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Publication Details

Wang, X (2008), Proposal for a new class of materials: spin gapless semiconductors, Physical Review Letters, 100(15), pp. 156404-1-156404-4.

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Keywords
Proposal, for, class, materials, Spin, Gapless, Semiconductors

Disciplines
Engineering | Physical Sciences and Mathematics

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Proposal for a New Class of Materials: Spin Gapless Semiconductors

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(Received 15 May 2007; revised manuscript received 13 August 2007; published 18 April 2008)

The concept of the spin gapless semiconductor in which both electron and hole can be fully spin polarized is proposed, and its possibility is presented on the basis of first-principles electronic structure calculations. Possible new physics and potential applications in spintronic devices based on the spin gapless semiconductors are discussed.

DOI: 10.1103/PhysRevLett.100.156404 PACS numbers: 71.55.Ak, 73.61.Le

In quantum solid-state band theory, materials in nature are generally classified as insulators, semiconductors, metals, and semimetals based on the electronic band structures. The valence and conduction bands overlap in metals, causing the Fermi level to penetrate into the conduction band [Fig. 1(a)], while these bands are separated by large gaps for insulators and small gaps for semiconductors [Fig. 1(b)]. With a small energy overlap of conduction and valence bands, the substance is a semimetal [Fig. 1(c)]. Half-metallic materials, a new class of materials, which are metallic for one spin direction [Fig. 1(d)], while semiconducting for the other spin direction, were predicted in the 1980s [1]. Half-metallic antiferromagnets [2], a new system with full spin polarization of the conduction electrons, but without any net magnetization, were theoretically predicted in alloys, perovskite oxides, and diluted magnetic semiconductors [2–4]. The half metals with full electron spin polarization and the diluted magnetic semiconductors [5] are the most important candidates for applications as spintronic materials. If the conduction and valence band edges touch at the Fermi level [Fig. 2(a)], this represents a comparatively new class of solids, namely, the gapless semiconductors (GS) [6]. No threshold energy is required to move electrons from occupied states to empty states; thus, the gapless semiconductors, such as HgCdTe, HgTeSe, HgZnSe, etc., have unique properties as their band structures are extremely sensitive to external influences, e.g., pressure or magnetic field. The electron mobility of a GS is two to four orders of magnitude higher than the mobility of classical semiconductors.

The very recent exciting discovery of two-dimensional gapless graphene [7] has aroused great interest worldwide. In classical semiconductors, the relation between energy and momentum is quadratic. However, the graphene has a two-dimensional gapless band structure, and the relation between energy and momentum is linear [Fig. 2(b)]. As the results of the gapless and linear dispersion, the electrons can travel at $0.0025c$, where c is the speed of light, much higher than speeds typical of electrons in semiconductors. Fascinating properties, from the quantum Hall effect [8,9] to the absence of localization [8], have been discovered in graphene.

Inspired by the unique superior properties of the above-mentioned gapless semiconductors and two-dimensional gapless graphene, the concept of the spin gapless semiconductor (SGS) is proposed in this work. There are four possible band structure configurations with spin gapless features as illustrated in Figs. 3(a)–3(d). These are based on gapless semiconductors (Fig. 2) with parabolic or linear dispersion between energy and momentum. For the first case [Fig. 3(a)] one spin channel is gapless, while the other spin channel is semiconducting. In the second case (b) there is a gap between the conduction and valence bands for both the majority and minority electrons, while there is no gap between the majority electrons in the valence band and the minority electrons in the conduction band. In the third case (c) one spin channel is gapless, and the other spin channel is semiconducting with the top of the valence band being lower than the Fermi level. In the fourth case (d) one spin channel is gapless while the bottom of the conduction band for the other spin channel touches the Fermi level, which is separated from its corresponding valence band by a gap. The same four configurations of the gapless parabolic bands also apply for linear dispersion between energy and momentum as shown in Fig. 4. By swapping the minority and majority bands, one can have another four gapless configurations for both parabolic and linear bands.

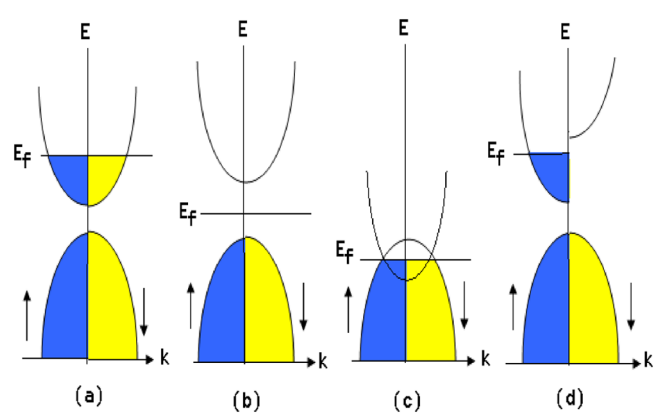

FIG. 1 (color online). Energy band diagrams for a (a) metal, (b) semiconductor (small gap) or insulator (big gap), (c) semimetal, and (d) half metal.

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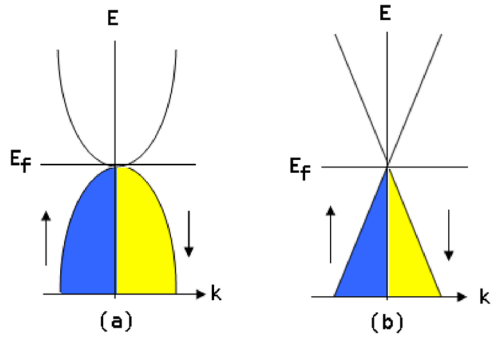

FIG. 2 (color online). Energy band diagrams for a direct gapless semiconductor with parabolic (a) and linear (b) dispersion between energy and momentum.

What can be directly seen from all these spin gapless band structures is that no energy is required to excite electrons from the valence band to the conduction band, which is the same as what we see for the Hg-based gapless semiconductors and graphene. What is more interesting is that, for an excitation energy up to the band gap energy of the other spin channel, the excited electrons are 100% spin polarized for all the spin gapless configurations except the third case [Fig. 3(c) or Fig. 4(c)], and more excitingly, the holes can also be 100% spin polarized except the first case. Therefore the phenomena that have been observed in classical gapless semiconductors could also be possible for the fully spin polarized carriers in the spin gapless semiconductors. Novel physics, novel phenomena, and novel applications could also be expected for this new class of SGS, as will be discussed later.

One of the methods used to design a SGS material is to introduce magnetic ions into the parent compounds, which should be gapless semiconductors or semiconductors with a narrow direct or indirect band. It is well-known that the GS are very rare and have been only found in Hg-based IV-VI compounds such as HgCdTe, HgCdSe, HgZnSe, etc. [6]. These materials have direct gapless bands, but they are toxic and easily oxidized, limiting their applications at elevated temperatures under oxidizing conditions. No oxide GS has been reported to date. In this work, we present an oxide gapless semiconductor, $PbPdO_2$, and discuss the

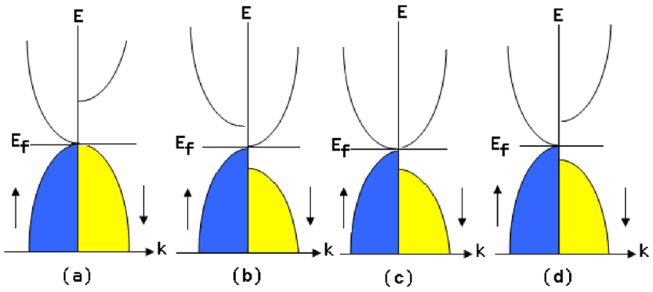

FIG. 3 (color online). Energy band diagrams for spin gapless semiconductors with parabolic dispersion between energy and momentum.

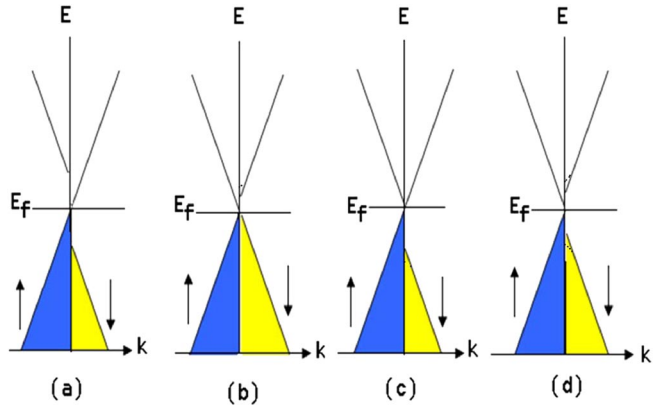

FIG. 4 (color online). Energy band diagrams for spin gapless semiconductors with linear dispersion between energy and momentum.

possibility of the proposed concept of SGS, based on doping this compound with magnetic ions.

To verify the concept of the spin gapless semiconductor, first-principles electronic band structure calculations were performed for $PbPdO_2$ using density functional theory implemented in the DMol3 package [10]. The local density approximation was used for the exchange-correction functional. A Monkhorst-Pack grid ($4 \times 4 \times 6$) with 96 summarized k points was used for Brillouin sampling with a cutoff energy of 340 eV, a self-consistent field tolerance of 10^{-6}. The quality of the k point separation for the band structure calculation is 0.015 Å^{-1}. Relativistic electrons were used for the core treatment as both Pd and Pb are heavy atoms.

$PbPdO_2$ crystallizes in the orthorhombic structure shown in Fig. 5 (space group, Imma). It consists of PbO layers stacked along the a axis. Each Pd is fourfold coordinated by oxygen in a square planar configuration. The PdO layers are separated by PbO layers. PdO squares face each other diagonally in the unit cell and form a honeycomblike structure along the b and c axes, enclosing the Pb

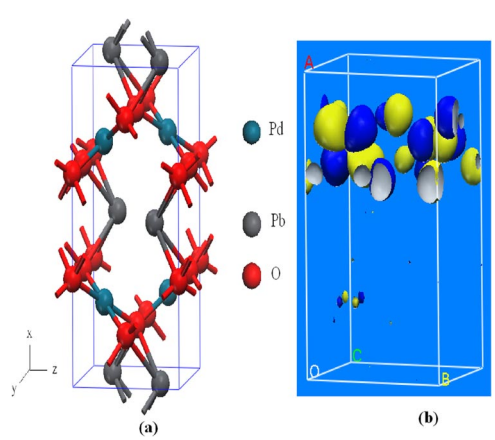

FIG. 5 (color online). Crystal structure of $PbPdO_2$ (a) and the HOMO for Co-doped $PbPdO_2$ (b) in which one Pd atom is replaced by Co.

atoms inside it. It has recently been reported that the polycrystalline $PbPdO_2$ samples showed p-type charge carriers and behaved like a metal at high temperature and turned to be semiconducting below 90 K [11], indicating possible gapless or narrow bands for the $PbPdO_2$. Figure 6 displays a band pattern of $PbPdO_2$ calculated by this work for high symmetry points in the Brillouin zone. As can be seen, no forbidden band or energy band is present at the Γ point; i.e., the lowest conduction band and the highest valence band touch at the Fermi level at the same point. These results clearly indicate that $PbPdO_2$ is a typical direct gapless semiconductor. The calculation results indicated that the Pd^{2+} is present in the low spin state with $S = 0$. Thus, the pure $PbPdO_2$ is nonmagnetic gapless semiconductor. It should be noted that the $PbPdO_2$ is the first oxide-based gapless semiconductor. Further studies on this new gapless oxide material both theoretically and experimentally and potential applications would be very exciting and interesting.

In order to introduce electron spin into the system, Co is introduced to replace one Pd in one unit cell. This corresponds to a 25% doping level of Co for Pd. The spin-resolved band structure for the Co-doped $PbPdO_2$ is shown in Fig. 7. The band structure shows that the highest valence band of the majority electrons touches the Fermi level at the Γ points. The lowest conduction band of the minority electrons touches the Fermi level as well, but at the U point and between the T and Y points. This means that the valence band of majority electrons and the conduction band of minority electrons is gapless, but indirectly. This band structure is the second case of spin gapless band structures shown in Fig. 3(b). The isosurface of the orbital electrons near the E_f shown in Fig. 5(b) reveals that it is the d orbitals from both Co and Pd and the p orbitals from oxygen that contribute to such an indirect spin gapless band structure in the Co-doped $PbPdO_2$.

It should be pointed out that the Co-doped $PbPdO_2$ is only one example of such spin gapless semiconductors. The SGSs should constitute a boundary between half metals and magnetic semiconductors, and they could be either ferromagnetic or antiferromagnetic without net magnetic moments, similar to that of ferromagnetic or antiferromagnetic half metals [1–4]. It should be possible to realize the spin gapless features in a wide range of other gapless or narrow band oxides and nonoxide semiconductors, ferromagnetic or antiferromagnetic semiconductors or oxides, or even in conductive ferromagnetic oxides and nonoxides with proper elemental substitutions. Attention also ought to be paid to perovskite structured parent compounds, as it has been widely observed that doping often changes those compounds from metallic to semiconducting. A spin gapless state could exist in between.

Some special properties are expected from the SGS. In addition to the 100% spin-polarized conduction carriers, it is important to note that all the related properties are tunable by external influences, such as pressure, electric fields, magnetic fields, electromagnetic radiation, impurities, etc. The devices based on SGS with full spin polarization could be used over a very wide temperature range from low temperature to elevated temperature depending on the values of the gap.

For the spin gapless structure shown in Fig. 3(b) or Fig. 4(a), if the Fermi level can be shifted up and down by external influences such as changing the sign of gate voltages, the directions (up or down) of spins in either the conduction or the valence band are tunable, and the spins of the resulting carriers are fully polarized. The feature of the tunable spin direction may be useful to design qubits for quantum computing, data storage, and coding or decoding. The speed of the 100% polarized spin electrons in the SGS could be much faster than in diluted magnetic semiconductors, and the speed will be significantly enhanced if the SGS could be realized as in the case of Fig. 4. Linear dispersion combined with a finite gap, as shown in Fig. 4, may not really exist, since there is no space group that will allow a linear dispersion combined with a finite band gap. Any interaction opening up a band gap will destroy the linear dispersion. Therefore, a deviation from linear dis-

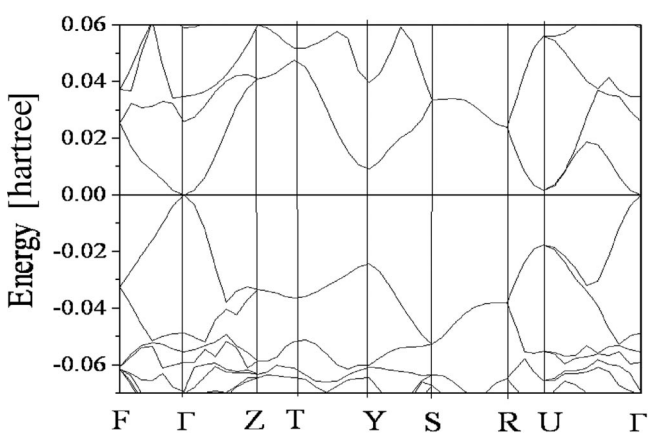

FIG. 6. Band structure of $PbPdO_2$.

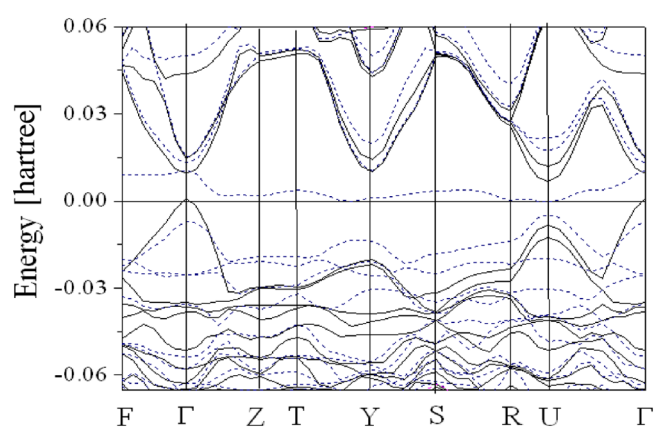

FIG. 7 (color online). Spin-resolved band structure of $PbPdO_2$. Majority spin (solid lines) and minority spin (dashed lines).

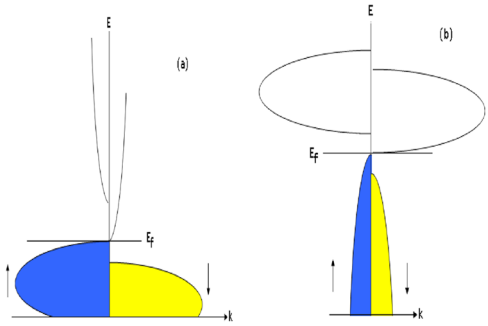

FIG. 8 (color online). Energy band diagrams of spin gapless semiconductors with heavy hole and light electrons (a) and light holes and heavy electrons (b).

persion should take place at both the bottom of the conduction band and the top of the valence band, as shown by the dotted curves in Fig. 4(d). However, the linear dispersion may still hold at some random point in the reciprocal space at proper "tuning" by pressure and doping, as proposed by a model for quantum magnetoresistance [12], or it might be realized in low-dimensional materials similar to what has been seen in graphene.

For the SGS with the band structure configuration as shown in Fig. 8(a), the spin of the electrons excited from the valence band to the conduction band is 100% polarized, and their speed is much faster than that of the corresponding 100% polarized holes. On the other hand, the 100% spin polarized electrons move much more slowly than the fully polarized light holes for the gapless band structures shown in Fig. 8(b). This means that the speed of the 100% polarized carriers could be significantly different. This feature could be useful for injecting or emitting either 100% polarized holes or electrons selectively.

Using the Hall effect, one can easily separate fully spin-polarized electrons or holes. For example, when a magnetic field is applied perpendicular to the current direction, fully polarized spin-down electrons and spin-up holes can be easily separated for case Fig. 3(b), fully polarized spin-up holes for case Fig. 3(c), and fully polarized both spin-up electrons and holes for the case Fig. 3(d). We can call this feature the field-induced self-spin filtering effect or self-spin filter.

For the SGS with the linear relation between energy and momentum, the mass of both electrons and holes should be very small. It is expected that the speed of the 100% polarized electrons should be much faster than that of the 2D nonpolarized electrons in graphene or in 3D conventional semiconductors, as the electron scattering is significantly reduced in the SGSs.

The SGS band structures could be either direct or indirect gapless. The spin gapless band structure for the $PbPd_{0.75}Co_{0.25}$ O_2 (Fig. 7) is indirect, which means that the momentum does not conserve. In contrary, the momentum conserves in the direct gapless bands seen in $PbPdO_2$, TeCdHg, and graphene. The combination of polarized holes and electrons occurs with the mediation of a phonon or a crystallographic defect which allows for conservation of momentum. This means that the absorption of light of an indirect SGS should depend more on temperature than that of a direct SGS. The devices based on direct spin gapless semiconductors are expected to be more sensitive than those based on indirect spin gapless semiconductors.

The spin gapless semiconductors should open up a new direction for the exploration of materials for spintronics and wide prospects for practical spintronic applications. Generally all the applications for gapless semiconductors [6] could be suitable for SGS. These include spin detectors and generators for electromagnetic radiation over a wide range of wavelengths based on the spin photoconductivity. Spin photodiodes and spin image detectors with high mobility of fully spin-polarized carriers might also be possible.

In summary, $PbPdO_2$ is predicted to be an oxide-based gapless semiconductor. The concept of a new class of materials, spin gapless semiconductors, is verified in Co-doped $PbPdO_2$ by band structure calculations. The excited carriers can be 100% spin polarized with tunable capabilities, and the SGS can be used as spintronic materials with superior performance to half metals and diluted magnetic semiconductors. The SGS provides a new platform and new opportunities for spintronics, electronics, and optics.

This work is supported by funding from the Australian Research Council under a Discovery project (No. DP0558753) and under the QEII program. The author thanks Dr. A. Goldberg and Dr. P. Kung from Accelrys Inc., Professor C. Zhang, Professor S. Dou, Dr. T. Silver, and Dr. G. Peleckis for helpful discussions.

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