] discussed the mechanisms of collision-induced proton transfer reactions and thermally-activated H/D exchange and demonstrated that TOF-SIMS is a quite powerful technique for investigating the solvation and hydrogen-bond reactions on the water–ice surface.

In the present paper, we report on the reaction of  $\text{HCl}$  and  $\text{NH}_3$  molecules by using TP-TOF-SIMS. Three adsorption systems are investigated in the temperature range from 15 to 180 K; (a) the  $\text{HCl}$  molecules adsorption on the  $\text{NH}_3$  layer, (b) co-adsorption of the  $\text{HCl}$  and  $\text{NH}_3$  molecules on the  $\text{H}_2\text{O}$  layer and (c) co-adsorption of the  $\text{HCl}$  and  $\text{NH}_3$  molecules on the  $\text{D}_2\text{O}$  layer. So far, the  $\text{NH}_4\text{Cl}$  formation from the  $\text{NH}_3$  and  $\text{HCl}$  molecules have been discussed extensively for the gas phase [16–18] as well as the condensed phase [19,20]. The sputtering of cations and anions from the  $\text{NH}_4\text{Cl}$  molecules is interesting, in comparison with the unreacted  $\text{NH}_3$  and  $\text{HCl}$  molecules, in terms of its ionic nature in bonding. It is well known that amorphous solid water transforms into crystalline phase at 140 K. Therefore, it is of interest to know the temperature evolutions of the reaction and solvation of the  $\text{HCl}$  and  $\text{NH}_3$  molecules on the water–ice surface. In addition, the system (c) would give us information on the contribution of the water–ice surface to the hydrogen-bond reaction by investigating the rate of the thermally-induced H/D exchange.

## 2. Experiment

Experiments were conducted in a stainless steel ultrahigh-vacuum chamber of base pressure below  $1 \times 10^{-8}$  Pa. The vacuum system was equipped with an electron-impact-type ion source, a linear-TOF tube, a quadrupole mass spectrometer for gas analysis, a hemispherical electrostatic analyzer, an X-ray source, a UV source, and a low-energy electron gun.  $\text{He}^+$  ions were chopped by an electrostatic deflector into pulses with width of 200 ns and frequency of 40 kHz. The TOF-SIMS measurements were made in such a man-

ner that the sample, floated with a bias voltage of +500 eV (in case of negative ions, the bias voltage was set –500 eV), was irradiated with a primary  $\text{He}^+$  beam of 2 keV through a grounded stainless-steel mesh placed 4 mm above the sample surface (the ion impact energy was 1.5 keV for cations and 2.5 keV for anions), and the positive or negative ions extracted into the field-free region of the TOF tube were detected with a channel electron multiplier. To minimize charging and damage of a surface, a pulsed  $\text{He}^+$  beam with a low incident flux ( $0.2 \text{ nA/cm}^2$ ) was used. The substrate was a polycrystalline Ni sheet mounted on a sample holder cooled to 15 K by means of a closed-cycle He refrigerator. The surface was cleaned by annealing around 1200 K. The  $\text{NH}_3$ ,  $\text{HCl}$ , and  $\text{H}_2\text{O}$  ( $\text{D}_2\text{O}$ ) molecules were dosed from separate gas inlet systems to the substrate by backfilling the vacuum system. One-monolayer (1-ML) coverage of the adsorbed molecules was determined from the decay curve of the sputtered ion yields from the substrate as a function of exposure, and the film thickness was estimated on the basis of this value.

## 3. Experimental results and discussion

### 3.1. $\text{HCl}$ (2-ML) on $\text{NH}_3$ (50-ML)

Fig. 1 shows evolutions of typical secondary-ion intensities sputtered from the  $\text{HCl}$ -adsorbed  $\text{NH}_3$ -ice surface as a function of temperature; the  $\text{NH}_3$  (50-ML) and  $\text{HCl}$  (2-ML) molecules were deposited successively at 15 K. Fig. 1(a) and (b) show positive and negative ions and electrons. In this system,  $\text{H}^+$  and  $\text{NH}_4^+$  are the dominant cation species. The  $\text{NH}_4^+$  yield at 15–60 K is about five times as high as that from the pure  $\text{NH}_3$  layer. The  $\text{NH}_4^+$  ion is caused by the proton transfer reaction during collisions between  $\text{HCl}$  and  $\text{NH}_3$  molecules ( $\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-$ ), where the probability for the proton transfer reaction depends on the proton affinities. The yields of  $\text{H}^+$  and  $\text{NH}_4^+$  ions decreases at 60 K. These ion yields in the 70–100 K range are almost the same as those of the thick  $\text{NH}_3$  layer. This result indicates that the surface is covered by the pure  $\text{NH}_3$  molecules. Furthermore, the  $\text{e}^-$  yield is enhanced markedly, implying that the  $\text{NH}_3$  molecules tend to emit electrons efficiently. Above 110 K, the yields of  $\text{NH}_4^+$  and

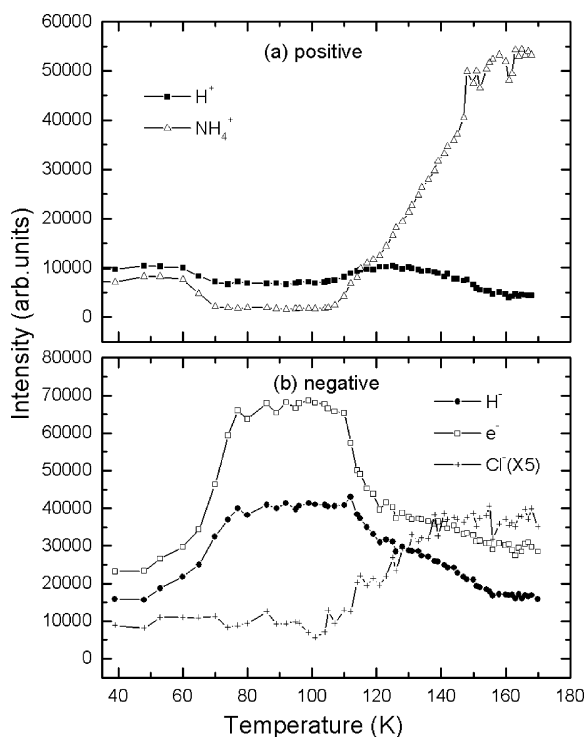


Fig. 1. Temperature evolutions of some secondary ion yields from the HCl-adsorbed NH<sub>3</sub> layer. The HCl molecules (2-ML) were deposited on the NH<sub>3</sub> layer (50-ML) at temperature of 15 K. The results for (a) positive ions and (b) negative ions and electrons are shown.

Cl<sup>-</sup> ions are enhanced markedly, whereas the yields of e<sup>-</sup> and H<sup>-</sup> ion steeply decay. These changes show that the NH<sub>4</sub>Cl molecules remain on the surface after desorption of the NH<sub>3</sub> molecules at 110 K. Judging from the fact that the Ni<sup>+</sup> ion is not detected above 110 K, we conclude that the surface is completely covered by the NH<sub>4</sub>Cl molecules. The yield of the NH<sub>4</sub><sup>+</sup> ion sputtered from the NH<sub>4</sub>Cl molecules is enhanced due to the polarization based on proton transfer reactions during energetic molecular collisions.

Regarding the electron emission, the amount of detectable electron depends on the electron affinity levels. Hence, the electron yield may have information about the state of the topmost surface layer. Note that the evolution curve of the yields of H<sup>-</sup> and e<sup>-</sup> is correlated; the H<sup>-</sup> ion would be produced by accommodating such hot electrons into the affinity level

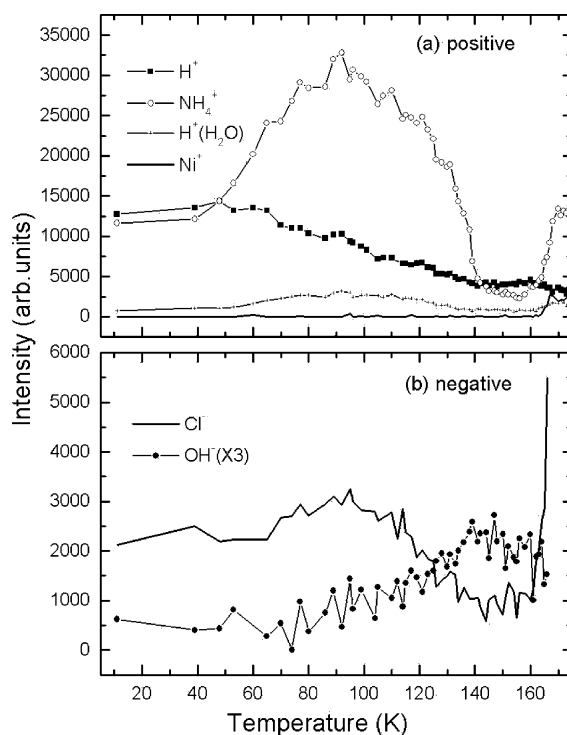


Fig. 2. Temperature evolutions of some secondary ion yields from the HCl and NH<sub>3</sub> molecules coadsorbed on the H<sub>2</sub>O layer. The H<sub>2</sub>O (50-ML) molecules were deposited at 100 K, and then the HCl (2-ML) and NH<sub>3</sub> (2-ML) molecules were coadsorbed after cooling down to 15 K. The results for (a) positive ions and (b) negative ions and electrons are shown.

(0.7 eV). On the other hand, the H<sup>+</sup> ion is originated from the dissociative ionization of the dangling N–H bond at the topmost surface layer.

### 3.2. HCl (2-ML) and NH<sub>3</sub> (2-ML) on H<sub>2</sub>O (50-ML)

Fig. 2 shows the yields of some secondary ions sputtered from the HCl and NH<sub>3</sub> molecules codeposited on the H<sub>2</sub>O–ice surface as a function of temperature; the H<sub>2</sub>O (50-ML) molecules were deposited at 100 K, and then the HCl (2-ML) and NH<sub>3</sub> (2-ML) molecules were coadsorbed on the surface after cooling down to 15 K. Thus, we prepared the nonporous amorphous solid water (ASW) to exclude the possibility that molecules are incorporated in the cavities of ASW [21]. Regarding the mechanism of the sputtered ion formation, the bare H<sup>+</sup> and H<sup>-</sup> ions come from the dangling O–H or N–H bond. On the other hand, the

hydrated  $H^+$  ion is created in the course of the breakage of hydrogen bond ( $H_2O + H_2O \rightarrow H_3O^+ + OH^-$ ). The  $H^+(HCl)$  ion (not shown in Fig. 2) would be created as well ( $HCl + HCl \rightarrow H^+(HCl) + Cl^-$ ), but it is hardly detectable because the HCl molecules have the highest ability to donate the proton in this system ( $NH_3 + HCl \rightarrow NH_4^+ + Cl^-$  or  $H_2O + HCl \rightarrow H_3O^+ + Cl^-$ ).

The yield of the  $NH_4^+$  ion from this surface is higher than that from the pure  $NH_3$  layer by more than an order of magnitude. Probably, the proton is not only donated from the HCl molecules but also from the  $H_2O$  molecules because of the higher proton affinity of the  $NH_3$ . In contrast to the results shown in the preceding section, the yield of  $NH_4^+$  ion is enhanced considerably above 50 K. This result suggests that the  $NH_4Cl$  molecules begin to be produced on the surface at 50 K. Moreover, the yield of the  $H^+(H_2O)$  ion increases above 50 K. This behavior should be ascribed to the proton transfer reactions enhanced by the HCl molecule ( $H_2O + HCl \rightarrow H_3O^+ + Cl^-$ ) since the  $H^+(H_2O)$  yield in this system is higher than that of the pure water–ice layer. The  $NH_4^+$  yield tends to decay above 100 K despite that the  $NH_4Cl$  molecules would not desorb. This is because the  $NH_4Cl$  molecules are gradually hydrated by the mobile  $H_2O$  molecules. Thus, the broad peak of the  $NH_4^+$  yield at 100 K occurs as a result of the competition between the hydration and the formation of the  $NH_4Cl$  molecules. The phase transition occurs from ASW to crystalline ice at 140 K and, hence, the  $NH_4Cl$  molecules can be hydrated efficiently by the water molecules with higher mobility above 140 K. This presumption is supported by the fact that the yield of the  $OH^-$  ion (the  $Cl^-$  ion) is increased (decreased) above 120 K, providing the evidence that the water molecules cover the topmost layer. The yield of the  $H^+(H_2O)$  ion sputtered from this system at 140 K is almost the same as that from the pure  $H_2O$  layer. Moreover, the  $NH_4^+$  ion does not disappear completely. This result may suggest that a small amount of the hydrated  $NH_4Cl$  molecules remain on the surface and do not diffuse completely into the thin-layer bulk of water–ice. It is thus concluded that the  $NH_4Cl$  molecules are basically hydrated on the surface at 140 K. Above 160 K, the  $NH_4^+$  yield increases due to desorption of the water molecules. But desorption of the  $NH_4Cl$  molecules is not complete at this temperature,

as inferred from the fact that the yield of  $Ni^+$  ion sputtered from the Ni substrate is negligibly small.

### 3.3. HCl (2-ML) and $NH_3$ (2-ML) on $D_2O$ (50-ML)

Fig. 3 shows evolutions of typical secondary ions sputtered from the HCl and  $NH_3$  molecules coadsorbed on the  $D_2O$ -ice surface as a function of temperature. This experiment is essentially the same as that in Fig. 2(a) except for utilizing the isotopic water molecules. At 15 K, the yields of the  $D^+(NH_3)$  ion [ $NH_3 + D_2O \rightarrow D^+(NH_3) + OD^-$ ] relative to the  $H^+(NH_3)$  ion [ $NH_3 + NH_3 \rightarrow H^+(NH_3) + NH_2^-$ ] would give us information about the relative amounts of the  $NH_3$  molecules wetting the  $D_2O$  surface to those forming islands. The enhancement of the  $NH_4^+$  and  $D^+(NH_3)$  ions above 50 K may be ascribed to the formation of the polarized  $NH_4Cl$  and  $NH_3DCl$  molecules, respectively. Furthermore, the deuterated ammonium ions, such as  $D^+(NH_3)$ ,  $D^+(NDH_2)$ ,

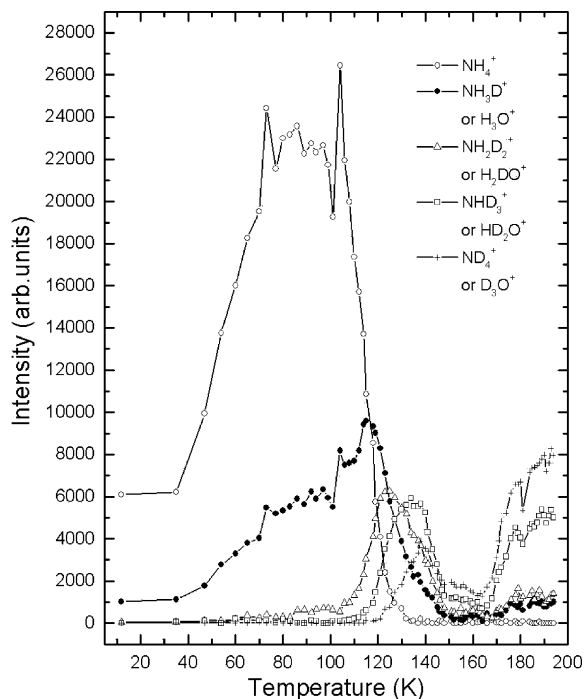


Fig. 3. Temperature evolutions of some secondary ion yields from the HCl and  $NH_3$  molecules coadsorbed on the  $D_2O$  layer. The  $D_2O$  (50-ML) molecules were deposited at 100 K, and then the HCl (2-ML) and  $NH_3$  (2-ML) molecules were coadsorbed after cooling down to 15 K.

$D^+(ND_2H)$  and  $D^+(ND_3)$ , become dominant above 120 K;  $m/e = 19, 20, 21, 22$  can be assignable not only to the deuterated ammonium ion but also to the protonated heavy water ion, but the former should be dominant species by taking into account the proton affinities (see also Fig. 2(a) in which the yield of  $H^+(H_2O)$  is much smaller than that of  $NH_4^+$ ). With increasing temperatures, the relative yields of the deuterated ammonium ions increase but the absolute yields decay steeply in order of mass number as a result of the hydration. This result suggests that the hydration and the H/D exchange, respectively, occur drastically between the hydrophilic groups of the  $D_2O$  and  $NH_4Cl$  molecules above 100 and 120 K. These two processes are almost completed above 140 K. In order for the H/D exchange to occur in crystalline ice, proton transfer and molecular rotation are required [3,5,6,22]. However, this may not hold for the present case in which the mobile water molecules play a role. The deuteration rate of the detectable ammonium ion is determined by the amount of mobile  $D_2O$  molecules; i.e., the H/D exchange is correlated to how many  $NH_4Cl$  molecules are hydrated. The hydrated  $NH_4Cl$  molecules undergo almost complete H/D exchange as inferred from the dominance of the  $ND_4^+$  ions sputtered from the ammonium chloride remaining on the surface above 170 K.

#### 4. Conclusion

Temperature evolution curves of the sputtered secondary ions provide information about the hydrogen-bond reactions and hydration on the water–ice surface. The  $NH_4Cl$  molecules are produced from the  $HCl$  and  $NH_3$  molecules above 50 K and remain above 180 K. The enhancement of the  $NH_4^+$  ion occurs provided that the counter  $Cl^-$  ion is present in the nearest neighbors. Specifically, the yield of the  $NH_4^+$  ion sputtered from the  $HCl$  and  $NH_3$  molecules coadsorbed on the water–ice exhibits a broad peak at around 100 K. This result is interpreted by the competition between the reaction of the  $HCl$  and  $NH_3$  molecules and the hydration of the resulting  $NH_4Cl$  molecules. The phase transition occurs from ASW to

crystalline ice at 140 K, where the water molecules become mobile remarkably and would hydrate the  $NH_4Cl$  molecules considerably. This presumption is supported by the fact that the H/D exchange is induced drastically above 120 K via the hydrogen-bond formation between the  $D_2O$  and  $NH_4Cl$  molecules. Furthermore, the fact that the  $NH_4^+$  and  $Cl^-$  ions do not vanish completely suggests that the  $NH_4Cl$  molecules are hydrated on the surface, but not incorporated deep in the bulk.

#### References

- [1] B.J. Gertner, J.T. Hynes, *Science* 271 (1996) 1563.
- [2] H. Kang, T.-H. Shin, S.-C. Park, I.K. Kim, S.-J. Han, *J. Am. Chem. Soc.* 122 (2000) 9842.
- [3] J.P. Devlin, H.H. Richardson, *J. Chem. Phys.* 81 (1984) 3250.
- [4] N. Uras, M. Rahman, J.P. Devlin, *J. Phys. Chem. B* 102 (1998) 9375.
- [5] P.J. Wooldridge, J.P. Devlin, *J. Chem. Phys.* 88 (1988) 3086.
- [6] W.B. Collier, G. Ritzhaupt, J.P. Devlin, *J. Phys. Chem.* 88 (1984) 363.
- [7] C.J. Pursell, M. Zaidi, A. Thompson, C. Frank-Gaston, E. Vela, *J. Phys. Chem. A* 104 (2000) 552.
- [8] Q.B. Lu, T.E. Madey, *Surf. Sci.* 451 (2000) 238.
- [9] M.T. Sieger, T.M. Orlando, *Surf. Sci.* 390 (1997) 92.
- [10] M.J. Campbell, J. Liesegang, J.D. Riley, R.C.G. Leckey, J.G. Jenkin, *J. Electr. Spectr. Relat. Phenom.* 15 (1979) 83.
- [11] S. Krischok, O. Hoff, V. Kempter, *Surf. Sci.* 507 (2002) 69.
- [12] G.M. Lancaster, F. Honda, Y. Fukuda, J.W. Rabalais, *J. Am. Chem. Soc.* 101 (1979) 1951.
- [13] S.-C. Park, K.-W. Maeng, T. Pradeep, H. Kang, *Nucl. Instrum. Meth. Phys. Res. B* 182 (2001) 193.
- [14] R. Souda, *J. Chem. Phys.* 119 (2003) 2774.
- [15] R. Souda, H. Kawanowa, M. Kondo, Y. Gotoh, *J. Chem. Phys.* 119 (2003) 6194.
- [16] R. Cazar, A. Jamka, F.-M. Tao, *Chem. Phys. Lett.* 287 (1998) 549.
- [17] F. He, J. Ramirez, C.B. Lebrilla, *J. Am. Chem. Soc.* 121 (1999) 4726.
- [18] B. Cherng, F.-M. Tao, *J. Chem. Phys.* 114 (2001) 1720.
- [19] C.J. Pursell, M. Zaidi, A. Thompson, C. Fraser-Gaston, E. Vela, *J. Phys. Chem. A* 104 (2000) 552.
- [20] L. Andrews, X. Wang, Z. Mielke, *J. Phys. Chem. A* 105 (2001) 6054.
- [21] K.P. Stevenson, G.A. Kimmel, Z. Dohnalek, R.S. Smith, B.D. Kay, *Science* 283 (1999) 1505.
- [22] J.P. Cowin, A.A. Tsekouras, M.J. Iedema, K. Wu, G.B. Ellison, *Nature* 398 (1999) 405.