Photovoltaic effect for narrow-gap Mott insulators

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(Received 2 June 2010; published 10 September 2010)

We discuss the photovoltaic effect at a *p-n* heterojunction, in which the illuminated side is a doped Mott insulator, using the simplest description of a Mott insulator within the Hubbard model. We find that the energy efficiency of such a device, if we choose an appropriate *narrow-gap* Mott insulator, can be significantly enhanced due to impact ionization caused by the photoexcited "hot" electron-hole pairs. Namely, the photoexcited electron and/or hole can convert its excess energy beyond the Mott-Hubbard gap to additional electrical energy by creating multiple electron-hole pairs in a time scale which can be shorter than the time characterizing other relaxation processes.

DOI: 10.1103/PhysRevB.82.125109 PACS number(s): 71.10.Fd, 71.27.+a, 72.40.+w, 73.50.Pz

I. INTRODUCTION

Solar cells based on conventional single-gap band semiconductors have low internal quantum efficiency for conversion of solar into electrical energy.[1] The main reason is that the photon energy absorbed by a single electron-hole pair with energy above the semiconductor band gap is lost in heat through electron-phonon scattering and phonon emission through which electrons and holes relax to their band edges. The solar-energy spectrum contains photons with energies in a rather broad energy range compared to any particular semiconductor energy gap. If instead semiconductors with a relatively large band gap are chosen in order to avoid the above-mentioned problem, this cuts off most of the energy spectrum of the solar radiation. Using a stack of cascaded multiple *p-n* junctions with various band gaps is an expensive approach to build efficient solar cells.

A variety of other ideas have been suggested in order to increase solar-cell efficiency.[2–5] One particular approach which increases the photocurrent is one in which the energetic carriers produce additional electron-hole pairs through impact ionization[6–8] at a much faster rate than the rate characterizing the relaxation process through phonon emission. In order to achieve this, it has been suggested that[9,10] using confining geometries, such as quantum wells, quantum wires, quantum dots, superlattices, and nanostructures, the relaxational time scales can be significantly affected[11–13] and this allows the possibility for impact ionization. Ross and Nozik[3] have argued that an efficiency of approximately 66%, much larger than Shockley-Queisser efficiency limit[1] for photovoltaics, can be theoretically achieved using an unusual inversion, in which the chemical potential of the excited electronic band is below that of the ground band. Other ideas to increase solar-cell efficiency by utilizing the possibility of carrier multiplication[14–16] via impact ionization by removing and isentropically cooling the carriers through special membranes were proposed by Würfel.[17]

In this paper we discuss the photovoltaic effect for materials which are based on doped Mott insulators, as opposed to the familiar semiconductors which are band insulators. A variety of transition-metal oxides that are predicted to be conductors by band theory (because they have an odd number of electrons per unit cell) are, in fact, insulators. Mott and Peierls[18] predicted that this anomaly can be explained by including interactions between electrons. Today, this can be described within the simple Hubbard model, as arising from the strong on-site Coulomb interaction. In this case the half-filled band leads to an insulator; the added holes or added extra electrons beyond half filling lead to conduction. In this case also we can imagine that we can form a *p-n* junction separating a region of hole-doped from a region of electron-doped Mott insulator.

There are recent reports[19–22] where the photovoltaic effect is observed in a *p-n* heterojunction of a doped maganite (a doped Mott-like insulator) and doped strontium titanate (a doped band insulator). In addition, there are reports of the photoelectric effect observed on heterojunctions of doped maganites and doped silicon[23,24] and on a heterostructure[25] of $YBa_2Cu_3O_{7-x}$ on Nb-doped $SrTiO_3$. Here, we demonstrate that in the case of *narrow-gap* Mott insulators the photovoltaic effect can lead to solar cells of high quantum efficiency, where a single solar photon can produce multiple electron-hole pairs.

II. MODEL AND CONCEPTS

In the simplest model of a Mott insulator, a single conduction band is formed from one localized orbital (which is, in general, a linear combination of atomic orbitals) per unit cell (or site). In the case of half filling, i.e., when one electron per site occupies the band made from this orbital, the material is a Mott insulator. In Fig. 1(a) the half-filled state is shown where the motion of an electron from one site to the nearest-neighbor (nn) site leads to an empty site (or hole) and a doubly occupied site (DO) [Fig. 1(b)]; this state, because of the DO, is characterized by a high energy cost, which is denoted by the so-called Hubbard on-site Coulomb repulsion energy U, and this effectively prohibits electron motion through the band. In order to have a concrete framework to facilitate the discussion we consider the so-called Hubbard model,

$$\hat{H} = \hat{H}_t + \hat{H}_U, \tag{1}$$

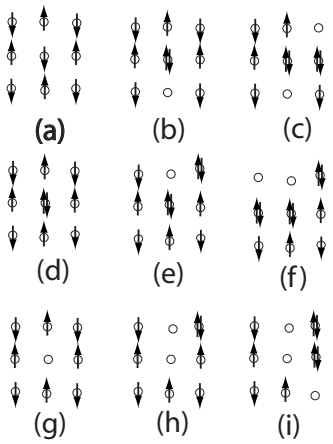

FIG. 1. Representative states from the S_m^n subspaces.

$$H_t = -t\sum_{\langle ij\rangle}(c_{j\sigma}^{\dagger}c_{i\sigma} + \text{H.c.}), \tag{2}$$

$$\hat{H}_U = U\sum_i \hat{n}_{i\uparrow}n_{i\downarrow}, \tag{3}$$

where $n_{i\sigma}=c_{i\sigma}^{\dagger}c_{i\sigma}$ and $c_{i\sigma}^{\dagger}$ creates an electron of spin σ at site i.

First, let us consider the limit of $U \gg t$ because in this case there is a well-defined concept for the origin of the Mott-insulator gap and this simplifies the conceptual part of the discussion. If we assert that the $\hat{H}_U$ term is the unperturbed part and we treat $\hat{H}_t$ as a perturbation, the eigenvalues of the unperturbed part are equally spaced by an energy U. For the case of half filling, i.e., in an N-site system with N electrons, each energy level corresponds to a massive number of states forming subspaces S_0^n characterized by the same eigenvalue $E_n=nU$, where n is the number of pairs of DO holes (DO-H). Figures 1(a)–1(c) illustrate examples of states $n=0$, 1, and 2 pairs of DO-H. The subspaces S_0^n are spanned by the states obtained by all allowed spin rearrangements. In a Mott insulator, the Coulomb energy cost for two electrons to occupy the same orbital leads to an insulating state at half filling. Replacing some atoms in the lattice with different atoms, which act as donors or acceptors of additional electrons beyond half filling thereby creating DO sites (n-type doping) or holes (p-type doping), leads to a conducting state with an effective carrier density given, respectively, by the density of DO or hole sites. In a doped system, i.e., an N-site system with $N+m$ or $N-m$ electrons, the subspaces S_m^n or S_{-m}^n are spanned by m DO or holes and n DO-H pairs. Examples for S_1^n and S_{-1}^n (for $n=0$, 1, and 2) are illustrated in Figs. 1(d)–1(f) and in Figs. 1(g)–1(i). For the rest of the paper, we will denote by U^* the renormalized gap, namely, the energy required to promote a particle and to create a DO-H pair starting from the half-filled lattice and by W the bandwidth of the quasiparticle or quasihole dispersion.

In the half-filled case and at low enough temperature, the model exhibits antiferromagnetic order,[26] which, however, will not play a significant role in our discussion, because the Mott-insulator phase can exist at temperatures higher than the Néel ordering temperature. The quasiparticle (hole or DO) spectral function and dispersion relation, as well as the spectral weights, have been computed using the t-J model[27] [which is the strong-coupling limit ($U \gg t$) of the Hubbard model with $J=4t^2/U$] within the so-called noncrossing approximation for two dimensions (2D). In this paper we have carried out the same calculation for three dimensions (3D) and the conclusions are qualitatively similar to the 2D case. There is a well-defined quasiparticle which corresponds to a low-energy peak in the spectral function, and we will use the operator $\alpha_{\mathbf{k}}^{\dagger}$ which, by acting on the undoped state $|0\rangle$, creates this quasiparticle with energy dispersion $E_{\mathbf{k}}$ and residue $Z_{\mathbf{k}}$. In this limit, while the bandwidth of the quasiparticle dispersion $E_{\mathbf{k}}$ is on the order of J, the width of the density of states is on the order of $2td$ (where d is the dimensionality).

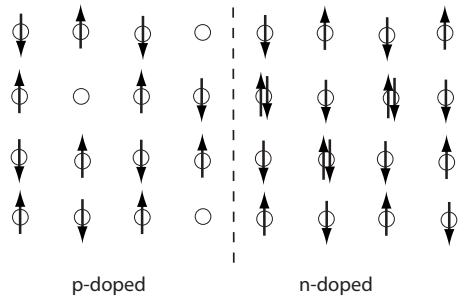

FIG. 2. An interface between a p- and an n-doped Mott insulator before carrier diffusion across the interface takes place. Some of the DO sites can be relieved from the energy cost due to Coulomb repulsion via diffusion of the extra electron to the p-doped region to fill a hole. This process stops when the electric field, which gradually develops across the interface due to this charge redistribution, becomes strong enough to oppose further carrier diffusion. The idea discussed here is also applicable when the illuminated side is a doped Mott insulator and the other side a doped band insulator.

Now we wish to consider a p-n heterojunction as illustrated in Fig. 2 based on an interface between two narrow-gap Mott insulators, one of which is p-doped (left side of the interface) and the other which is n-doped (right side). Because of the energy gain that is achieved when a hole of the p-doped material is filled by an electron from a DO site on the n-doped part, diffusion of electrons from the n-doped side will occur and this leads to a positively charged layer in the n-doped side adjacent to the interface and, vice versa, a negatively charged layer in the p-doped side. The potential-energy difference acts as a unidirectional collector of the DO and holes created upon the incident light.

III. NARROW-GAP NARROW-BAND CASE

Let us, first, consider a narrow-band narrow-gap Mott insulator. An incident photon of energy several times the Mott-gap U^* has enough energy so that several electron-hole pairs could be created. In practice, since the range of the solar spectrum is from 0.5–3.5 eV, we can consider a Mott insulator with a gap on the order of 0.5–1.0 eV and a bandwidth in the same range. We need a narrow-gap Mott insulator in order to increase the efficiency but on the other hand the gap should be large enough to avoid decay of the excited quasi-

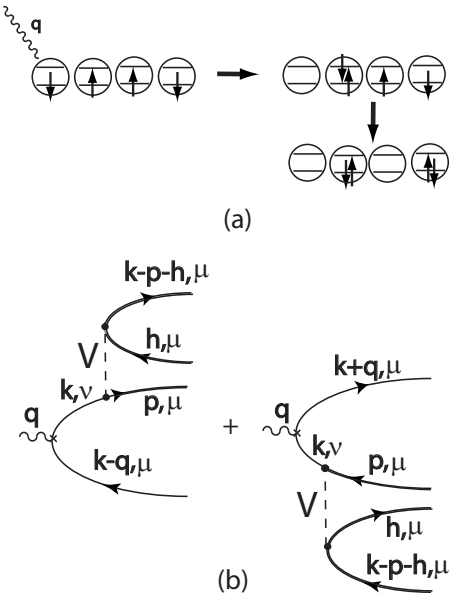

FIG. 3. See the text for explanation.

particles (by phonon emission, spin-wave emission, or through other possible excitations).

If the energy $\hbar\omega_q$ of the solar photon is between $U^* < \hbar\omega_q < U^* + W$, the incident photon can create a single electron-hole pair by promoting an electron to the first Mott-Hubbard band. Figure 3(a) indicates a two-step process in which the incident photon can create a state with two pairs of DO-H, if its energy is higher than $2U^*$. In Fig. 3(a), within each atom we depict two atomic levels, one which forms the Mott-Hubbard band, and a higher level which forms a high-energy band. First, the incident high-energy photon is absorbed by an electron which hops to the high-energy band as indicated in Fig. 3(a). Subsequently, the charged atom, which carries the extra electron, transfers part of the excess energy via the Coulomb interaction to an electron of a different site which causes it to hop to a nn atom, while itself falls to the lowest level already occupied by one electron; this leads to the creation of two DO-H pairs. Figure 3(b) illustrates the same process in momentum space. If the energy of the photon is higher than $2U^*$, the electron (or the hole) can be temporarily photoexcited to a high-energy band which is different than the Mott band. The electron, for example, can be photoexcited to the state $|\mathbf{k}\nu\rangle$ of energy E denoted by the label $\mathbf{k},\nu$ in the first term of Fig. 3(b). This electron can decay quickly into two quasiparticles plus one quasihole state of the Mott band, provided that the energy of the initial and final state matches. This is caused by the matrix element $V \equiv \langle \mathbf{k}\nu, \mathbf{h}\mu | \hat{V} | \mathbf{p}\mu, \mathbf{k}-p+h\mu \rangle$ of the Coulomb interaction which couples the state $|\mathbf{k}\nu\rangle$, where the electron was initially excited by the incident high-energy photon, and the states $|\mathbf{h}\mu\rangle$, $|\mathbf{p}\mu\rangle$, and $|\mathbf{k}-\mathbf{p}-\mathbf{h}\mu\rangle$, which form the Mott band μ. Now, we would like to estimate the transition rate $\Gamma_\mathbf{k}$ for an electron or hole of momentum $\mathbf{k}$ from a high-energy band to undergo the decay processes illustrated in Fig. 3(b). Namely, Fig. 3(b) illustrates the following two processes: (a) the initially photoexcited particle can decay into two quasiparticles plus one quasihole given as $\alpha_\mathbf{h}\alpha^\dagger_\mathbf{p}\alpha^\dagger_{\mathbf{k}-\mathbf{p}-\mathbf{h}}|0\rangle$ [first term in Fig. 3(b)] or (b) the initially photocreated hole state can decay into two quasiholes plus one quasiparticle given as $\alpha^\dagger_\mathbf{h}\alpha_\mathbf{p}\alpha_{\mathbf{k}-p-h}|0\rangle$ [second term in Fig. 3(b)]. For simplicity, the Mott-band index μ has been omitted as a label of the α's. Using Fermi's golden rule we can obtain the decay rate of the bare electron (or hole) into two quasiparticles plus one quasihole as

$$\Gamma_\mathbf{k}(\epsilon) = \frac{2\pi}{\hbar}\sum_{\mathbf{p},\mathbf{h}} |M|^2 \delta(\epsilon - E_{\mathbf{k}-\mathbf{p}+\mathbf{h}} - E_\mathbf{p} + E_\mathbf{h}), \tag{4}$$

where $\epsilon \equiv E - 2U^*$ and M stands for the interaction matrix element which couples the initially excited particle state $c^\dagger_{\mathbf{k},\nu}|0\rangle$ ($|0\rangle$ is the ground state) to which the incoming solar photon couples directly, and the final two quasiparticles and one quasihole given as $\alpha_\mathbf{h}\alpha^\dagger_\mathbf{p}\alpha^\dagger_{\mathbf{k}-\mathbf{p}-\mathbf{h}}|0\rangle$, i.e., $\langle 0|\alpha^\dagger_\mathbf{h}\alpha_\mathbf{p}\alpha_{\mathbf{k}-\mathbf{p}+\mathbf{h}}\hat{V}c^\dagger_{\mathbf{k},\nu}|0\rangle$. As can be inferred from the main contribution to the decay of the photoexcited high-energy electron-hole pair into two DO-hole pairs is due to the two processes shown by the diagrams in Fig. 3(b). Namely, when the Mott electron absorbs most of the photon energy and it is excited to a high-energy band, it becomes possible for the electron to decay into two DOs and one hole in the Mott band. When the created hole absorbs most of the photon energy, i.e., it corresponds to an excitation of an electron from an inner valence state to the Mott conduction band, it becomes possible for the hole to decay into two holes from the Mott band and one DO state from the Mott band. Each case can be approximated by the calculation of the decay rate of the high-energy electron or the decay rate of the high-energy hole because the other particle (the hole or electron, respectively), in this order in perturbation theory, behaves only as a spectator. The later rates are given by the above Eq. (4). The matrix elements M in this expression is given by

$$M = \frac{V}{N} Z_\mathbf{h} Z_\mathbf{p} Z_{\mathbf{k}-\mathbf{p}+\mathbf{h}}, \tag{5}$$

where the Z's are the quasiparticle residues and N is the total number of lattice sites. The effect of the Hubbard interaction U has been approximately taken into account by the Z, where $Z_p = \langle 0|\alpha_p|\mathbf{p}\mu\rangle$, and by using the renormalized Mott-band dispersion $E_\mathbf{k}$. In order to obtain an order of magnitude estimate for Γ, we will take V to be on the order of 1 eV. In a Mott insulator, where the atomic limit is appropriate, the charged highly excited atom in the intermediate state of Fig. 3(a) is expected to interact rather strongly with the electrons of the other atoms in its neighborhood.

This decay rate can be estimated by the following further approximation:

$$\Gamma_\mathbf{k}(\epsilon) \simeq \frac{2\pi}{\hbar} V^2 \bar{Z}^6 D(\mathbf{k}, \epsilon), \tag{6}$$

where $\bar{Z}$ is the average quasiparticle/quasihole spectral weight throughout the entire Mott-Hubbard band and

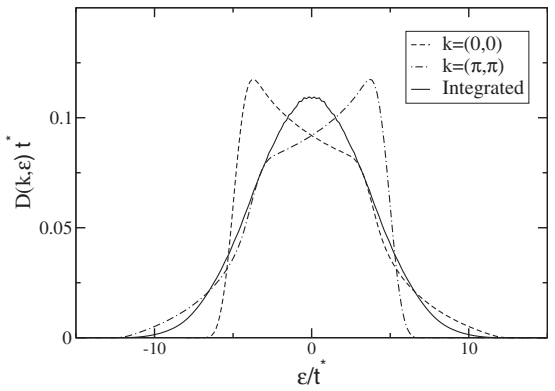

FIG. 4. The two-particle/one-hole density of states for the simple tight-bindinglike dispersion $E(\mathbf{k})=-2t^*[\cos(k_x a)+\cos(k_y a)]$ for a square lattice.

$$D(\mathbf{k},\epsilon)=\frac{1}{N^2}\sum_{\mathbf{p},\mathbf{h}}\delta(\epsilon-E_{\mathbf{k}-\mathbf{p}-\mathbf{h}}-E_{\mathbf{p}}+E_{\mathbf{h}}), \tag{7}$$

the two-particle/one-hole density of states. The approximation of Eq. (6) is obtained by using the average Z throughout the integration.

The two-particle/one-hole density of states can be illustrated using an effective tight-binding dispersion, i.e., $E_{\mathbf{k}}=-2t^*\Sigma_{\mu=1}^{d}\cos(k_\mu a_\mu)$, where d is the number of dimensions and k_μ, a_μ, are the component of the momentum and the lattice constant along the direction μ. In Fig. 3 we show $D(\mathbf{k},\epsilon)$ for a square lattice. Notice, that it is nonzero in an energy range on the order of the single-particle/single-hole bandwidth $W=8t^*$ and the value of the density of states is on the order of $1/W$. The rate averaged over all momenta in the tight-binding band can be written as

$$\bar{\Gamma}(\epsilon)\simeq\frac{2\pi}{\hbar}V^2\bar{Z}^6\Delta(\epsilon), \tag{8}$$

$$\Delta(\epsilon)=\frac{1}{N}\sum_{\mathbf{k}}D(\mathbf{k},\epsilon), \tag{9}$$

which is the density of states given in Fig. 4 for 2D averaged over all momenta $\mathbf{k}$. Note that $\Delta(\epsilon)$ is on the order of $1/W$ in the energy range where there are available states.

The value of the residue Z has been estimated in the strong-coupling limit using the t-J model in Ref. 27 for 2D. We have carried out the same calculation in 3D and we found that the value of Z is somewhat larger than in the 2D case because the role of quantum fluctuations is less important in 3D. Because we are interested in obtaining an approximate estimate of Γ, we will use the results of Ref. 27 for 2D. Since the t-J model is the strong-coupling limit of the Hubbard model with $J/t=4t/U$, we need to choose $U\gg t$. Choosing $J/t=1$ (i.e., $U=4t$) from Table IV of Ref. 27 we obtain, $W=0.96t$ and $Z=0.53$. Thus, taking $V=U=1$ eV yields $t=0.25$ eV, $W=0.24$ eV, and $\Gamma\simeq 0.9\times 10^{15}$ s^{-1} [using $\Delta(\epsilon)\sim 1/W$]. As can be inferred from the trend in Table IV of Ref. 27, larger values of t/U will give larger values both for Z and for the bandwidth W (similar to the value of the gap as needed) and consequently a larger Γ. However, while we believe this trend to be qualitatively correct, the regime $4t/U>1$ is not accessible by the strong-coupling limit discussed in Ref. 27. Nevertheless, the above estimate indicates that this process can be significantly faster than the decay processes through phonon[2,6,11,28] or spin-wave excitations which are expected to be on the order of $10^{12}-10^{13}$ s^{-1}. In addition, the Mott-Hubbard gap and W can be tuned to be several times smaller than the range of the energy of solar photons and, thus, a photon has the energy required to create more than one quasielectron-hole pairs.

IV. NARROW-GAP WIDE-BAND CASE

Now, let us consider the case of a narrow-gap but a wide-band Mott insulator, i.e., the case where $W\gg U^*$. It is believed and supported by calculations that for any value of W we can tune the value of U to provide a small value of the gap U^*. It is also known that the value of U required to produce a small gap should be greater than $W/2$. Therefore, if we choose $W=8$ eV and $U^*=0.5$ eV we will need a U greater than 4 eV. The exact value of U is not required for the following calculation, suffice it to know that it is greater than 4 eV. When the incident photon promotes an electron from the lower Hubbard band to the upper Hubbard band, the energy E of the excited electron can be large compared to the gap, say, $E>nU^*$, and, thus, it can decay into n quasiparticles plus $n-1$ quasiholes ($n=2,3,\ldots$). The main process is depicted by the diagram of Fig. 3(b), where all the lines in this case denote quasiparticles/quasiholes of the same (Mott) band (i.e., $\nu=\mu$), and the interaction is the Hubbard on-site Coulomb interaction U instead of the V discussed previously.

In this case the decay of the high-energy DO-hole pair, produced by the solar photon, into two DO-hole pairs is due to the two processes shown by the diagrams of Fig. 3(b) where the interaction is U instead of V and the decay rate is given by Eq. (4) with the matrix element M given by Eq. (5) where V is replaced by the Hubbard on-site Coulomb repulsion U. Namely, (b) when the electron absorbs most of the photon energy and it is excited to the upper-Hubbard band to become a high-energy DO site, it becomes possible for the DO to decay into two DO states and one hole. (b) When the created hole absorbs most of the photon energy, it becomes possible for the hole to decay into two holes in the Mott band and one DO state in the Mott band. Here also, either (a) or (b) can be estimated by the calculation of the decay rate of the high-energy DO or the decay rate of the high-energy hole because the other particle (the hole or DO, respectively), behaves only as a spectator.

Therefore, an estimate of the decay rate is given by Eq. (4) by replacing V with U which can be approximated by $\hbar\Gamma\sim 2\pi U^2\bar{Z}^6/W$ [see discussion leading to Eq. (8) starting from Eq. (4)]. Using this expression and $W=8$ eV and $U=4$ eV, the lower bound required to yield $U^*=0.5$ eV, we also obtain a large $\Gamma\sim 0.5\times 10^{15}$ s^{-1} (taking the same value of $\bar{Z}$ used in the previous paragraph).

V. ISSUES REGARDING EFFICIENCY

A. Impact ionization, Auger recombination, and other processes

Impact ionization increases the number of charge carriers per absorbed phonon. However, Auger recombination which is the inverse process should not be omitted. First, let us begin our discussion from the open-circuit situation. We found that for the type of Mott insulators discussed in the previous section, the characteristic time scale for thermalization of the photoexcited electrons and holes is much shorter than the time needed for phonons to thermalize the electronic system with the lattice. Therefore, it is reasonable to assume that the photocreated DOs and the holes in a Mott insulator thermalize among themselves at a temperature T_e higher than the lattice temperature T_L, by means of the electron-electron interaction (the interaction V defined in the previous section in the case of narrow band or the Hubbard on-site U in the case of a wide-band Mott insulator). This interaction between the electronic degrees of freedom leads to processes such as impact ionization and Auger recombination, as well as carrier-carrier scattering. This equilibrium state is achieved as follows.

The energy current of the absorbed solar photons is given by

$$J_{absorbed} = \frac{\Omega_s}{4\pi^3\hbar^3c^2}\int_{U^*}^{\infty} d\epsilon \frac{\epsilon^3}{\exp\left(\frac{\epsilon}{k_BT}\right)-1}, \tag{10}$$

where Ω_s is the solid angle under which the Sun is seen, and T is the Sun's surface temperature $T \simeq 5760$ K. Here, the lower energy cutoff is set by the value of the Mott gap U^*.

First, there is the impact ionization process, and, then, the Auger recombination process, i.e., the inverse of the impact ionization process, shown as the reverse process of the one shown in Fig. 3. These two processes can be also denoted as follows:

$$\mathrm{DO}_1 \leftrightarrow \mathrm{DO}_1' + \mathrm{DO}_2 + \mathrm{H}, \tag{11}$$

where DO_1 is the initial DO which creates the additional DO-H pair in the Mott insulator denoted as DO_2, H, by changing its energy-momentum state to become DO_1'. In addition, there is the analogous processes for high-energy holes, i.e.,

$$\mathrm{H}_1 \leftrightarrow \mathrm{H}_1' + \mathrm{DO} + \mathrm{H}_2. \tag{12}$$

Furthermore, there is the electron-electron scattering (due to the matrix element V defined in Sec. III or the on-site Coulomb repulsion U), which leads to DO-DO, hole-hole, and DO-hole interaction processes,

$$\mathrm{DO}_1 + \mathrm{DO}_2 \leftrightarrow \mathrm{DO}_1' + \mathrm{DO}_2', \tag{13}$$

$$\mathrm{H}_1 + \mathrm{H}_2 \leftrightarrow \mathrm{H}_1' + \mathrm{H}_2', \tag{14}$$

$$\mathrm{DO} + \mathrm{H} \leftrightarrow \mathrm{DO}' + \mathrm{H}'. \tag{15}$$

If these scattering processes are excluded, and we consider only impact ionization and Auger recombination, then, only those processes involving DOs and holes in certain energy and momentum range which allow for impact ionization and its inverse through energy-momentum conservation would take place and everything else would be excluded. As a result, the final distribution of carriers would depend on energy and momentum and, thus, it cannot be described by a Fermi-Dirac distribution. Therefore, in the absence of electron-phonon interaction, the above scattering processes are important in order to establish a common temperature and a Fermi-Dirac distribution.

If we now consider the equilibrium of all of the above processes, we realize that they produce a distribution of DO-H pairs in equilibrium with a distribution of photons over energy due to the emission process,

$$\mathrm{DO} + \mathrm{H} \leftrightarrow \gamma, \tag{16}$$

in which a DO and a hole (H) combine and a photon (γ) is emitted (luminescence) or the inverse where a photon produces a DO-H pair in the Mott insulator. This distribution of photons in equilibrium with a gas of quasiparticles consisted of DOs and holes is analogous to the case of electrons and holes in a band insulator which can be described[17,29] by a thermal distribution of photons at a temperature T_e and a chemical potential $\mu_\gamma = \mu_{\mathrm{DO\text{-}H}} = 0$ (see Refs. 17 and 29). The value of T_e is determined from the equation,

$$J_{emitted} = J_{absorbed}, \tag{17}$$

$$J_{emitted} = \frac{\Omega_e}{4\pi^3\hbar^3c^2}\int_{U^*}^{\infty} d\epsilon \frac{\epsilon^3}{\exp\left(\frac{\epsilon-\mu_\gamma}{k_BT_e}\right)-1}. \tag{18}$$

Here Ω_e is the solid angle of the emitter and it is π for a planar emitter. This equation defines a temperature T_e of the electronic system which is considered decoupled from the lattice and the phonons. A value of $\mu_{\mathrm{DO\text{-}H}} = 0$ is expected for a system in which the particle number is not conserved as is the case for the DO and holes in the equilibrium state of impact ionization and Auger recombination.

Assuming that the density of the DO and of holes near the interface is not large, the above process produces an equilibrium Fermi distribution of DO and holes at the above temperature T_e with no separation of the quasi-Fermi energies, i.e., the chemical-potential difference between DO and holes $\mu_{\mathrm{DO\text{-}H}}$ is zero.

Now, equilibrium is achieved (under open-circuit conditions) at the temperature T_e which is higher than the lattice temperature T_L. As shown in the previous sections, the time scale for the Mott insulator to reach equilibrium (through impact ionization, Auger recombination, and electron-electron scattering) is much shorter that the time scale required for such a system to reach thermal equilibrium with the lattice through the process,

$$\mathrm{DO} + \mathrm{H} \leftrightarrow \Gamma, \tag{19}$$

where Γ denotes a phonon. This is so because of the facts that (i) the time scale for the decay processes described by Eqs. (11) and (12) is much faster than the process of electron decay via phonons and (ii) the interaction matrix elements

involved in the processes described by Eqs. (13)–(15) are much stronger than the electron-phonon interaction matrix elements leading to the processes, Eq. (19). These facts allow first equilibration of the electronic system to a temperature T_e, which is different than T_L by creating multiple DO-H carriers per incident photon. This has been argued in Refs. 14–16 to lead to a significant increase in the efficiency by means of carrier multiplication[15,16] for a conventional solar cell. By treating the carriers in the Mott insulator as weakly interacting quasiparticles which obey Fermi-Dirac statistics, which may allow us to apply the same assumptions and approximations used by Brendel *et al.*[15] to calculate the efficiency of a conventional solar cell, we also find that the maximum efficiency is bounded from above by the maximum of the following function of the voltage V and the Mott gap U^*,

$$\eta(V,U^*) = qV\frac{g(U^*) - \xi r(V,U^*)}{P_{in}}, \tag{20}$$

$$g(U^*) = \int_{U^*}^{\infty} d\epsilon \frac{m(\epsilon)\epsilon^2}{\exp(\epsilon/k_B T_e) - 1}, \tag{21}$$

$$r(V,U^*) = \int_{U^*}^{\infty} d\epsilon \frac{m(\epsilon)\epsilon^2}{\exp[(\epsilon - qV)/k_B T_e] - 1}, \tag{22}$$

$$P_{in} = \int_{0}^{\infty} d\epsilon \frac{\epsilon^3}{\exp(\epsilon/k_B T_s) - 1}. \tag{23}$$

In the above expression, apart from a multiplicative constant common in the numerator and denominator expressions which cancels out, $g(V)$ corresponds to the generation current, $r(V,U^*)$ to the recombination current and P_{in} the total power carried by the sunlight; $m(\epsilon)=\min([\epsilon/U^*],m_0)$ is the number of DO-H pairs corresponding to each photon in dynamic equilibrium, where $[\epsilon/U^*]$ stands for the integer part of ϵ/U^* and m_0 is a maximum allowed value of the carrier multiplication. Furthermore, q is the carrier charge and $\xi = \pi/\Omega_s$ is the ratio of π to the solid angle through which the Sun is seen from the Earth and the case $\xi=1$ corresponds to fully concentrated sunlight. If we follow Werner *et al.*[14] and Brendel *et al.*[15] and use a value of $T_e=300$ K, we reproduce the same upper bounds for the solar-cell efficiencies as a function of U^* as those reported in Figs. 1 and 2 of Ref. 15. The calculated values for these upper bounds for solar-cell efficiencies reach up to 85% for fully concentrated sunlight and in the limit of vanishing value of U^* when m_0 becomes very large.

B. Further efficiency improvement

As argued by Würfel,[17] however, since the phonons are excluded from the equilibration process, the DO and holes through Eq. (17) will reach an equilibrium temperature T_e which should be higher than 300 K; as a result of the fact that the equilibrium temperature of the electronic degrees of freedom is higher than 300 K assumed in the calculation of Brendel *et al.*,[15] the efficiency should be lower than the values calculated using $T_e=300$ K. As was argued in the previous sections, the electronic equilibration is achieved much faster than the equilibration with the lattice, and this is important for another reason, namely, it allows the application of an idea discussed by Würfel,[17] which is summarized below, in order to improve the efficiency further.

The photovoltaic cell can achieve maximum efficiency when there is a way to cool the gas of carriers to the lattice temperature T_L via an isentropic process[17] where the relatively high energy of the carriers is not dissipated by heating the lattice but rather by creating electrical energy. Following Würfel[17] we assume that (a) impact ionization (and Auger recombination) occurs at much higher rate than photon absorption/emission, which as argued above is more likely in a Mott-insulator based solar cell and (b) the carriers are removed from the solar cell through membrane leads which are attached to the solar cell on each side[17] and which can be semiconductors of n type and p type with narrow bands of bandwidth $\delta\epsilon$ and large band gaps.

Because of the assumption (a) discussed above, the equilibrium of the carriers is not disturbed by the withdrawal of electrons and holes when the circuit is short. Now, the interaction with the slower acting phonons of the membranes cannot be avoided; in this case, however, this interaction is utilized in a favorable way. Namely, the hot electrons and holes with energies ϵ_e and ϵ_h in a narrow interval $\delta\epsilon$ and with temperature T_e can be cooled to the temperature of the lead membranes T_L by keeping the entropy constant. This can occur due to the above-mentioned assumption (b) where the carriers, whose concentration is constant, are transported via an approximately flat band, which prevents energy losses because the carriers keep approximately the same energy. This works as a Carnot engine which produces work $\mu_{eh} = (1-T_L/T_e)(e_e+e_h)$ which appears as a difference of the quasi-Fermi levels between the electron and hole carriers in the two membranes and is given by qV. The details of how this works as well as the calculation of the efficiency can be found in Ref. 17. This calculation leads to a maximum energy efficiency of 85% also in the limit of a vanishing Mott gap and for maximum concentration of solar-cell radiation. Therefore, in this section, we conclude that the idea proposed by Würfel may be utilized in solar cells based on Mott insulators.

C. Other issues regarding efficiency

A significant reason why a narrow-band Mott insulator may be preferred over the wide-band case is that the threshold for impact ionization to occur for the latter case (and in a wide-band semiconductor[1,30,31]) is approximately 3 times the Mott-insulator gap. This is because energy and momentum are conserved together via the impact ionization (or Auger recombination) and presence of a wide band implies a strong dependence of the energy with momentum. On the other hand, a narrow-band Mott insulator of the case discussed in Sec. III gives a much smaller energy threshold for impact ionization.

Finally, there is an important issue to address which is that in a Mott insulator the carrier mobility might be low. How-

ever, the effective collection length, as well as the drift field of the minority carriers can be large in such a Mott insulator, due to the following reasons. The main reason why a DO diffuses from the *n*-doped region inside the *p* region to fill a hole, is the large energy gain which will be resulted by the fact that the double occupancy in a Mott insulator of the type considered here, costs several electron volts. These materials become Mott insulators precisely because of this large on-site Coulomb repulsion which prevents the electrons from hopping from one site to a nearest-neighboring site and this leads to an insulator in the half-filled band case. Therefore, this strong on-site Coulomb repulsion between electrons produces high diffusivity because the DO in the *n*-doped region move to the *p*-doped region to gain a large amount of energy by filling the hole and this may lead to a high drift voltage and large diffusion length regardless of the fact that the electron mobility might be low.

VI. CONCLUSIONS

What should be the nature of the absorption spectrum in the case of the Mott insulator considered here in order for it to be a candidate for the basis of an efficient solar cell? There are two cases as discussed in the paper for the case of a narrow gap Mott insulator. (a) Narrow Mott-band materials. In this case in order for the effect considered in the present paper to be significant, we need other bands present, not necessarily of Mott type. The incident solar photon may be absorbed by an electron from another such valence band or the Mott conduction band and be promoted to a highly excited band. If there are no issues related to selection rules, these electrons are expected to decay very quickly (for the reasons discussed in the paper) to produce one or multiple DO-hole pairs from the Mott band. Therefore, if the material is appropriately selected, a large fraction of the solar spectrum, could be absorbed leading to a much larger photocurrent than in band semiconductors. (b) In a wide-band Mott insulator, almost the entire solar spectrum could be absorbed by the same single Mott band. As analyzed in the present paper, in this case the initially photoexcited single DO-hole pair decays into two or more DO-hole pairs by means of the on-site Coulomb repulsion within a time scale much shorter than other internal processes which dissipate the excess energy of the DO or hole beyond the Mott gap.

In conclusion, it was argued that a *p*-*n* heterojunction in which the illuminated side is a narrow-gap Mott insulator, if fabricated, should be expected to behave as a high quantum efficiency solar cell. This can be achieved when the Mott insulator's energy spectrum for multiple quasielectron-hole pairs falls within the energy range of solar photons. We find that in such case, a relatively high-energy incident photon initially creates a high-energy electron-hole pair which quickly dissociates into multiple quasielectron-hole pairs and this leads to an increased photocurrent. As required for the device to work, it is estimated that this dissociation occurs in a time scale shorter than the time needed for the excited electron-hole pair to relax through the emission of phonons or other intrinsic excitations. This allows equilibration of the electronic degrees of freedom among themselves, with excitation of multiple DO-H pairs for every absorbed photon, at a different temperature, on a time scale significantly shorter than the time required for the system to reach equilibrium with the lattice. This separation of time scales also allows the application of other previously proposed ideas to improve solar-cell efficiency by cooling the carriers isentropically to a lower temperature.[17]

ACKNOWLEDGMENTS

I wish to thank V. Dobrosavljevic, B. I. Halperin, C. S. Hellberg, P. Schlottmann, and S. von Molnár for useful discussions.

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