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# Unusual Conduction Mechanism of n-type $\beta$ -Ga<sub>2</sub>O<sub>3</sub>: A shallow donor Electron Paramagnetic Resonance analysis

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## Abstract

We have investigated by electron paramagnetic resonance (EPR) spectroscopy the conduction mechanism in n-type, Si doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> bulk samples and evidenced carrier dynamics in the GHz frequency range at room temperature. The Si shallow donor EPR and conduction electron spin resonance (CESR) spectra show an unusual temperature dependence of the linewidth and lineshape, which reveals a variable range hopping conduction and donor clustering. The temperature dependence of the EPR signal intensity can be fitted with two thermally activated processes with energies of 4meV and 40meV in the below and above 40K temperature range. The value of 40meV is attributed to the ionization energy of the Si shallow donor, indicating that hopping proceeds via the conduction band. Above T=130K and up to room temperature the conduction electron spin resonance (CESR) can be observed with decreasing linewidth of  $\Delta B < 1G$ , which indicates negligible spin flip scattering. To illustrate the unusual behavior of the shallow donor in Ga<sub>2</sub>O<sub>3</sub>, we have analyzed the hydrogen shallow donor in ZnO, for which we observe a different “classical” behavior, characterized by donor localization below 40K and thermal ionization in the conduction band above T=90K. In ZnO the CESR can only be observed in a small temperature range at 90K due to excessive line broadening for higher temperatures.

## Introduction

$\beta$ -Gallium oxide is an emerging semiconductor material [1], which due to its high bandgap and suitable n-type conductivity is well suited for microelectronic devices requiring high breakdown voltages.  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> can be obtained as bulk material [2,3] or in the form of epitaxial layers [4] grown by various techniques such as PLD, MBE, MOCVD and LPCVD. Contrary to standard semiconductors such as Si, SiC or GaAs  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has a low symmetry, monoclinic crystal structure, giving rise to two nonequivalent Ga sites and three nonequivalent oxygen lattice sites. Like many oxide wide bandgap semiconductors Ga<sub>2</sub>O<sub>3</sub> can be easily made n-type conductive. Doping with Si, Ge or Sn has been predicted and shown to introduce shallow donors with ionization energies of 30..40meV and high donor doping levels up to  $10^{19}cm^{-3}$  and room temperature conductivities of  $10^{-2}\Omega^{-1}cm^{-1}$  have been achieved [4-7]. The room temperature mobilities are in the range 10 to  $100cm^2V^{-1}s^{-1}$  with highest values in homoepitaxial layers. Sn and Si donors have been predicted to occupy preferentially different lattice sites, octahedral and tetrahedral Ga sites respectively [5,6]. As the lowest conduction band is composed of 4s orbitals of octahedral Ga, the lattice site of shallow donors might have an influence on the conductivity properties.

The conduction mechanism in n-type  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> has been investigated before [7-12] but some issues remain to be investigated in more detail. In one recent study of highly doped Sn doped  $\beta$ -Ga<sub>2</sub>O<sub>3</sub> with donor concentration above the Mott limit a variable range hopping conductivity for impurity band conduction has been reported [11]. In this work we have studied the conduction mechanism in n-type bulk samples, where the carrier concentration was below the Mott limit for

metallic conduction. We had shown recently [13] in a correlated electrical transport and EPR study of  $\epsilon$ -Ga<sub>2</sub>O<sub>3</sub>, that the conduction mechanism in Si doped epitaxial layers with a carrier concentration of  $2.8 \times 10^{18} \text{cm}^{-3}$ - close to but below the Mott transition- is characterized by variable range hopping. Variable range hopping conductivity is quite unusual for a crystalline semiconductor and generally a property of amorphous semiconductors. To investigate, whether this process is related to the particular multidomain microstructure of the  $\epsilon$ -polytype, we have undertaken a similar study in monocrystalline, n-type bulk  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>, which does not have any microstructure. We have equally addressed the issue of negative U properties, recently evoked [10] for the Si donor in  $\beta$ -Ga<sub>2</sub>O<sub>3</sub>.

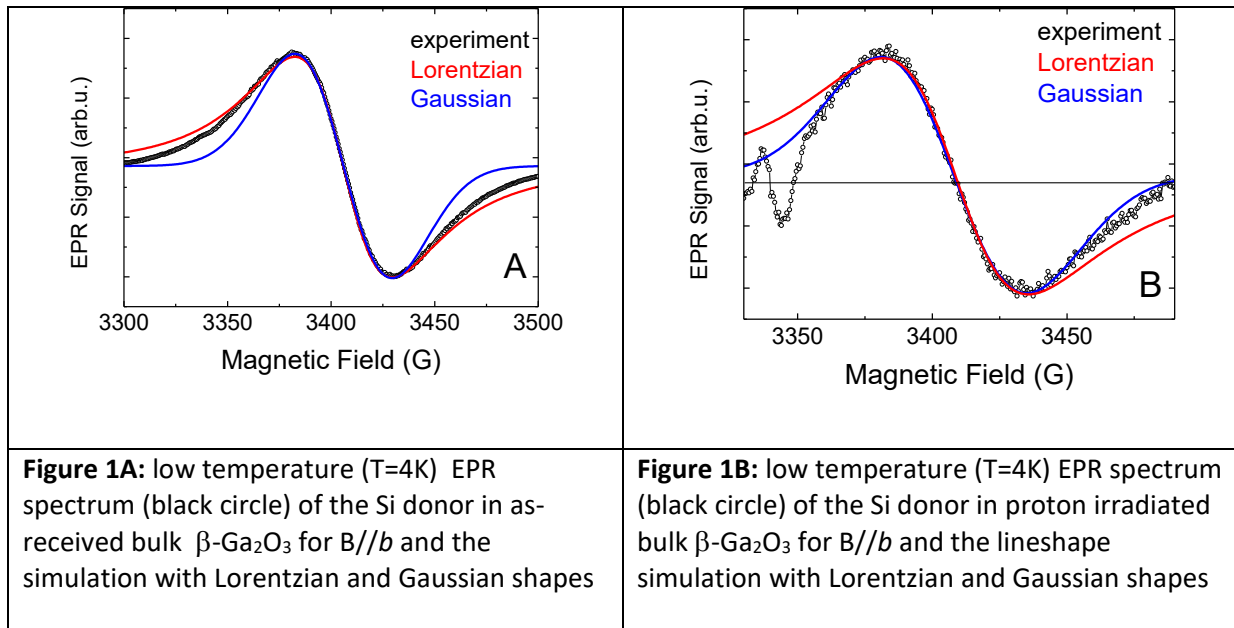
Both neutral shallow donors and conduction electrons are spin  $S=1/2$  centers, thus electron paramagnetic resonance spectroscopy is an adequate tool for the study of both. At low temperature the electron is localized on the donor and the g-tensor, lineshape and linewidth as well as the spin concentration can be determined. For a localized donor a Gaussian lineshape is expected due to inhomogeneous broadening induced by the hyperfine interaction with the Ga nuclei. In case of delocalization the hyperfine interaction is averaged out and the lineshape becomes Lorentzian. In this work we have focused on the temperature dependence of the EPR parameters. They provide information about the delocalization of the electrons, their dynamics and their emission in the conduction band.

To demonstrate the singularity of the conduction mechanism in Ga<sub>2</sub>O<sub>3</sub>, we have performed a similar investigation for a shallow donor in n-type ZnO, which on the contrary shows a “classical” behavior.

#### **Experimental details:**

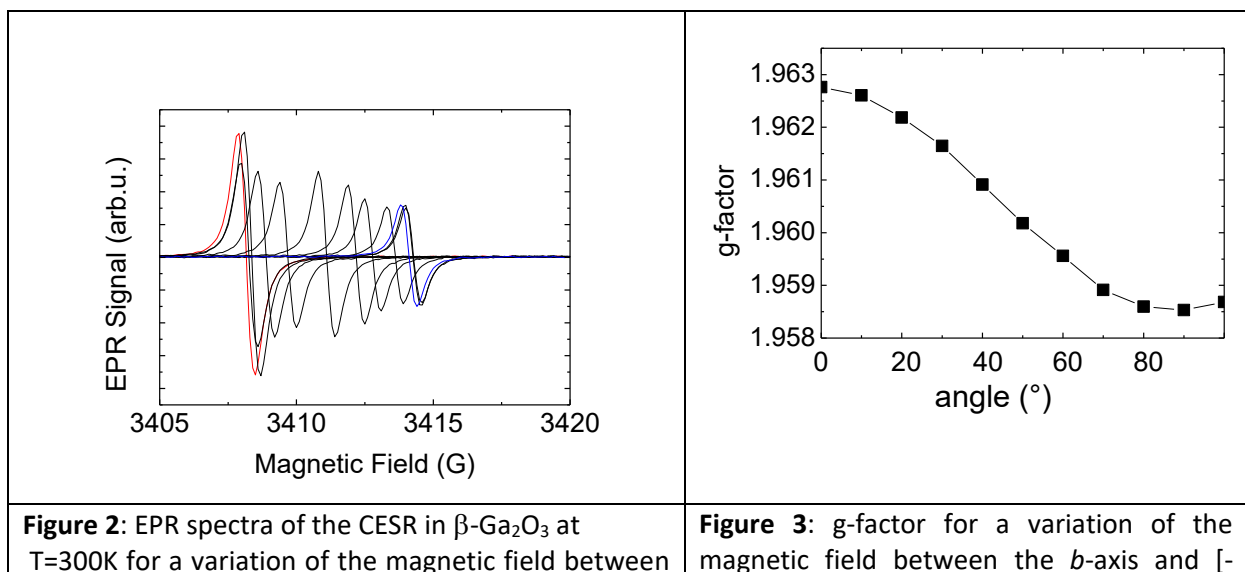
The bulk samples were commercial purchased from Tamura Comp. (Japan); they were grown by the edge-defined film-fed (EFG) technique [2,3] and even though not intentionally doped, are n-type conducting due to Si contamination. The room temperature carrier concentration was  $2 \times 10^{17} \text{cm}^{-3}$ . No additional thermal treatment was performed. The samples were (010) b-plane oriented and of rectangular shape with edges along [102] and  $[\perp 102]$ . The thickness was  $400 \mu\text{m}$  and the EPR sample dimensions  $5 \times 5 \text{mm}^2$ . To verify the influence of electrical compensation and conductivity on the EPR spectra, we have equally investigated one proton-irradiated sample, in which the carrier concentration was reduced. This sample was irradiated at room temperature with protons of kinetic energy  $E=12 \text{MV}$  at a fluence of  $1 \times 10^{16} \text{cm}^{-2}$ . For this energy the proton will completely cross the sample with a predicted end-of-range region at  $450 \mu\text{m}$  and no hydrogen will be incorporated. Due to the formation of Ga vacancies, which are deep acceptors, the increased compensation will reduce the neutral donor concentration. The irradiated sample is still n-type conductive and the neutral donor resonance is observed at  $T=4 \text{K}$ . The n-type bulk ZnO samples were grown by vapor phase epitaxy. The dominant shallow donor was hydrogen with a bulk concentration of  $7 \times 10^{17} \text{cm}^{-3}$ . Transport measurements have been performed on this sample by D.C. Look (Ohio State Univ.). The sample size was  $5 \times 5 \times 0.5 \text{mm}^3$  and it was (0001) plane oriented.

The EPR measurements were performed with a Bruker X-band spectrometer in the temperature range from  $T=4 \text{K}$  to  $T=300 \text{K}$ . For each scan the microwave frequency was also monitored in order to determine the g-values with a precision of  $\Delta g=0.0002$ . The principal values and axes orientation of the g-tensor were obtained from the angular variation of the donor resonance in three lattice planes and deduced in a standard procedure. The EPR lineshape was analyzed with the EPR simulation program of V.Grachev [14]. The linewidth  $\Delta B$  is defined as the peak-to-peak width of the first derivative line.

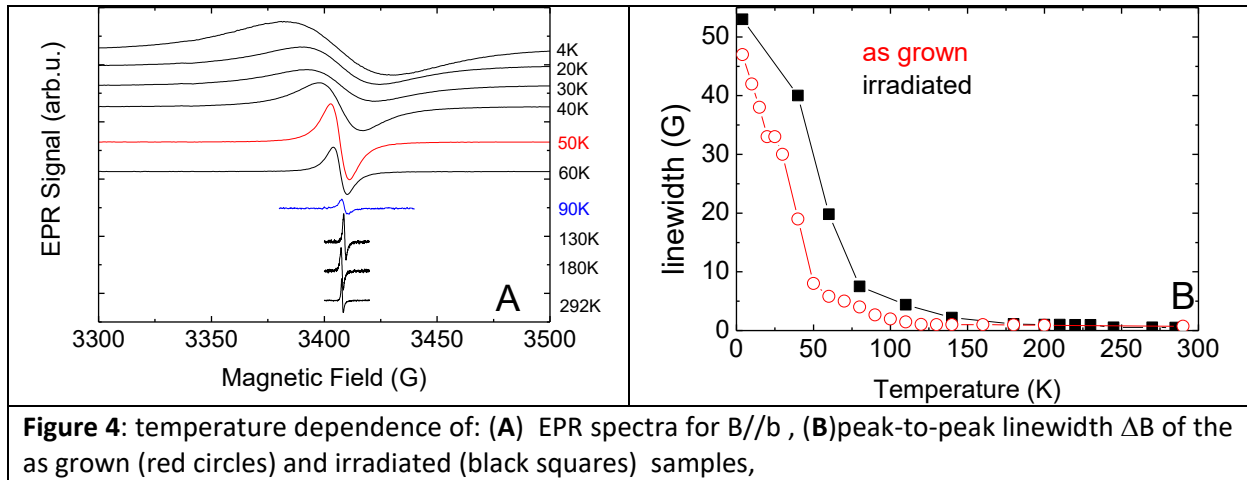


### EPR results in $\beta\text{-Ga}_2\text{O}_3$

The as-received samples show only one anisotropic single line spectrum, which can be observed in the whole temperature range from 4K to 300K (fig.1, 2). At  $T=4K$  we observe the neutral shallow donor, which has an electron spin of  $S=1/2$  and at  $T=300K$  the electron spin resonance of conduction electrons. At  $T=4K$  the EPR spectrum has a linewidth of 50G and a Lorentzian shape. The observation of a large linewidth of  $\sim 50G$  is not unexpected for localized electrons as the presence of 100% Ga nuclei with spin  $I=3/2$  gives rise to large inhomogeneous broadening. Inhomogeneous broadening normally produces a Gaussian lineshape, which is not observed here. The observed shape is Lorentzian, an indication of dynamic effects already operating at temperatures as low as  $T=4K$ . If the carrier concentration is reduced by particle irradiation, the EPR spectrum is changed into a "normal" Gaussian shape (Fig.1B). From the angular dependence of the resonance fields (fig.3) in three lattice planes its spin  $S=1/2$  and  $g$ -tensor have been determined:  $g_{xx}=1.9575$ ,  $g_{yy}=1.9603$  and  $g_{zz}=1.9630$  with the principle axes  $zz$  aligned with the  $b$ -axis and the  $xx$  and  $yy$  axes lying in the  $b$ -plane with  $xx$  at an angle of  $23^\circ$  from the  $c$ -axis. The  $g$ -values are close to those previously reported for shallow donors in  $\beta\text{-Ga}_2\text{O}_3$  and conduction electrons (table I) [8-10].



When the temperature is increased from  $T=4K$  the  $g$ -values vary only marginally with temperature and the orientation of the principal axes is not changed. The linewidth however decreases rapidly. In the range between  $T=4K$  and  $T=40K$  it decreases drastically from 50G to  $<1G$  (Fig.4A, 4B) and the lineshape becomes asymmetric, an indication of increasing conductivity of the sample. The asymmetric Dyson-like lineshape is characterized by a small asymmetry  $A/B$  ratio of  $<1.6$ , whereas for metallic conduction higher values of  $A/B > 2$  should be observed.  $A$  and  $B$  are the amplitudes of the positive and negative lobes of the first derivative line. The comparison with the EPR parameters in the proton irradiated sample (Fig.4B) shows only small differences in the absolute value of the linewidth and their temperature dependence. The only notable difference is the lineshape, which now is Gaussian at low temperature. The fact that the donor linewidth is changing at a temperature as low as  $T=4K$  is surprising; for example, the linewidth of deep centers such as transition metal ions is temperature independent. The mechanism leading to a reduction of the EPR linewidth is motional narrowing, which will average out the superhyperfine interactions, when the time scale of motion is sufficiently small, i.e. if the condition  $\Delta\nu \tau > 1$ , where  $\Delta\nu$  is the linewidth in frequency units and  $\tau$  the correlation time, corresponding to the inverse of the hopping frequency. For a linewidth of 50G the hopping frequency must be higher than GHz to lead to a reduction of the linewidth.

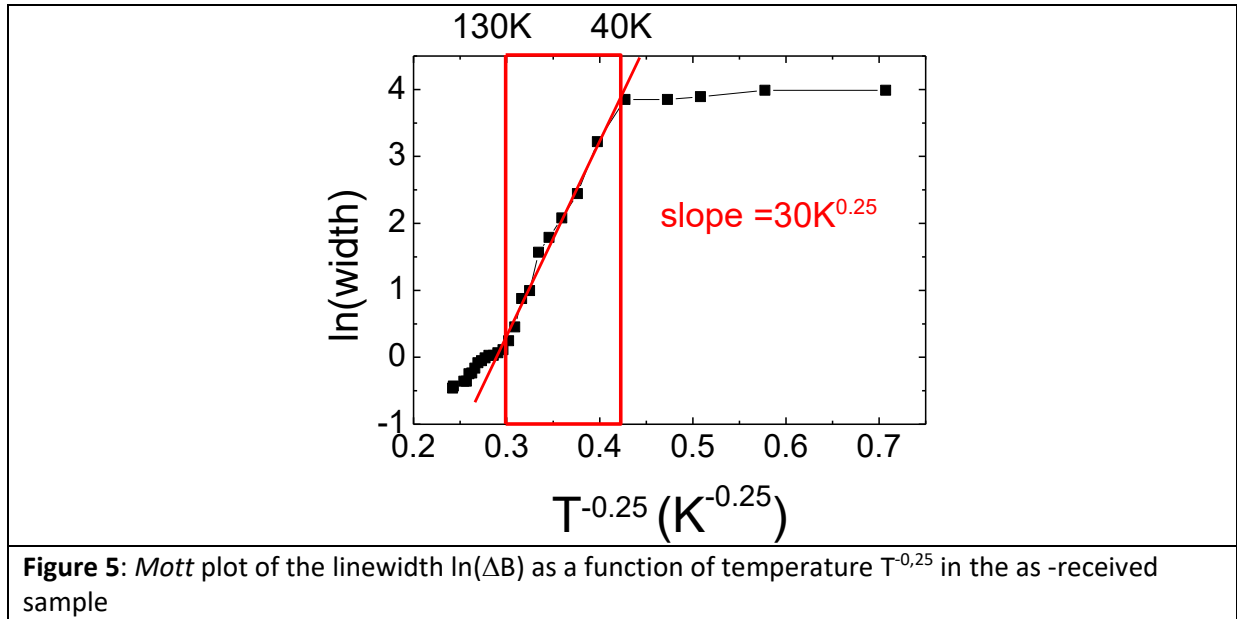


To get further insight in the dynamic processes of the donor electrons we have tested whether the temperature variation of the linewidth can be simulated by a variable range hopping process [15] such as previously demonstrated for shallow donors in  $\epsilon$ - $Ga_2O_3$  [13]. In fig.5 we have plotted the results in a so-called Mott plot, i.e.  $\ln(\Delta B)$  vs  $T^{-1/4}$ , the expression for 3-dimensional variable range hopping (VRH).

This expression has been derived for the temperature variation of the electrical conductivity  $\sigma$ :

$$\sigma = \sigma_{00} \exp \left[ - \left( \frac{T_0}{T} \right)^{1/4} \right] \quad (\text{eq.1})$$

Where  $\sigma_{00}$  is a prefactor,  $T_0$  a material parameter [11],



Assuming the same expression for the linewidth we obtain:

$$\Delta B = \Delta B_{00} \exp \left[ - \left( \frac{T_0}{T} \right)^{\frac{1}{4}} \right] \quad (\text{eq.2})$$

The motionally narrowed EPR line will be of Lorentzian shape with a width  $\omega_p^2 \tau_c$  with  $\omega_p$  the low temperature linewidth in frequency units. Its width follows the same law as the correlation time  $\tau_c$ , which is correlated with the hopping frequency. The plot  $\ln(\Delta B)$  vs  $T^{-1/4}$  shows two linear regions  $T=4\text{K}..T=40\text{K}$  and  $T=40\text{K}..T=130\text{K}$ , which are in agreement with the model of VRH conduction. The parameter  $T_0$  is defined as

$$T_0 = \frac{\beta}{k_B D(E_F) a^3} \quad (\text{eq.3})$$

and its value can be obtained from the slope in fig.5:  $T_0=8 \times 10^5 \text{K}$ . Assuming a localization length equal to the effective Bohr radius  $a_B=1.9\text{nm}$  and a numerical constant  $\beta=18$ , we find a density of states near the Fermi level of  $D(E_F)=4 \times 10^{19} \text{eV}^{-1} \text{cm}^{-3}$ . The concentration of localized states at  $T=100\text{K}$  is thus

$$n(E_F) = 1/4 D(E_F) k_B T (T/T_0)^{-1/4} = 1.6 \times 10^{18} \text{cm}^{-3}$$

and the average hopping length at  $T=100\text{K}$  is  $6.6\text{nm}$ .

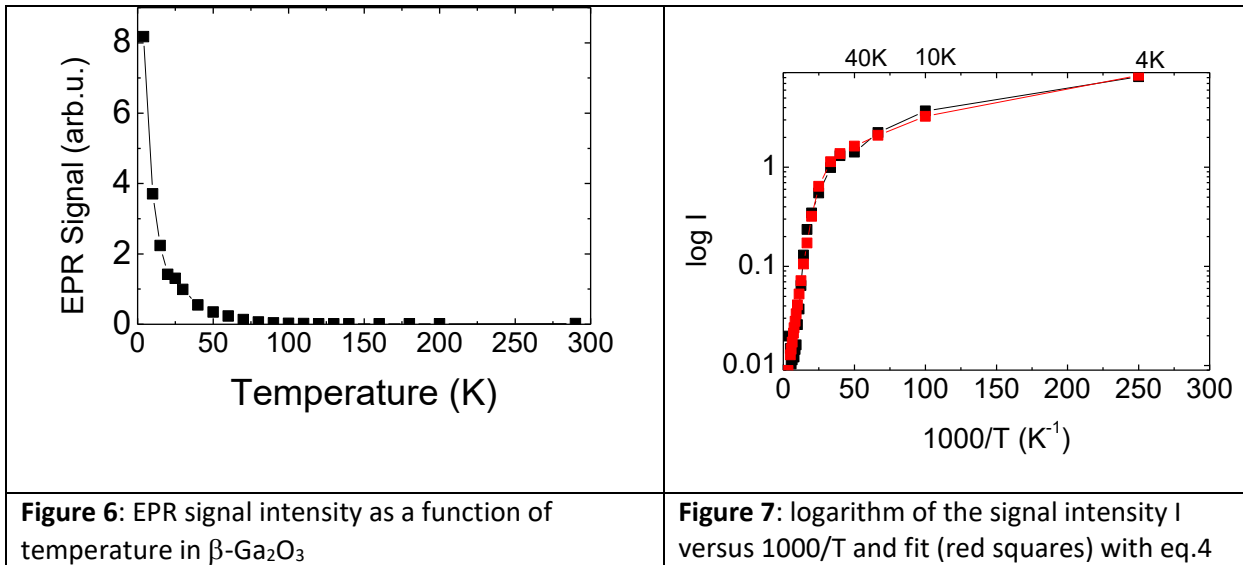
However, given the thermal ionization energy of the Si shallow donor of  $31\text{meV}$  [7,12] and a concentration of only  $10^{17} \text{cm}^{-3}$ , one should a priori expect carrier localization below  $T=40\text{K}$  and delocalization above this temperature. However, the drastic reduction of the linewidth already in the low temperature range  $T < 40\text{K}$  indicates a more complex situation. We have reported [13] in a previous study of Si shallow donors in epitaxial  $\varepsilon\text{-Ga}_2\text{O}_3$ , that donor clustering is a possible explanation of this phenomenon. It might give rise to close neighbor hopping at low temperature and variable range hopping at  $T > 40\text{K}$  between donor clusters. The temperature dependence of the EPR

linewidth cannot be analyzed above 130K, as the linewidth is already close to the intrinsic one, determined by lifetime broadening.

At temperatures above  $T=130\text{K}$ , we will have coexistence of delocalized electrons and conduction electrons thermally emitted in the conduction band. The observation of conduction electron spin resonance (CESR) is possible and has been studied in all main semiconductorssuch as Si [16], GaN[18] or SiC [17]. In all cases due to life time broadening the CESR lines becomes rapidly (within some K) unobservable above the temperature, for which thermal ionization becomes dominant. In the case of the Si shallow donor in  $\beta\text{-Ga}_2\text{O}_3$  the observation of the CESR at temperatures higher than  $T=100\text{K}$  is unexpected and the monotonous decrease of the linewidth is opposite to the findings in most semiconductor materials. To illustrate this phenomenon, we have performed a similar study for the Hydrogen shallow donor and CESR inZnO, as shown below.

We have equally analyzed the temperature dependence of the EPR signal intensity  $I$ . A plot of  $I$  vs  $T$  is shown in fig6. We observe a monotonous variation of  $I$  with temperature with no indication of a negative U behavior, which would have introduced a maximum at an intermediate temperature. These results are different from those reported by Son et al[10]. We have analyzed the temperature dependence in a standard model, which considers Curie type paramagnetism and thermally activated emission of the donor electrons (fig.7). The Curie type paramagnetism decreases the EPR signal intensity as  $I \sim 1/T$  in the high temperature approximation and applies to the case of localized electrons. For the thermal emission of the donor electrons we have considered two activation energies:

$$\frac{I}{I_0} = (1 + \sum_i k_i e^{-\frac{E_i}{2k_B T}})^{-1} \quad (\text{eq.4})$$



Where  $E_i$  is the thermal activation energy of process  $i$  with prefactor  $K_i$ . As shown in fig.7 the experimental data can be well fitted with two activation energies:

$$E_1=4\text{meV} \text{ and } K_1=12$$

$$E_2= 40\text{meV} \text{ and } K_2=1550.$$

The second activation energy is in fair agreement with the shallow donor value (36+/-5) meV as reported before [7,12]. The smaller activation energy of  $E_1=5\text{meV}$  in the low temperature range has been observed also for other shallow donor systems but its origin has not been identified; we tentatively assign it to the thermal activation energy for hopping conduction.

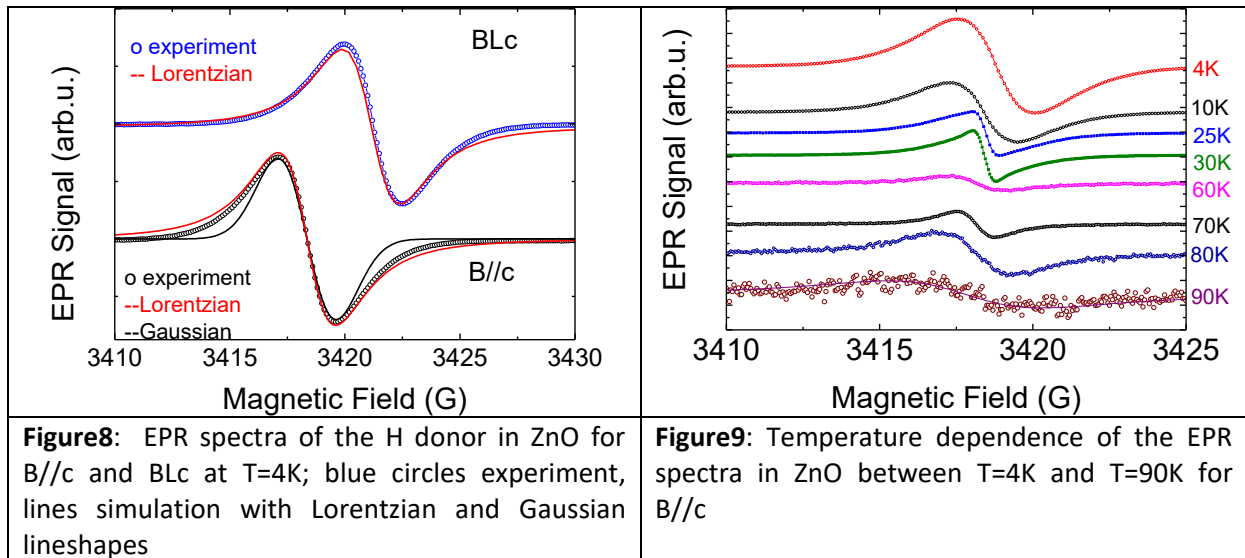
Model	g-tensor principal values : $g_{xx}, g_{yy}, g_{zz}$ T=4K T=300K		Sample	Reference
Neutral donor $D^\circ$ T=4K	1.9603 1.9575 1.9622 $\alpha=23+/-3^\circ$		EFG grown As grown	This work
Conduction electrons T=300K		1.9606 1.9578 1.9628 $\alpha=23+/-3^\circ$	EFG grown As grown	This work
Conduction electrons T=300K		1.9616 1.9590 1.9635 $\alpha=27+/-3^\circ$	Float zone growth Verneuil method	Binet 1994 [24]
Donor cluster Oxygen vacancy T=300K		1.960 1.958 1.962 $\alpha=24^\circ$	Float zone growth Non int. doped	Yamaga 2003 [8]
Donor (DX) T=300K/80K	1.9606 1.9577 1.9630 $\alpha=23^\circ$	1.9606 1.9577 1.9623 $\alpha=23^\circ$	Bulk plus 1100°C anneal	Son (2016) [10]

**Table I:** EPR parameters of the shallow donor and conduction electrons in  $\beta\text{-Ga}_2\text{O}_3$ : principal values of the g-tensor and the orientation  $\alpha$  of the principal axes xx, yy in the crystal *b*-plane; the zz axis is parallel to the crystal *b*-axis

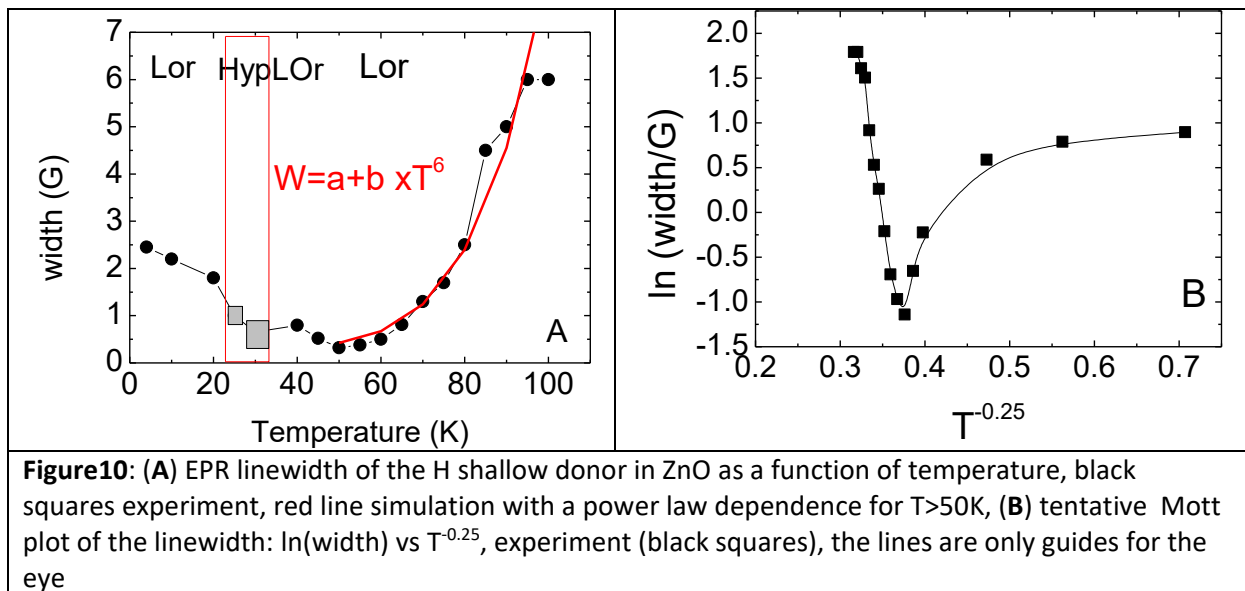
### ZnO:H

To illustrate the particularity of the shallow donor properties and conduction electron properties in  $\beta\text{-Ga}_2\text{O}_3$  we have also investigated the case of ZnO by EPR spectroscopy. This sample is n-type conductive due to doping with the hydrogen shallow donor (fig.8). The EPR spectra can be observed in the range T=4K to T=90K only (fig.9). The EPR spectrum of the H donor has an axial symmetry with two principal values of the g-tensor due to the hexagonal symmetry of the ZnO lattice. The values are  $g_{//c}=1.9570$  and  $g_{\perp c}=1.9554$  at T=4K. At T=4K the shape of the EPR line is





Lorentzian and the peak-to-peak linewidth 2.5G (fig.8). The linewidth for the localized donors in ZnO is much smaller than in the case of Si in  $\beta$ -Ga $_2$ O $_3$  due to the small abundance of nuclei with non-zero



nuclear spin ( $^{67}\text{Zn}$ ,  $I=3/2$ , 4.1%). The linewidth is slightly decreasing up to T=50K with a hyperlorentz lineshape in a small temperature range at (25 $\pm$ 5)K. For T>60K, when the electrons are thermally emitted into the conduction band, the linewidth is rapidly increasing and the observation of the EPR signal becomes impossible for temperatures T>90K due to excessive line broadening (fig.9). As the lineshape is still symmetric and not Dyson like the decrease of the EPR signal amplitude is not due to the reduced microwave absorption, which does occur when the skin depth becomes inferior to the sample thickness.

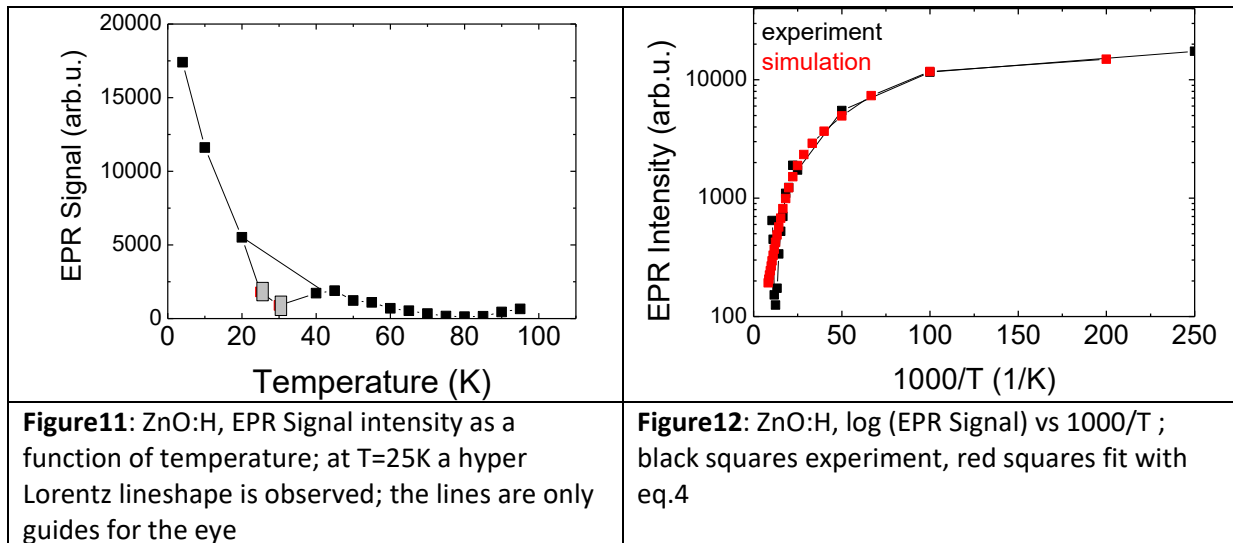
The temperature dependence of the linewidth is opposite to the case of  $\beta$ -Ga $_2$ O $_3$ . As shown in fig. 10B a “Mott plot” has no physical significance; but its variation can be fitted with a power law (fig.10A). Such strong broadening of the EPR line, when the electrons are moving in the conduction band, has been observed in many semiconductors and is generally attributed to phonon scattering. As the g-values of the conduction electrons are close to those of the shallow donor, their EPR lines are often undistinguishable.

We have equally analyzed the temperature dependence of the EPR signal intensity in the range  $T=4\text{K}$  to  $T=80\text{K}$  (fig.11) within the same model of Curie type paramagnetism and thermal emission of the donor electrons in the conduction band [19]. Again the data can be well fitted with two activation energies (fig.12). The fit gives the values of:

$$E_1=7\text{meV}$$

$$E_2=40\text{meV}$$

These values are close to those reported previously for the hydrogen donor in ZnO in samples with comparable donor concentrations of  $10^{17}\text{cm}^{-3}$  [19].



### Discussion:

EPR studies of donors and/or conduction electrons in  $\beta\text{-Ga}_2\text{O}_3$  have been reported before [8-10,20-22] but the issue of the conduction mechanism has not been analyzed sufficiently. The early results can be classified in two phases. In the 90's EPR studies have been undertaken on undoped, melt grown, "laboratory" crystals, which without intentional doping showed already extremely high electron concentrations of  $>10^{19}\text{cm}^{-3}$ . The origin of the high electron concentration was at that time attributed to the presence of oxygen vacancies [20-22] believed to be shallow donors and the EPR spectra were associated with conduction electron spin resonance. More recent results have shown, that the donor responsible for this high electron concentration cannot not be an oxygen vacancy[5]. Later Yamaga et al [8] reported an EPR study of n-type conducting, laboratory, bulk samples grown by the float zone technique. They were non-intentionally doped and showed a RT conductivity of  $20\ \Omega^{-1}\text{cm}^{-1}$ . They observed a single line anisotropic EPR spectrum with g-values typical for donor defects. They noticed already a strong temperature dependence of EPR linewidth, which they attributed to the effect of motional narrowing for  $T>50\text{K}$  but the conduction mechanism was not analyzed. Our results indicate that conduction is determined by three-dimensional variable range hopping with two different activation energies. The model retained by us is that the donors are not randomly distributed but forming local clusters in these non intentionally doped bulk samples. Within this model low temperature hopping occurs within the clusters and at high temperatures hopping between different clusters becomes possible. A recent study by terahertz spectroscopy on comparable bulk samples has equally concluded on the presence of carriers moving in localized

potential minima at temperatures below  $T=50\text{K}$  [23]. Interestingly an activation energy of  $E=5\text{meV}$  has been reported similar to our results.

The observation of the CESR with extremely small linewidth below  $\Delta B=1\text{G}$  must be related to a nonstandard spin-phonon interaction. It is a quite unique feature different from the case of silicon [16], silicon carbide [17], GaN [18] or as shown here ZnO, where phonon scattering rapidly increases the CESR linewidth with increasing temperature. Binet et al [24] have attributed the strongly reduced linewidth to the conduction band structure of  $\beta\text{-Ga}_2\text{O}_3$ . They showed the lowest conduction band to be composed of 4s states of octahedral Ga, having a quasi one-dimensional property along the  $b$ -axis. According to these authors the conduction electrons are moving along the octahedral chains, which are separated through an energy barrier by the tetrahedral Ga chains.

Finally, we want to comment on the DX properties of Si shallow donors. In a recent EPR study on donors in bulk  $\beta\text{-Ga}_2\text{O}_3$  Son et al [10] have proposed a DX model. The term "DX center" has been used previously for donors in AlGaAs alloys [25], where from a particular Al composition on a deep donor state becomes the equilibrium configuration of the Si donor. The samples investigated in [10] were Si doped at a concentration of  $7.1 \times 10^{17} \text{cm}^{-3}$  but showed surprisingly no neutral donor EPR spectrum in the as-grown state. Only after an annealing at  $1100^\circ\text{C}$  in  $\text{N}_2$  gas flow, the samples became conductive and the EPR spectrum of a neutral donor was observed. These authors concluded that the shallow donor, supposed to be Si, is a negative-U center, similar to DX centers in AlGaAs. The DX like character of the Si donor, which has been questioned [7] later on the basis of transport measurements in Si doped n-type thin films and is also not confirmed by our results. For more details on negative U properties see the discussions in [7, 10] concerning  $\text{Ga}_2\text{O}_3$ .

In conclusion we have shown that EPR spectroscopy of the shallow donor can be efficiently used to investigate the conduction properties in  $\beta\text{-Ga}_2\text{O}_3$ . As EPR is a volume sensitive technique, it is "free" from surface conductivity effects, which often complicate the transport measurements in oxide semiconductors. We have shown that carrier transport in  $\beta\text{-Ga}_2\text{O}_3$  occurs via a VRH process even in samples with carrier concentrations below the Mott transition. The carrier dynamics already observed at the lowest temperature evidence that the donor distribution in the bulk samples is not uniform but gives rise to cluster formation. The small linewidth of the CESR might be attributed to a quasi-one-dimensional character of the lowest conduction band.

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