Low temperature magnetic field effects on the efficiency of aluminium tris(8-hydroxyquinoline) based organic light emitting diodes in the absence of magneto-resistance

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Abstract

This paper presents low temperature results of the magnetic field effect on current and efficiency in Alq_3 based light emitting diodes (OLEDs). We report a magnetic field effect on light output at driving voltages where no magnetic effect is measured on the current. This is attributed to the presence of significant trapping, where trapped carriers are unable to de-trap at low temperature. At high current densities and corresponding bias, magnetoresistance is observed as a result of trap filling or field assisted tunnelling. A negative magnetic field effect (MFE) on efficiency at low temperatures and a deviation from the linear relationship between organic magnetoresistance (OMR) and singlet population are also observed. The latter are attributed to significant triplet-triple annihilation (TTA) occurring within the device.

1 Introduction

In 2003 Kalinowski *et al.*[1] observed that for aluminium *tris*(8-hydroxyquinolate) (Alq_3) devices significant increases in the current, light emission and efficiency could be obtained with the application of magnetic fields of magnitude<0.5T. Since then the study of these phenomena has been made great progress[2-27], but there is still some debate as to the model to understand the organic magnetoresistance (OMR). A successful OMR model will be essential for understanding the underlying mechanisms for the magnetic field effect on the organic semiconductors. Generally, the existing OMR models can be divided into two contrasting approaches: the bipolaron and excitonic models. The bipolaron model is based on the role of bipolarons on the current transport and the effect that a magnetic field is expected to have on their formation rate. This bipolaron based model suggests that OMR may be observed in unipolar structures[11, 12, 16, 17, 25]. On the other side, the excitonic models are based primarily on the effect of magnetic fields on excitons or the pair states prior to exciton formation [1, 5-10, 26] and the role these excitons play on the current in the device. These excitonic models are receiving particular attention because the majority of experiments suggest OMR can only be seen in devices above the turn-on voltage for light emission. The one of excitonic models is the pair states model[1, 5-7, 10], it suggests that the singlet and triplet pair states initially can be mixed by the hyperfine fields. The magnetic field could modulate the ratio of pair states between the singlet pair states and triplet pair states, resulting in the rates changes of recombination and dissociation of pair states. Therefore, a change in the mixing of these pair states by a magnetic field results in a change in the current. Another of excitonic model is TPI model[8, 9] which suggests that triplet polaron interaction decreases the polaron mobility due to two processes: spin blocking or weak trapping and interactions between triplets and polarons. When the magnetic field affects on an operating OLED, the ratio of triplets to singlets could be shifted, resulting in the decrease in the triplet concentration and increase the polaron mobility.

It has been observed that the TPI model can be described using a double Lorentzian function, where the two Lorentzians correspond to the two processes: spin blocking or weak trapping and interactions between triplets and polarons. The TPI can include a number of processes such as polaron induced triplet dissociation [8, 28] or polaron induced triplet quenching[29]. Each of these components would in turn be dependent on the triplet population which can be modified by a magnetic field through changes to the intersystem crossing rate of either polaron pairs or excitons[8, 10, 20]. In addition, it has been demonstrated that the OMR data over a range of thicknesses, cathodes and temperatures can be fitted by the TPI model [21, 24] and that the pre-factor for each process linearly scales with exciton concentration. Whilst this model has been shown to successfully fit a wide range of data for thick devices it is clear that other process can occur and contribute towards OMR. For example we have demonstrated that in thin devices a negative OMR component can exist and this has been attributed to triplet dissociation at the cathode [30]. It is not unreasonable to conclude that OMR is a complex phenomenon where several processes are occurring simultaneously and that considerable effort will be required to elucidate all the processes operating and which dominate in different devices.

In this paper we show that, whereas at room temperature magnetically induced changes in the electroluminescence and efficiency of devices coincide with changes in the device current, this is not the case at low temperature. We report measured changes in the electroluminescence and device efficiency under conditions where no magnetically induced change in the current occurs and that this is consistent with considerable charge trapping within the device. In addition, at room temperature, the percentage change of efficiency in an Alq_3 based OLED always increases with applied magnetic field, at low temperature (100K) a change in behaviour is observed with the efficiency starting to fall at fields greater than ~30mT. Although the MFE on efficiency starts to become negative at these low temperatures the OMR remains positive and can still be fitted using the double Lorentzian approach from the TPI model. However, once this negative component in the MFE on efficiency occurs the fitted OMR data is found to no longer be linear with exciton concentration. Whilst at

high temperatures the magnitude of each of the processes found from the fitting scaled linearly with exciton concentration, the linear relationship breaks down at high operating voltages and low temperatures. This deviation from the linear behaviour corresponds to the onset of the negative component in the MFE on efficiency data and is probably due to the onset of triplet-triplet annihilation (TTA) which means that the triplet concentration is no longer linear with the light emission (i.e. singlet concentration).

2 Experimental

For the measurements we have used a standard device structure which consisted of indium tin oxide (ITO)/50 nm of N,N′-diphenyl-N,N′bis (3-methylphenyl) -(1,1′-biphenyl)- 4,4′diamine (TPD)/50 nm of Alq_3/1 nm of LiF/ 100 nm of aluminium. The devices were grown in a Kurt J. Lesker SPECTROS thermal evaporation system under continuous vacuum of ~10^{-7} mbar. The ITO coated substrates are purchased from Merck and undergo photolithographic patterning and oxygen plasma treatment prior to growth. The plasma treatment is ~3 min at 30 W and 2.5 mbar pressure and is performed using a Diener Electronic Femtoplasma system. The Alq_3 and TPD are purchased from Sigma Aldrich and are purified prior to use by train sublimation. The rate of deposition of organic materials was ~0.2 nm/s while that of the aluminium was varied from ~0.1 to 1 nm/s.

The temperature dependent OMR measurements are carried out in a liquid nitrogen flow cryostat operated between 100K and 300K with the sample held in the nitrogen exchange gas. The magnetic field is applied perpendicular to the current direction using an electromagnet. The magnetic field measurements were taken with the device in constant voltage mode and alternated with null field measurements to remove any effects due to drifting in the device characteristics. Voltage sourcing and current measurements were performed using a Keithley 236 source-measure unit with current measurements being averaged over 320 readings. Electroluminescence intensity was measured using a Newport 818SL silicon detector placed against the cryostat window, coupled with a Newport 1831 optical power meter.

3 Result and discussion

Figure 1 shows the current and luminescence against voltage for a 50nm Alq_3 OLED at 100K. It can be observed that the voltage for the onset of light emission that can be detected in our experimental setup is 6.8V. Figure 2 shows the onset of the percentage changes in light emission, current and efficiency with magnetic field at 100K. It has been reported that the onset voltage for OMR at 300K and 200K coincides with the onset of light emission at 2.4V and 3.2V respectively and this suggests that OMR is the result of excitonic processes [24]. What is of greater interest is the difference between the onset of light emission and the onset of OMR observed at 100K. In this case, the presence of a magnetic field effect on the light emission was measured at 7V, corresponding to the onset of light emission. This onset of light emission reflects the measured formation of excitons and furthermore the magnetic field effects on the light emission confirm the occurrence of ISC from the triplet to the singlet state, probably through interactions at the pair state level. Despite this, no OMR could be detected until the device was driven at voltages greater than 13V. It is worth noting that increased averaging was undertaken (1280) to improve signal to noise, however any effect remained below the detection limit. In addition, we prefer to present the data as a percentage change in the efficiency rather than the electroluminescence, in contrast to other research groups. This is because the percentage change in light emission is dependent on the driving conditions, whereas the percentage change in efficiency depends only on excition formation, that is, on the relative numbers of singlet and triplet excitons formed by the injected electrons and holes. The calculation of the percentage change in efficiency, however, is related to the percentage change in the current. This may result in additional noise appearing in the efficiency data, compared to the electroluminescence data, because of variations in the current (as demonstated in figure 2, 7V driving conditions).

In an earlier paper, Desai *et al.*[8] suggested that the OMR may be due to the interaction of polarons with triplets within the device. There are two primary methods through which we have suggested excitons, and predominantly triplets, can affect the current.

The first is through a direct change in the carrier mobility due to spin blocking or weak trapping of the polarons at the triplets. The second is through spin interactions between polarons and triplets which may modulate triplet quenching or dissociation. According to the first mechanism, any process that reduced the concentration of triplets would have the effect of increasing the mobility of free carriers within the device, hence increasing the current. As a modulation in the light emission with magnetic field can be observed from ~7V it might be expected that this would give a corresponding change in the current as observed at higher voltages.

According to Agranovich *et al.* [31] triplets can act as shallow traps for polarons. It is well known that Alq_3 has highly dispersive carrier transport, for example when measured using time-of-flight, and that the transport is dominated by trapping with a significant number of deep traps[32]. Therefore at low temperatures and low current densities the transport will be dominated by the deepest traps. It is probable that carriers will become trapped at these sites and will not have sufficient thermal energy to escape. This deep trapping will not be affected by the presence of a magnetic field. It will not be until all these trap states are filled, i.e. at high current densities, or when the electric field in the device is high, to allow the carriers to tunnel out, that the role of the shallow triplet-induced traps can be observed[33]. Hence there is an offset, at low temperatures, between the onset of the magnetic field effect on light emission and the onset of OMR.

In an earlier paper, Zhang *et al.*[24] reported that the OMR data for 50nm Alq_3 device can be fitted using the triplet polaron interaction (TPI) model that includes two independent processes, namely the exciton trapping and the triplet polaron interaction components, which both scale linearly with exciton concentration over the temperature range from 300K to 150K. This TPI model can be presented as a double Lorentzian equation as follow,

$$f(B) = a_t \frac{B^2}{\left(B^2 + B_t^2\right)} + a_i \frac{B^2}{\left(B^2 + B_i^2\right)} \qquad \text{Equation (1)}$$

Where B is the applied magnetic field, a_t an a_i are the pre-factors for the Lorentzians and B_t and B_i are the saturation fields, the subscripts t and i stand for trapping and

interaction respectively. The constraints used in the fit, taken from reference [21, 24], were 5mT<B_t<7mT, a_t>0, B_i=160 mT and a_i>0.

Figure 3 shows the OMR curves (plotted as the relative change in current) for a 50nm Alq_3 device at 100K and over a range of operating voltage. It can be seen that when the temperature is reduced to 100K the quality of the fits by Equation (1) to the OMR data is not as good as that obtained at higher temperatures (300K-150K) previously observed by Zhang *et al.*[24]. This may indicate that another process is occurring in the devices at low temperatures. Figure 4 shows the percentage change in efficiency in a 50nm Alq_3 OLED at 100K with applied field for several drive voltages. It was reported that the change in efficiency for an Alq_3 device at 300K with magnetic field is that a rapid increase in efficiency during the first tens of mT followed by a slow increase at higher magnetic fields[8, 9]. At 100K, however, following the initial rapid rise in efficiency observed at low fields there is a subsequent negative component to the delta efficiency which becomes more pronounced with increasing drive voltage.

A similar phenomenon has also been reported by other research groups. Johnson *et al.* [34] observed a small increase in delayed fluorescence of anthrancene at low fields, followed by a decrease as the magnetic field increases. This was attributed to a modulation of the TTA rate induced by the magnetic field. Similar results have also been observed in delayed electroluminescence of Alq_3 OLEDs[35] and delayed photoluminescence of PtOEP-doped DPA films[36]. More recently Xiong *et al.*[37,38] observed an identical effect to that obtained here in the electroluminescence of Alq_3 at low temperatures which was also attributed to TTA. The magnitude of the TTA process we have observed increases dramatically with increasing operating voltage, with there being no evidence of it below 10V but with it dominating the delta efficiency data at 15V. This is to be expected as the TTA should be proportional to the square of the triplet concentration[39]. It is possible that the presence of TTA in these devices at low temperature may also be having a role on the OMR and account for the fact that the fits to the OMR are not as good at low temperature as those obtained at higher temperature.

Figure 5 shows the pre-factors for the trapping component, a_t, obtained using Equation (1) fits to the OMR data at 300K and 100K, plotted against singlet concentration. The singlet concentration is calculated using the light output and assuming a recombination wavelength of 520nm, a singlet lifetime of 10ns and that the recombination occurs throughout the Alq_3 layer. Zhang *et al.*[24] previously reported that for OLEDs at temperatures above 150K both pre-factors for trapping and TPI scale linearly with exciton concentration. However, it can be seen in figure 4 that the pre-factors for the trapping component results from the fitting to the OMR data at 100K deviate significantly from this linear behaviour. We have suggested that as the primary cause of the OMR is interactions with triplets the linearity with the singlet concentration is due to the fact that the formation rate and decay rate of singlets and triplets are proportional and hence the singlet concentration is a good measure of the triplet concentration in the device. In the presence of TTA this relationship breaks down as TTA results in two triplets combining to produce a new singlet. This means that when TTA is occurring the triplet concentration rises more slowly than the singlet concentration and therefore the data points would be expected to lie on a line with a slope greater than one, as can be seen in figure 4.

4 Conclusion

In conclusion we have investigated the temperature dependencies of the magnetic field effect on current and efficiency of Alq_3 based OLEDs. A large difference between the onset of light emission and onset of OMR was observed at low temperatures. This phenomenon is abnormal compared with OMR data at room temperature. This is attributed to the trapped carriers being unable to de-trap at low temperatures. We observe a negative MFE on efficiency at low temperatures and suggest it is probably due to triplet-triplet annihilation (TTA) and that due to the effect this has on the triplet population there is a deviation from the linear relationship between OMR and singlet population.

5 Reference

1. J. Kalinowski, M. Cocchi, D. Virgili, P. Di Marco and V. Fattori, Chemical Physics Letters **380**, 710 (2003).
2. A. H. Davis and K. Bussmann, Journal of Vacuum Science & Technology A **22**, 1885 (2004).
3. O. Mermer, M. Wohlgenannt, T. L. Francis and G. Veeraraghavan, Ieee Transactions on Magnetics **41**, 3682 (2005).
4. Y. Sheng, T. D. Nguyen, G. Veeraraghavan, O. Mermer, M. Wohlgenannt, S. Qiu and U. Scherf, Phys Rev B **74**, 045213 (2006).
5. H. Odaka, Y. Okimoto, T. Yamada, H. Okamoto, M. Kawasaki and Y. Tokura, Appl Phys Lett **88**, 123501 (2006).
6. V. N. Prigodin, J. D. Bergeson, D. M. Lincoln and A. J. Epstein, Synthetic Metals **156**, 757 (2006).
7. Y. Wu and B. Hu, Appl Phys Lett **89**, 203510 (2006).
8. P. Desai, P. Shakya, T. Kreouzis, W. P. Gillin, N. A. Morley and M. R. J. Gibbs, Phys Rev B **75**, 094423 (2007).
9. P. Desai, P. Shakya, T. Kreouzis and W. P. Gillin, Phys Rev B **76**, 235202 (2007).
10. B. Hu and Y. Wu, Nature Materials **6**, 985 (2007).
11. F. L. Bloom, W. Wagemans, M. Kemerink and B. Koopmans, Physical Review Letters **99**, 257201 (2007).
12. P. A. Bobbert, T. D. Nguyen, F. W. A. van Oost, B. Koopmans and M. Wohlgenannt, Physical Review Letters **99**, 216801 (2007).
13. Y. Sheng, T. D. Nguyen, G. Veeraraghavan, O. Mermer and M. Wohlgenannt, Phys Rev B **75**, 035202 (2007).
14. T. D. Nguyen, Y. G. Sheng, J. Rybicki, G. Veeraraghavan and M. Wohlgenannt, Journal of Materials Chemistry **17**, 1995 (2007).
15. T. D. Nguyen, Y. Sheng, J. Rybicki and M. Wohlgenannt, Phys Rev B **77**, 235209 (2008).
16. F. L. Bloom, W. Wagemans and B. Koopmans, J Appl Phys **103**, 07F320 (2008).
17. F. L. Bloom, W. Wagemans, M. Kemerink and B. Koopmans, Appl Phys Lett **93**, 263302 (2008).
18. B. F. Ding, Y. Q. Zhan, Z. Y. Sun, X. M. Ding, X. Y. Hou, Y. Z. Wu, I. Bergenti and V. Dediu, Appl Phys Lett **93**, 183307 (2008).
19. L. Y. Xin, C. N. Li, F. Li, S. Y. Liu and B. Hu, Appl Phys Lett **95**, 123306 (2009).
20. S. J. Zhang, J. Y. Song, T. Kreouzis and W. P. Gillin, J Appl Phys **106** (043511) (2009).
21. W. P. Gillin, S. J. Zhang, N. J. Rolfe, P. Desai, P. Shakya, A. J. Drew and T. Kreouzis, Phys Rev B **82**, 195208 (2010).

22. T. D. Nguyen, B. R. Gautam, E. Ehrenfreund and Z. V. Vardeny, Physical Review Letters **105**, 166804 (2010).
23. T. D. Nguyen, G. Hukic-Markosian, F. J. Wang, L. Wojcik, X. G. Li, E. Ehrenfreund and Z. V. Vardeny, Nature Materials **9** (4), 345 (2010).
24. A. J. D. S.J. Zhang, T. Kreouzisa and W.P. Gillin, Synthetic Metals **161**, 628 (2011).
25. W. Wagemans, A. J. Schellekens, M. Kemper, F. L. Bloom, P. A. Bobbert and B. Koopmans, Physical Review Letters **106**, 196802 (2011).
26. A. Buchschuster, T. D. Schmidt and W. Brutting, Appl Phys Lett **100**, 123302 (2012).
27. S. Zhang, N. J. Rolfe, P. Desai, P. Shakya, A. J. Drew, T. Kreouzis and W. P. Gillin, Phys Rev B **86**, 075206 (2012).
28. E. L. Frankevich, A. A. Lymarev, I. Sokolik, F. E. Karasz, S. Blumstengel, R. H. Baughman and H. H. Horhold, Phys Rev B **46**, 9320 (1992).
29. V. E. a. R. E. Merrifield, Phys. Rev. Lett. **21**, 609 (1968).
30. P. Desai, P. Shakya, T. Kreouzis and W. P. Gillin, J Appl Phys **102**, 073710 (2007).
31. V. M. Agranovich, D. M. Basko, K. Schmidt, G. C. LaRocca, F. Bassani, S. Forrest, K. Leo and D. Lidzey, Chemical Physics **272**, 159 (2001).
32. R. G. Kepler, P. M. Beeson, S. J. Jacobs, R. A. Anderson, M. B. Sinclair, V. S. Valencia and P. A. Cahill, Appl Phys Lett **66**, 3618 (1995).
33. K. Schwarzburg and F. Willig, Appl Phys Lett **58**, 2520 (1991).
34. R. C. Johnson and Merrifie.Re, Phys Rev B **1**, 896 (1970).
35. C. Garditz, A. G. Muckl and M. Colle, J Appl Phys **98**, 104507 (2005).
36. J. Mezyk, R. Tubino, A. Monguzzi, A. Mech and F. Meinardi, Physical Review Letters **102**, 087404 (2009).
37. Y. Zhang, R. Liu, Y. L. Lei and Z. H. Xiong, Appl Phys Lett **94**, 083307 (2009).
38. R. Liu, Y. Zhang, Y. L. Lei, P. Chen and Z. H. Xiong, J Appl Phys **105** (9), - (2009).
39. M. Colle and C. Garditz, Appl Phys Lett **84**, 3160 (2004).

Figure Captions

Figure 1. The current versus voltage and luminescence versus voltage for a 50nm Alq_3 based OLED at 100K.

Figure 2. The panels show the percentage in light emission, current and efficiency with magnetic field at 100K with the drive voltages at 7V and 13V.

Figure 3.The change in current in a 50nm Alq_3 OLED at 100K with applied magnetic field for several drive voltages. The fits are obtained using Equation(1).

Figure 4. The percentage change in efficiency in a 50nm Alq_3 OLED at 100K with applied magnetic field for several drive voltages.

Figure 5: The pre-factors for the trapping component, a_t, obtained using Equation (1) fits to the OMR data at 300K and 100K, plotted against singlet concentration. The straight lines are of slope 1.

Figure 1.

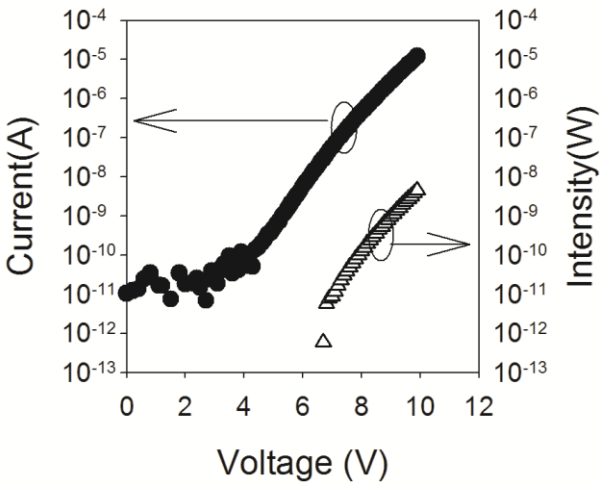


Figure 2

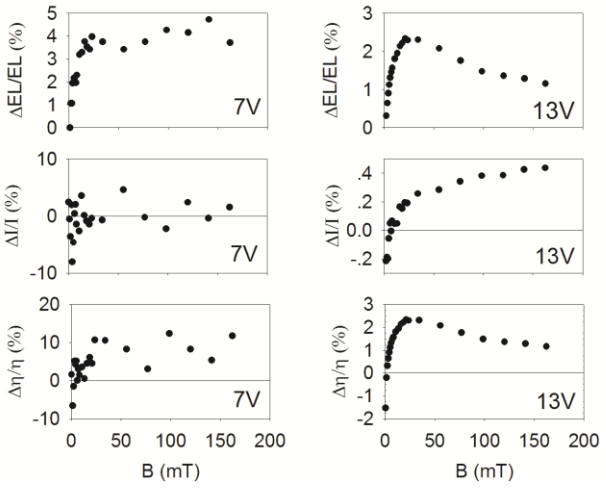


Figure 3

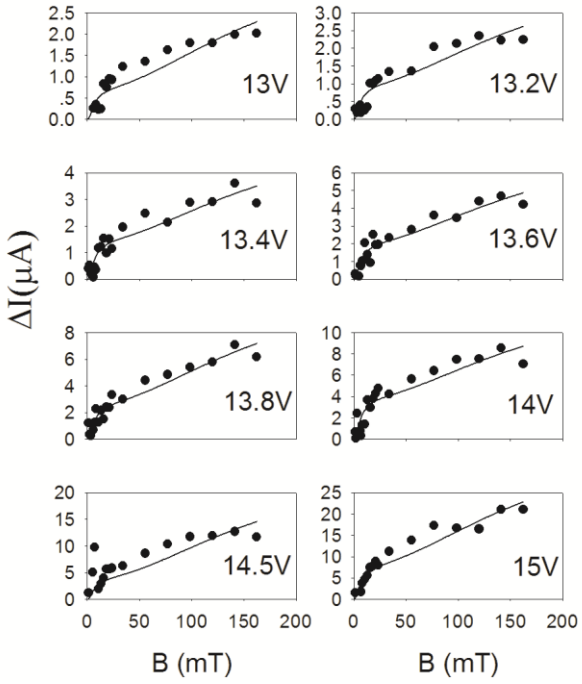


Figure 4.

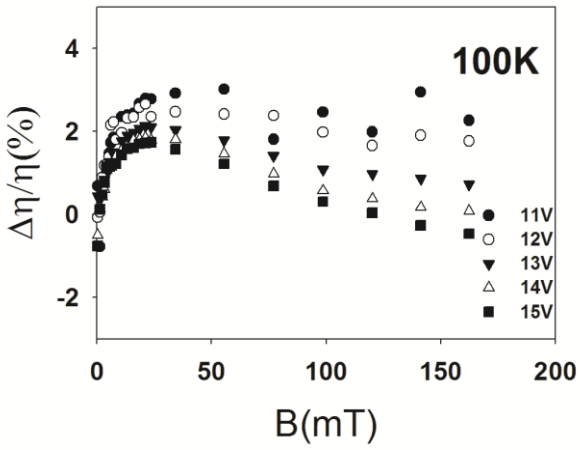
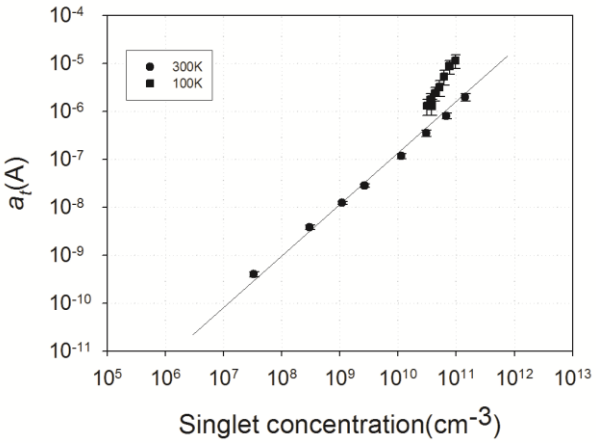


Figure 5


300K
100K
a_f(A)
10^{-4}
10^{-5}
10^{-6}
10^{-7}
10^{-8}
10^{-9}
10^{-10}
10^{-11}
10^{5} 10^{6} 10^{7} 10^{8} 10^{9} 10^{10} 10^{11} 10^{12} 10^{13}
Singlet concentration(cm^{-3})