Magnetic resonance studies of tris-(8-hydroxyquinoline) aluminum-based organic light-emitting devices

G. Li,[1] C. H. Kim,[1] P. A. Lane,[2,*] and J. Shinar[1]
[1]*Ames Laboratory-U.S. DOE and Department of Physics and Astronomy, Iowa State University, Ames, Iowa 50011, USA*
[2]*C. S. Draper Laboratory, 555 Technology Square, Cambridge, Massachusetts 02139, USA*
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The electroluminescence (EL)-, electrical current density (J)-, and photoluminescence (PL)- detected magnetic resonance (ELDMR, EDMR, and PLDMR, respectively) of tris-(8-hydroxyquinoline) aluminum (Alq_3)-based organic light-emitting devices (OLEDs) and Alq_3 films is described. At low temperatures, a positive spin-1/2 resonance is observed, i.e., the changes in J, the EL intensity I_{EL}, and the PL intensity I_{PL} are positive ($\Delta J/J$, $\Delta I_{EL}/I_{EL}$, and $\Delta I_{PL}/I_{PL}>0$). $\Delta J/J$ and $\Delta I_{EL}/I_{EL}$ are insensitive to the nature of the Alq_3/cathode interface. They weaken with increasing T and become unobservable above 60 K. $\Delta I_{PL}/I_{PL}$ also decreases with T, but is still observable at 250 K. Since the resonances all have the same g value, similar linewidths, and a similar dependence on T and the excitation level (J or the laser power), they are all attributed to the same mechanism. That mechanism is either the reduction of singlet exciton (SE) quenching by a reduced population of polarons in the bulk of the Alq_3 layer (''the quenching mechanism''), or the enhanced formation of SEs from singlet polaron pairs at the expense of triplet excitons (TEs) (''the delayed PL mechanism''). However, the latter mechanism implies that the yield of SEs in Alq_3-based OLEDs is greater than 25%. Due to evidence to the contrary, and other evidence which is inconsistent with the delayed PL mechanism, we conclude that the positive spin-1/2 resonance is due to the quenching mechanism. At $T\approx 60$ K, another spin-1/2 resonance, which reduces both J and I_{EL} (but is unobservable in the PL), emerges and grows with increasing T. This negative EDMR and ELDMR is sensitive to the buffer layer between Alq_3 and the cathode, and is attributed to the magnetic resonance enhancement of the spin-dependent formation of negative spinless bipolarons from spin-1/2 negative polarons at the organic/cathode interface. The increased trapping of injected electrons at the interface reduces J and consequently I_{EL}. However, at 295 K, the ratio $|\Delta I_{EL}/I_{EL}|$ in $Alq_3/AlO_x/Al$ devices to that in Alq_3/CsF/Al devices is significantly lower than the ratio of $|\Delta J/J|$ in these devices. Hence we suspect that other mechanisms, unidentified at this point, are also contributing to the negative ELDMR.

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I. INTRODUCTION

Organic light-emitting devices (OLEDs) have drawn extensive attention since electroluminescence (EL) was observed from devices based on tris-(8-hydroxy quinoline) Al (Alq_3) (Ref. 1) and poly(*para*-phenylene vinylene) (PPV).[2] The brightness, efficiency, and lifetime of OLEDs have increased dramatically over the past decade.[3] However, with the exception of OLEDs using phosphorescent dopants,[4] the external EL quantum efficiency η_{ext} remains stubbornly capped at $\sim 5\%$. This cap has been attributed to the product of the maximum formation efficiency of singlet excitons (SEs) from nongeminate polaron recombination $\eta_{SE}=25\%$ (Refs. 1–5) and the outcoupling efficiency of the emission to the front face of the device $\gamma=1/(2n^2)\sim 1/6$, where $n\sim 1.7$ is the refractive index of the organic layers.[3,5,6] Recent theoretical[7,8] and experimental[5,8–11] studies imply that η_{SE} could be as high as 60% and γ may be higher than $1/n^2 \sim 1/3$,[5] so η_{ext} could be as high as $\sim 20\%$. However, the experimental evidence for the high values of η_{SE} is either model dependent[8–10] (see below) or restricted to polymers containing Pt in their backbone.[11]

Nonradiative SE quenching processes, such as electric-field-induced SE dissociation,[12] energy transfer to the electrodes,[13] and quenching by polarons[14,15] and triplet excitons (TEs),[16] could contribute significantly to the large gap between the observed and theoretical η_{ext}. Since the dynamics of polarons and TEs are spin dependent, it is not surprising that the various optically detected magnetic resonance (ODMR) spectroscopies have proven to be powerful tools in studying the physics of these materials and devices.[8–10,14–23] These studies have provided direct evidence for the presence of long-lived polarons and TEs in both photoexcited films and biased OLEDs, and they have been used to explore the interactions of these excitations with SEs.

This paper describes EL- and electrical current density J-detected magnetic resonance (ELDMR and EDMR, respectively) studies of N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine(TPD)/Alq_3 OLEDs, as well as the photoluminescence (PL)- detected magnetic resonance (PLDMR) of Alq_3 films. The measurements yield a positive (i.e., EL-, J-, and PL-enhancing) spin-1/2 resonance at low temperatures, which is due either to reduced quenching of SEs by a reduced population of polarons (''the quenching mechanism'')[14,15,22,23] or to enhanced formation of SEs by nongeminate polaron pairs at the expense of TEs (''the delayed PL mechanism'').[8–10] However, this latter mechanism implies that $\eta_{SE}>25\%$ in Alq_3 OLEDs, which is contrary to existing evidence;[3,24,25] the delayed PL mechanism is also inconsistent with more recent experimental evidence (see Sec. IV A). Hence, we conclude that the positive spin-1/2 resonance is due to the

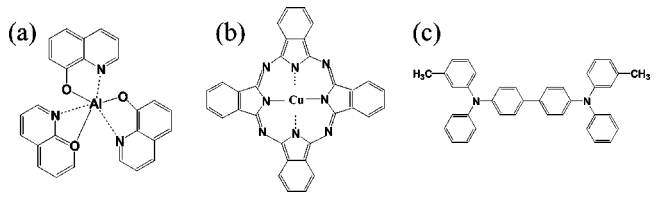

FIG. 1. Molecular structures of (a) tris-(8-hydroxy quinoline) Al (Alq_3), (b) copper phthalocya-nine (CuPc), and (c) N,N'-diphenyl-N,N'-bis(3-methylphenyl)-(1,1′-biphenyl)-4,4′-diamine (TPD).

quenching mechanism, and previous ODMR-based methods to determine η_{SE} (Refs. 8–10) are invalid.

Besides the low-T positive spin-1/2 resonance, a high-T negative spin-1/2 ELDMR and EDMR (but no negative PLDMR) is also observed. We conclude that it results from the spin-dependent formation of negative spinless bipolarons from spin-1/2 polarons[19,21,23] at the Alq_3/cathode interface, as it is highly sensitive to the presence and nature of the buffer layer between the Alq_3 and the cathode. The enhanced formation of negative bipolarons implies enhanced trapping of injected electrons at the organic/cathode interface, which reduces J and concomitantly the EL intensity I_{EL}. Indeed, several theoretical studies have predicted that a high density of negative bipolarons forms at the organic/cathode interface,[26–28] and UV and x-ray photoelectron spectroscopy measurements have confirmed their presence.[29,30]

II. EXPERIMENTAL PROCEDURE

The OLEDs consisted of an indium tin oxide (ITO) anode, a 15-nm-thick copper phthalocyanine (CuPc) hole-injection layer, a 25-nm-thick TPD hole-transport layer, and a 40-nm-thick emissive Alq_3 layer. An ~1-nm-thick CsF (Refs. 31–33) or an ~3-nm-thick AlO_x buffer layer[34] was evaporated on top of the Alq_3 layer, followed by evaporation of the Al cathode. The chemical structures of CuPc, TPD, and Alq_3 are shown in Fig. 1 and the device structure is shown in the inset of Fig. 2(a).

The OLEDs were fabricated by thermal vacuum evaporation in an $\sim 10^{-6}$ Torr vacuum chamber installed in an argon-filled glove box, typically containing ~0.5 ppm oxygen and water. Prior to deposition of the organic layers, the ITO coated glass was thoroughly cleaned as described elsewhere.[34,35] The deposition rates were monitored by a Maxtek TM-100 thickness monitor. The organic layers were deposited at ~2 Å/sec. The CsF was deposited similarly at ~0.1 Å/s. The AlO_x layer was fabricated by depositing an ~15 Å layer of Al, followed by 5-min exposure to air. The OLEDs had an active area of ~0.2 cm^2.

The magnetic resonance spectra were measured by placing an OLED or an Alq_3 film in an optically accessible microwave cavity between the pole pieces of a dc electromagnet, as described previously.[14–19,21–23] The ELDMR, EDMR, or PLDMR were measured by lock-in detection of the changes in I_{EL}, J, or the PL intensity I_{PL}, respectively, induced by the microwaves, which were chopped at 500 Hz. For $\Delta I_{EL}/I_{EL}$ and $\Delta J/J$, the microwave power was 360 mW at 9.45 GHz; for $\Delta I_{PL}/I_{PL}$, it was 811 mW at 9.34 GHz.

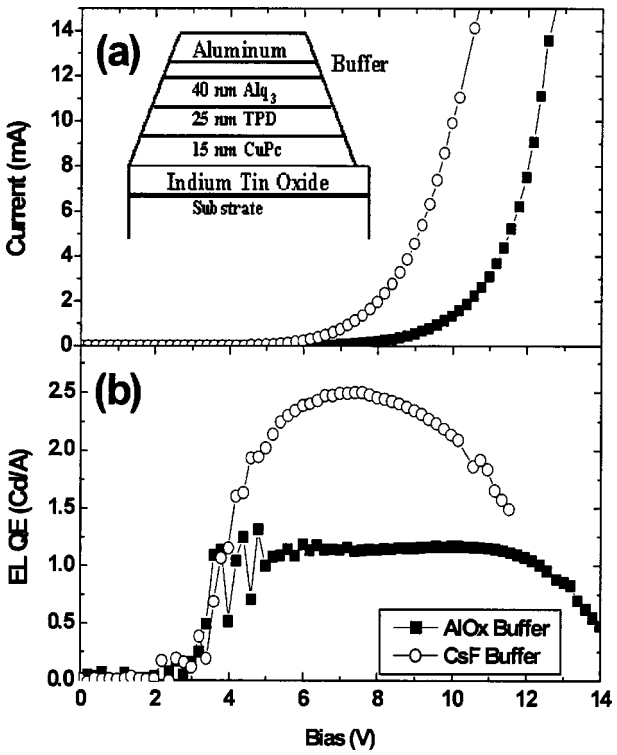

FIG. 2. The room-temperature (a) current density voltage and (b) EL quantum efficiency (ELQE) of OLEDs with CsF buffer layers (open circles) and AlO_x buffer layers (solid squares) vs the bias voltage V. Inset: The structure of the OLEDs.

Magnetic resonance conditions occur when the Zeeman splitting between two spin sublevels equals the microwave photon energy

$$h\nu = g\beta H, \tag{1}$$

where $h\nu$ is the microwave photon energy, g is the gyromagnetic ratio, β is the Bohr magneton, and H is the magnetic field strength.[36] Magnetic resonance conditions equalize the populations of the spin sublevels, which in turn affect the populations of the excited states.[36]

III. RESULTS

Figure 2(a) shows the room-temperature current density-voltage $J(V)$ characteristics of CsF- and AlO_x-buffered OLEDs. Both devices show rectifying behavior; the behavior of the EL-voltage curve $I_{EL}(V)$ was similar. Note that the buffer layer has a dramatic effect on $J(V)$. The AlO_x-buffered device requires roughly 2 V higher bias than the CsF-buffered device to achieve the same current density. The buffer layer also affects the EL efficiency η_{EL}, as shown in Fig. 2(b). The peak efficiency of the CsF-buffered OLED is more than double that of the AlO_x-buffered devices. The efficiency of both devices decreases at higher bias, owing to increasing quenching by the electric field and, possibly, quenching of SEs by polarons, either free or trapped, and TEs.

Figure 3 shows the spin-1/2 ELDMR spectra of (a) AlO_x-

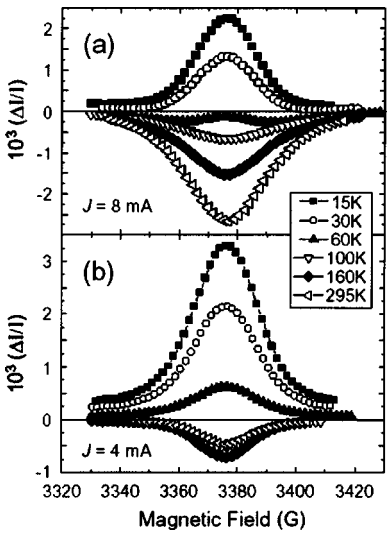

FIG. 3. The spin-1/2 ELDMR spectra of OLEDs with (a) AlO_x and (b) CsF buffer layers, at $15 \leqslant T \leqslant 295$ K.

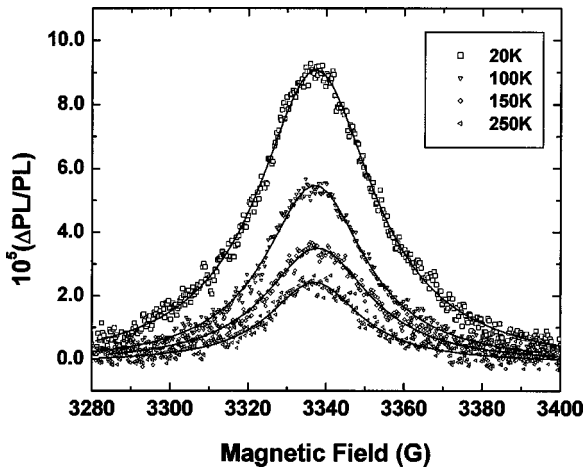

FIG. 5. The PLDMR of a 330-nm-thick Alq_3 film vacuum evaporated on a quartz substrate, at $T=20$, 100, 150, and 250 K (the amplitude decreases monotonically with increasing T). The PL was excited by the 65 mW UV multiline output of an Ar^+ laser at 351–363 nm.

and (b) CsF-buffered OLEDs at temperatures from 15 to 295 K. Both devices have a positive (EL-enhancing) resonance below 60 K that decreases in amplitude with increasing temperature and a negative (EL quenching) resonance that becomes evident at or above $T=60$ K and increases in amplitude with increasing temperature. The enhancing and quenching resonances have similar g values, though the linewidths are different. This can be seen in the 60 K ELDMR of the AlO_x device, which contains both positive and negative resonances. While the amplitude $|\Delta I_{EL}/I_{EL}|$ of the positive resonance is similar in the two types of devices, the negative resonance is much weaker in the CsF-buffered devices.

Figure 4 shows the dependence of the ELDMR amplitude $|\Delta I_{EL}/I_{EL}|$ on J. The positive ELDMR increases with J; its behavior is qualitatively similar to the laser power dependence of the PLDMR in polymers[10,15] and Alq_3 films (see below). The behavior of the quenching resonance amplitude $|\Delta I_{EL}/I_{EL}|$ differs qualitatively from that of the enhancing resonance and between the two devices. In the CsF-buffered OLEDs, it decreases with increasing J as $J^{-0.4}$, whereas in the AlO_x-buffered devices it increases from 2.2×10^{-4} at 0.5 mA/cm^2 to 2.9×10^{-4} at 7 mA/cm^2. In contrast to the positive resonance, the magnitude of the negative resonance increases with increasing temperature.

Figure 5 shows the spin-1/2 PLDMR spectrum of an Alq_3 film at several temperatures. The resonance is positive ($\Delta I_{PL}/I_{PL}>0$) and its amplitude decreases from 9.1×10^{-5} at $T=10$ K to 2.4×10^{-5} at $T=250$ K. This decrease with increasing T is much more moderate than that of the positive ELDMR $\Delta I_{EL}/I_{EL}$. It is suspected that the positive ELDMR decreases much more rapidly due to overlap with the negative resonance. The similarity between the positive ELDMR and PLDMR leads us to assign the positive resonance to enhanced polaron recombination under magnetic resonance conditions. This mechanism requires the presence of both positive and negative polarons, which occurs only in the bulk of an OLED under operation.

Figure 6 shows the laser power-dependence of the spin-1/2 PLDMR of the Alq_3 film. As clearly seen, at low power

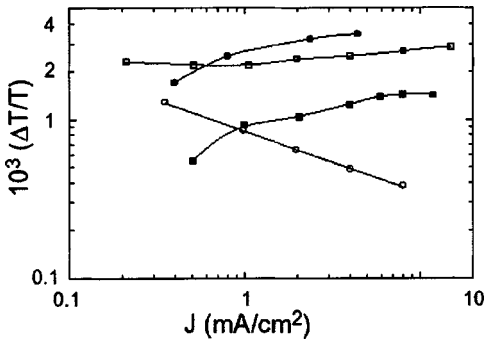

FIG. 4. The current density J dependence of the amplitude of the spin-1/2 ELDMR $|\Delta I_{EL}/I_{EL}|$. The enhancing (quenching) resonance of CsF-buffered devices is shown as filled (open) circles. The enhancing (quenching) resonance of AlO_x-buffered devices is shown as filled (open) squares.

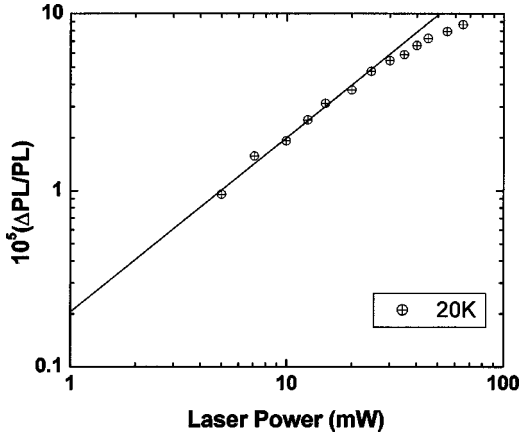

FIG. 6. Laser power dependence of the PLDMR of an Alq_3 film at 20 K. The slope of the straight line is 1.

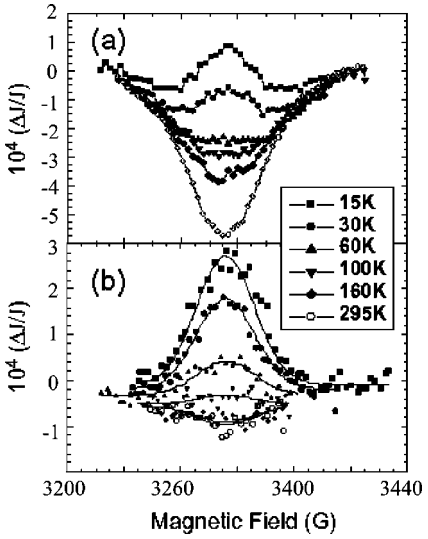

FIG. 7. The spin-1/2 EDMR spectra of OLEDs with (a) AlO_x and (b) CsF buffer layers, at $15 \leqslant T \leqslant 295$ K.

$\Delta I_{PL}/I_{PL}$ depends linearly on the power, but it saturates to a sublinear behavior at high power. This behavior is qualitatively similar to the J dependence of the positive spin-1/2 ELDMR above, and to the laser power dependence of the positive spin-1/2 PLDMR of several oligomers and polymers studied to date.[10,15]

Figure 7 shows the spin-1/2 EDMR spectra of both CsF- and AlO_x-buffered OLEDs from 15 to 295 K. Similar to the ELDMR, the EDMR is positive (J enhancing) below 60 K and negative (J quenching) above 60 K.

The distinct behavior of the positive and negative resonances suggests different origins. In turning to the discussion of these resonances, we consequently treat each resonance separately.

IV. DISCUSSION

A. The positive spin-1/2 resonance

In both devices the amplitude of the positive spin-1/2 ELDMR decreases rapidly with T and increases sublinearly with J (Figs. 3 and 4). This behavior is similar to the temperature and laser power dependence of the positive spin-1/2 PLDMR of Alq_3 films (see Figs. 5 and 6) and of various π-conjugated polymer films.[10,15,17,23] In all previous studies, this resonance was attributed to magnetic resonance enhancement of the overall polaron recombination rate. This enhancement of the overall polaron recombination rate is confirmed by several photoinduced absorption (PA)-detected magnetic resonance (PADMR) measurements, which demonstrated unambiguously that the overall polaron population decreases at resonance.[8–10,15,20]

Several mechanisms have been proposed for the origin of the positive spin-1/2 resonance.

(i) Ground-state recovery.[37] This mechanism simply takes into account the faster recombination of the polarons, which increases the ground-state population, and consequently the absorption and the emission. However, the PLDMR is observed in both optically thin and thick films, and the ELDMR (and EDMR; see below) is not due to optical absorption. We therefore rule out this mechanism.

(ii) Enhanced TE-TE annihilation to SEs.[38] This mechanism is inconsistent with the reduced population of TEs at the field-for-spin-1/2-resonance.[8,10,15,20]

(iii) ''The delayed PL'' mechanism. This mechanism is based on the assumption that the enhanced polaron recombination is due to a higher cross section for SE formation from singlet polaron pairs σ_{SE} than TE formation from triplet polaron pairs σ_{TE}.[8–10] Hence, off-resonance, the population of nongeminate singlet polaron pairs n_{SPP} is depleted relative to the population of nongeminate triplet polaron pairs n_{TPP}. On resonance, n_{SPP} increases at the expense of n_{TPP}, and the PL increases. Wohlgenannt *et al.* have shown that in several polymers the excitation power dependence of this resonance is in good agreement with a model based on this mechanism.[10] Yet if this scenario is the origin of the resonance in Alq_3, it implies that in this material $\sigma_{SE} > \sigma_{TE}$ and the yield of SEs in Alq_3-based OLEDs is significantly greater than 25%. This conclusion is contrary to that of several previous studies.[3,24,25] In addition, it is inconsistent with the following recent experimental results, which will be published elsewhere: (i) Double modulation-PLDMR (DM-PLDMR), in which the laser power is modulated at $\nu_L \gg \nu_c$, where ν_c is the microwave chopping frequency, show that the contribution of the prompt fluorescence to the PLDMR is essentially equal to that of the delayed fluorescence.[39] (ii) A combined PLDMR and thermally stimulated luminescence (TSL) study of high-quality PPV derivative films shows that as the excitation wavelength is decreased from the visible to the near UV, the TSL *increases* approximately 30-fold while the positive spin-1/2 PLDMR *decreases* approximately sixfold.[40] Since the delayed PL from nongeminate polaron pair recombination is roughly proportional to the TSL, the delayed PL model requires that the PLDMR *increase* approximately 30-fold. We therefore rule out the delayed PL model as the origin of the positive spin-1/2 ODMR (i.e., PLDMR, ELDMR, or PADMR). We note that this conclusion invalidates the conclusions of Wohlgenannt *et al.* on the yield of SEs in OLEDs.[8–10]

(iv) The only remaining scenario which has been proposed for the origin of the positive spin-1/2 resonance is based on the well-known evidence that polarons quench SEs.[15,22,23,41–44] At resonance a reduced polaron population reduces the SE quenching rate, thereby increasing the emission (''the quenching model''). List *et al.* have shown that in oligophenylenes and methyl-bridged ladder-type poly (p-phenylenes) the excitation power dependence of the resonance is in excellent agreement with a rate equation model based on this scenario.[15] Indeed, we note that the quenching model is the only model proposed to date, which is consistent with the entire body of ODMR results that have accumulated on π-conjugated materials and OLEDs. We therefore conclude that the positive spin-1/2 ODMR is due to the quenching mechanism.

B. The negative spin-1/2 resonance

As mentioned above, the J dependence of the amplitude of the quenching resonance (Fig. 4) differs qualitatively from

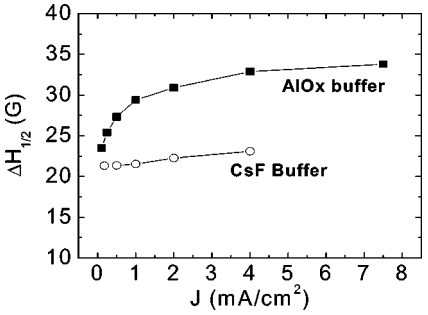

FIG. 8. The full-width-at-half-maximum linewidth $\Delta H_{1/2}$ of the negative ELDMR at 295 K vs injected current density J in AlO_x-buffered OLEDs (solid squares) and CsF-buffered OLEDs (open circles).

that of the enhancing resonance and between the two devices. In the CsF-buffered OLEDs, it decreases with increasing current as $J^{-0.4}$, whereas in the AlO_x-buffered devices it increases moderately with J, from 2.2×10^{-4} at 0.5 mA/cm^2 to 2.9×10^{-4} at 7 mA/cm^2. In contrast to the positive resonance, the amplitude of the quenching resonance increases with T.

There are two nonradiative species that can be generated from polaron recombination: spin-1 TEs and spinless bipolarons. Resonant enhancement of TE formation at the expense of SEs would reduce the EL intensity. However, it has been shown that the TE population decreases at the spin-1/2 resonance field.[8–10,15,20] Furthermore, this process would not affect the current density in the device and hence the EDMR spectrum should contain only a positive resonance. However, as mentioned above, Fig. 7 shows that similar to the ELDMR, the EDMR is positive (J enhancing) below 60 K and negative (J quenching) above 60 K. Hence, enhanced TE formation cannot account for the negative spin-1/2 resonance.

The observation of negative EL- and J-detected spin-1/2 resonances is, however, entirely consistent with bipolaron formation. Several theoretical studies have suggested that a high density of negative bipolarons—indeed a bipolaron lattice—may be generated to form a dipole layer at the organic/metal cathode interface of OLEDs.[26–28] UV and x-ray photoelectron spectroscopy (UPS and XPS, respectively) studies have confirmed the presence of bipolarons at the interface.[29,30] Furthermore, there is direct experimental evidence for enhanced bipolaron formation under magnetic resonance conditions in both small molecules and polymers.[43,44]

The mobility of bipolarons should be much lower than that of polarons, and their formation is obviously an electron- or negative polaron-trapping mechanism. Hence, the negative ELDMR may simply be due to the negative EDMR: A reduction in J causes a reduction in the EL. However, at 295 K, the ratio $|\Delta I_{EL}/I_{EL}|$ in AlO_x devices to that in CsF devices, $r_{ELDMR}\equiv|\Delta I_{EL}/I_{EL}|_{AlO_x}/|\Delta I_{EL}/I_{EL}|_{CsF}=4.0\pm0.3$, is significantly lower than the ratio of $|\Delta J/J|$ in these devices, where $r_{EDMR}\equiv|\Delta J/J|_{AlO_x}/|\Delta J/J|_{CsF}=5.8\pm0.3$. Any additional mechanism which would contribute to the ELDMR, e.g., enhanced quenching of SEs due to an enhanced electric field throughout the device which results from increased charge at the Alq_3/Al interface, should result in r_{ELDMR} being *higher* than r_{EDMR}, not *lower*. We therefore conclude that the EL- and J-quenching resonances are due to the spin-dependent formation of spinless bipolarons; their strong dependence on the buffer layer demonstrates that these bipolarons are located at the organic/cathode interface. Since the positive charge density is very low near the cathode, the resonance is assigned to the enhanced formation of negative bipolarons at this interface. However, due to the observation that $r_{ELDMR}<r_{EDMR}$, we suspect that other mechanisms, unidentified at this point, are also contributing to the negative ELDMR.

The negative ELDMR cannot be due to direct quenching of SEs by bipolarons since the recombination zone lies on the Alq_3 side of the TPD/Alq_3 interface while the bipolarons must be located at the Alq_3/Al interface region. Likewise, relatively few positive polarons will reach the counterelectrode and be quenched. However, increased trapping of injected electrons at the Alq_3/Al interface reduces J and consequently I_{EL}.

The bipolaron model also explains the J dependence of the Lorentzian linewidth $\Delta H_{1/2}$ and $|\Delta I_{EL}/I_{EL}|$. Figure 8 shows that in the CsF-buffered devices, $\Delta H_{1/2}\approx22$ G, almost independent of J. In contrast, in the AlO_x-buffered OLEDs, it increases from ~23 G at low J to ~34 G at $J=7.5$ mA/cm^2. The dipolar broadening contribution to $\Delta H_{1/2}$ can provide an estimate of the average distance d between polarons.[36] A residual linewidth of ~15 G was estimated from measurements on similar OLEDs with no intentional buffer layer and is attributed to mechanisms other than dipolar broadening (e.g., hyperfine interaction between the polarons and protons in Alq_3).[36] Taking into account the residual linewidth, $d\approx1.1$ nm in the CsF-buffered devices. In the AlO_x-buffered OLEDs, it decreases from ~1.0 nm to ~0.8 nm as J increases to 7.5 mA/cm^2. Since bipolarons require a counterion for stabilization,[45,46] the model implies that the density of counterions is much higher in AlO_x-buffered devices. Previous SEM and XPS measurements on the AlO_x-buffered devices revealed pinholes and a very high carbon content in the buffer region.[47] Other UPS and XPS studies have demonstrated a strong reaction between Al metal and Alq_3.[48] This issue clearly deserves additional attention.

The decrease of $|\Delta I_{EL}/I_{EL}|$ with increasing J in CsF-buffered devices implies that the density of bipolarons reaches its maximal value at low J. As J increases, the formation of bipolarons becomes less spin-dependent and $|\Delta I_{EL}/I_{EL}|$ consequently decreases. This behavior and scenario are consistent with previous studies of poly (p-phenylene vinylene) OLEDs.[15]

The bipolaron model also explains the temperature dependence of the quenching ELDMR. Since there is a Coulomb barrier to form bipolarons from polaron pairs, increasing T enhances their formation, so $|\Delta I_{EL}/I_{EL}|$ increases. Figure 9 shows $\log(|\Delta I_{EL}/I_{EL}|)$ vs $1000/T$ for the AlO_x-buffered devices. The behavior above $T=100$ K yields an activation en-

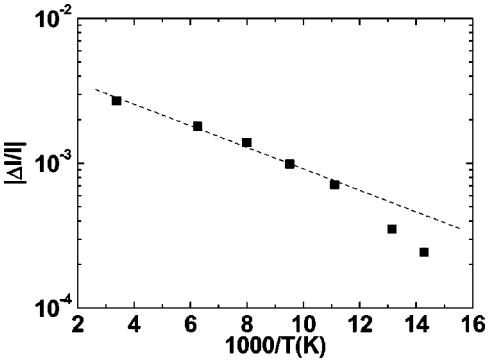

FIG. 9. The amplitude $|\Delta I_{EL}/I_{EL}|$ of the negative ELDMR vs $1000/T$ in the AlO_x-buffered OLEDs. The slope of the dashed line yields an activation energy of 11.6 meV.

ergy of 11.6 meV. The results deviate from the straight line below for $T=100$ K due to overlap of the positive and negative resonance.

The foregoing results and analysis demonstrate the importance of the buffer layer in determining the behavior of the OLEDs. The observation of the negative resonance in OLEDs with a CsF buffer layer demonstrates that further improvement in buffer layers is possible and desirable.

V. SUMMARY AND CONCLUDING REMARKS

In conclusion, the spin-1/2 ELDMR and EDMR of Alq_3-based OLEDs with thin CsF or AlO_x buffer layers between the Alq_3 and the Al cathode is positive (EL- and current enhancing) below 60 K and negative (EL quenching) above 60 K. The positive resonance is attributed to enhanced recombination of polarons in the recombination zone. The mechanism responsible for the resonance is concluded to be reduced quenching of SEs by a reduced population of polarons, since the ''delayed PL model'' would imply that the yield of SEs in Alq_3 OLEDs is significantly greater than 25%. The delayed PL model is also inconsistent with other recent experimental results, and we conclude that previous ODMR-based methods to determine the yield of SEs in OLEDs are invalid.

The negative resonance was shown to result from the magnetic resonance enhancement of the formation of negative spinless bipolarons at the organic/cathode interface. This enhanced electron or negative polaron trapping reduces the current density and consequently the EL. However, it is suspected that other mechanisms may also be contributing to the negative resonance. In any case, the superior performance of the CsF-buffered OLEDs relative to the AlO_x-buffered devices may be due to reduced trapping of electrons or negative polarons at the organic/cathode interface.

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*Present address: Naval Research Laboratory, 4555 Overlook Ave., Washington, DC 20375.

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