PRAMANA — journal of physics © Indian Academy of Sciences Vol. 66, No. 1 January 2006 pp. 239–246

Multiple superconducting phases in heavy fermion compounds $PrOs_4Sb_{12}$ and $CeCoIn_5$

YUJI MATSUDA[1,2]
[1]Department of Physics, Kyoto University, Kyoto 606-8502, Japan
[2]Institute for Solid State Physics, University of Tokyo, Kashiwa, Chiba 277-8581, Japan
E-mail: matsuda@scphys.kyoto-u.ac.jp

Abstract. In recently discovered heavy fermion compounds, quasi-two-dimensional $CeCoIn_5$ and skutterudite $PrOs_4Sb_{12}$, multiple superconducting phases with different symmetries manifest themselves below T_c. The angle-resolved magnetothermal transport measurements revealed that in $PrOs_4Sb_{12}$ a novel change in the symmetry of the superconducting gap function occurs deep inside the superconducting state. The ultrasound velocity measurements revealed that in $CeCoIn_5$ the Fulde–Ferrel–Larkin–Ovchinikov (FFLO) phase, in which the order parameter is spatially modulated and has planar nodes aligned perpendicular to the vortices, appears at low temperature and high field. These results open up a new realm for the study of the superconductivity with multiple phases.

Keywords. Multiple superconductivity; heavy fermion; Fulde–Ferrel–Larkin–Ovchinikov.

PACS Nos 74.20.Rp; 74.25.Bt; 74.25.Fy; 74.70.Tx

1. Introduction

In almost all superconductors, once the energy gap in the electronic spectrum opens at the critical temperature T_c, only the gap amplitude, but not the shape and symmetry around the Fermi surface, changes within the superconducting (SC) state. The only exception to this well-known robustness of the SC gap symmetry had been reported for UPt_3 with three SC phases with different symmetries, A-, B- and C-phase, in the B–T phase diagram. In UPt_3 the SC order parameter possesses a multiplicity, with a near-degeneracy of order parameters with different symmetries [1]. Tuning the pairing interaction by an external perturbation causes a SC state of given symmetry to undergo a transition to a different SC state.

Here we show that multiple superconducting phases are present in heavy fermion superconductors, $CeCoIn_5$ [2] and $PrOs_4Sb_{12}$ [3] , both of which were discovered very recently. The superconducting gap function of $PrOs_4Sb_{12}$ was investigated using thermal transport measurements in magnetic field rotated relative to the crystal axes [4]. We demonstrate that a novel change in the symmetry of the superconducting gap function occurs deep inside the superconducting state, giving a clear indication of the presence of two distinct superconducting phases with two-fold and four-fold symmetries. Ultrasound velocity measurements of $CeCoIn_5$ reveal an unusual structural transformation of the flux line lattice (FLL) at $T^*(H)$ in the vicinity of the upper critical field parallel to the two-dimensional (2D) planes $H_{c2}^{\parallel}$ [5]. These results provide a strong evidence of the presence of the Fulde–Ferrel-Larkin–Ovchinikov phase, in which the order parameter is spatially modulated and has planar nodes aligned perpendicular to the FLL [6].

2. Experimental

High-quality $PrOs_4Sb_{12}$ single crystals with a very sharp resistive transition $\Delta T_c/T_c < 0.01$ were grown by the Sb-flux method (T_c=1.82 K). We measured the c-axis thermal conductivity κ_{zz} (the heat current $\mathbf{q}\|c$) on the sample with a rectangular shape (0.40×0.37×2.20 mm^3) by the steady-state method. To apply **H** with high accuracy relative to the crystal axes, we used a system with two superconducting magnets generating **H** in two mutually orthogonal directions and a ^{3}He cryostat set on a mechanical rotating stage at the top of the Dewar. By computer-controlling the two magnets and the rotating stage, we were able to rotate **H** with a misalignment of less than 0.5° from each axis, which we confirmed by the simultaneous measurements of the resistivity [7].

The ultrasound velocity measurements were performed on high-quality single crystals of $CeCoIn_5$ with tetragonal symmetry, grown by the self-flux method. Ultrasonic waves, with a frequency of 90 MHz, were generated by a $LiNbO_3$ transducer glued on the surface of the crystal. A pulse echo method with a phase comparison technique was used for the sound velocity measurements. The relative change of the sound velocity was measured by the phase change of the detected signal. The resolution of the relative velocity measurements was about 1 part in 10^6.

3. Superconducting gap functions in $PrOs_4Sb_{12}$

Recently discovered heavy fermion superconductor $PrOs_4Sb_{12}$ with filled skutterudite structure should be distinguished from the other unconventional superconductors, in that it has a non-magnetic ground state of the localized f-electrons in the crystalline electric field (most likely the singlet Γ_1 state) [3]. Therefore, the relation between the superconductivity and the orbital fluctuation of f-electron state (i.e. quadrupole fluctuation) has aroused great interest; $PrOs_4Sb_{12}$ is a candidate for the first superconductor mediated by neither electron–phonon nor magnetic interactions. The subsequent measurements have revealed the unconventional superconductivity in $PrOs_4Sb_{12}$. The broken time reversal symmetry has been reported by the μSR experiments [8]. The thermal conductivity and penetration length showed the presence of point nodes in the SC gap function [4,9]. Here we determined the nodal structure by the angle resolved magnetothermal transport measurements, which have been shown to be a unique powerful probe for determining the gap structure.

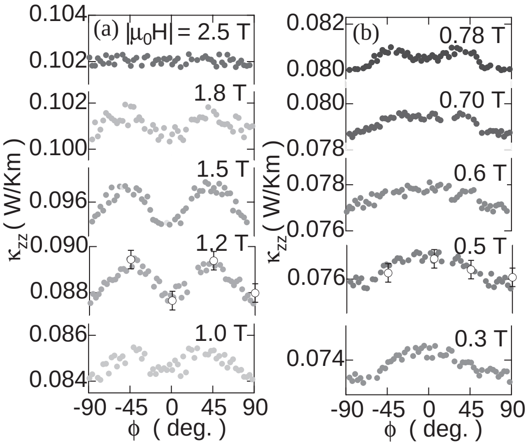

Figure 1(a) and (b). Angular variation of κ_{zz} with $\mathbf{H}$ rotating within the ab-plane at 0.52 K above and below H_{c2} ($\simeq$2.0 T). ϕ is the angle between $\mathbf{H}$ and the a-axis.

The theoretical understanding of the heat transport for superconductors with nodes has made significant advances during the past few years. The most significant effect on the thermal transport for such superconductors comes from the Doppler shift of the quasi-particle (QP) energy spectrum ($\varepsilon(\mathbf{p}) \rightarrow \varepsilon(\mathbf{p}) - \mathbf{v}_s \cdot \mathbf{p}$) in the circulating supercurrent flow $\mathbf{v}_s$ [10]. This effect becomes important at such positions where the local energy gap becomes smaller than the Doppler shift term ($|\Delta| < |\mathbf{v}_s \cdot \mathbf{p}|$), which can be realized in the case of superconductors with nodes. The maximum magnitude of the Doppler shift at a particular point strongly depends on the angle between the node direction and $\mathbf{H}$ [11–15]. Such an angle-dependent thermal conductivity or heat capacity has been observed in several nodal superconductors, but is absent in fully gapped s-wave superconductors [16–20]. Here we apply this technique to $PrOs_4Sb_{12}$.

Figures 1a and b depict the angular variation of the thermal conductivity along the c-axis, κ_{zz}, measured by rotating $\mathbf{H}$ within the ab-plane as a function of angle ϕ between $\mathbf{H}$ and a-axis at $T = 0.52$ K. Above H_{c2} ($\simeq$2.0 T at 0.5 K) $\kappa_{zz}(\mathbf{H}, \phi)$ is essentially independent of ϕ. A clear four-fold variation is observed just below H_{c2} down to $H \sim 0.8$ T. However, further decrease of H below 0.8 T causes a rapid decrease of the amplitude of the four-fold symmetry and eventually a discernible four-fold symmetry is not observed below 0.7 T. At the same time, the two-fold symmetry grows rapidly.

Figure 2 shows the T-dependence of the cross-over field H^* at which the four-fold symmetry changes to two-fold symmetry in κ_{zz}. H^* is obtained by decomposing $\kappa_{zz}(\mathbf{H}, \phi)$ into three terms with different symmetries: $\kappa_{zz}(\mathbf{H}, \phi) = \kappa_0 + \kappa_{2\phi} + \kappa_{4\phi}$, where κ_0 is a ϕ-independent term, $\kappa_{2\phi} = C_{2\phi} \cos 2\phi$, and $\kappa_{4\phi} = C_{4\phi} \cos 4\phi$ are terms with two-fold and four-fold symmetries with respect to ϕ-rotation. Therefore, the change from four-fold to two-fold symmetry provides a direct evidence for the change of the gap symmetry. The fact that $\kappa_{zz}(\mathbf{H}, \phi)$ possesses minima at $\phi = \pm 90°$ and $0°$ at high-field phase and at $\phi = \pm 90°$ for low-field phase immediately leads

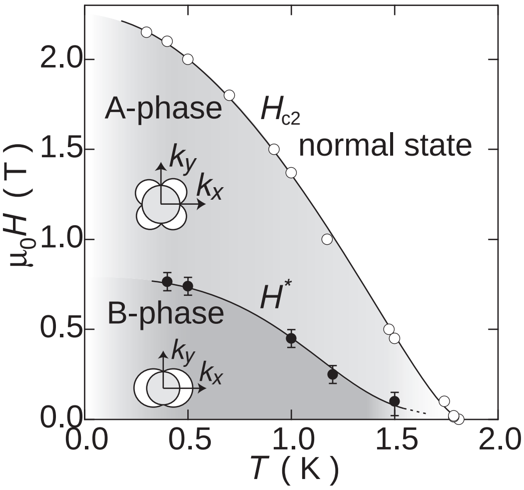

Figure 2. The phase diagram of the superconducting gap symmetry determined by the present experiments. The filled circles represent the magnetic field H^* at which the transition from four-fold to two-fold symmetry takes place. The open circles represent H_{c2}. The gap function above H^* has four-fold symmetry (A-phase) and the gap function below H^* has two-fold symmetry (B-phase).

to the conclusion that the nodes are located along the [1 0 0] and [0 1 0] directions in the high-field phase, while they are located only along the [0 1 0] direction in the low-field phase. We note that the two-fold symmetry of the gap function has been confirmed by the observation of the FLL by the small angle neutron scattering [21].

As suggested in ref. [22], the SC gap function with four point nodes is unlikely in the cubic T_h crystal symmetry, regardless of spin singlet or triplet symmetry. This naively suggests that the gap function at high-field phase has six point nodes, while that at low-field phase has two point nodes. The H–T phase diagram of the SC symmetry in figure 2 indicates that the H^*-line which separates two SC phases (high field A-phase and low field B-phase) lies deep inside the SC state. Thus the angle resolved magnetothermal transport measurements provide a strong evidence of the multiple superconducting phases in $PrOs_4Sb_{12}$.

4. New superconducting phase in $CeCoIn_5$

Recently it was reported that $CeCoIn_5$ is a new type of heavy fermion superconductor with quasi-2D electronic structure and an effective electron mass $m^* \approx 100m_e$ [2]. Subsequent measurements have identified that the gap symmetry of $CeCoIn_5$ is most likely to be d-wave with line nodes perpendicular to the 2D-planes [16,23]. The normal state of $CeCoIn_5$ reveals quite unusual properties [24,25]. One of the most striking phenomena observed in the superconducting state in $CeCoIn_5$ is that the superconducting transition at the upper critical field is of first order below approximately 1.3 K both in $H\|ab$-plane and in $H\|c$-axis [16,26,27]. This is in

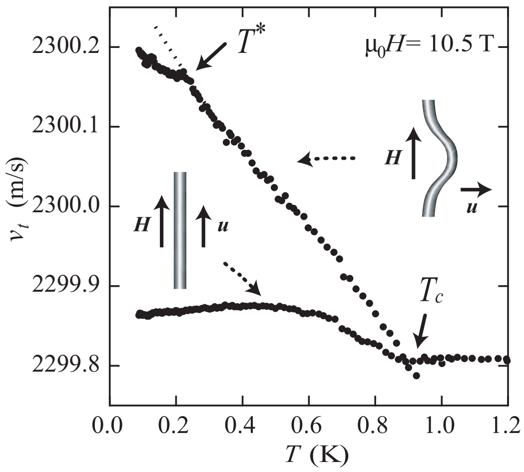

Figure 3. The transverse sound velocity $v_{\rm t}$ as a function of temperature at $H = 10.5$ T in two different configurations. (**a**) The Lorentz mode $\mathbf{H}\|\mathbf{k}\|$[1 0 0], $\mathbf{u}\|$[0 1 0] and (**b**) the non-Lorentz mode, $\mathbf{u}\|\mathbf{H}\|$[1 0 0], $\mathbf{k}\|$[0 1 0]. The configuration (a) corresponds to a flux line bending mode.

contrast to the other superconductors, in which the transition at $H_{\rm c2}$ is of second order. The simplest interpretation is as follows: In spin-singlet superconductors, superconductivity is suppressed by the orbital effect (vortices) and by the Zeeman effect (Pauli paramagnetism) of the conduction electron spins. It has been suggested that the phase transition from SC state to normal state becomes first order when H_{c2} is determined by the Zeeman effect and the system is very clean ($\xi \ll \ell$, where ξ is the coherence length and ℓ is the mean free path) [28]. Therefore, in $CeCoIn_5$ the superconductivity seems to be limited by the Pauli paramagnetism. The unusual SC state has also been reported by the very recent Knight shift measurements in NMR experiments [29], which imply the anomalous electronic structure of vortex cores, similar to high-$T_{\rm c}$ cuprates [30–34].

Very recent reports of heat capacity measurements in a field parallel to the *ab*-plane have raised great interest, because a second-order phase transition line, which branches from the first order $H_{\rm c2}^{\|}$-line and decreases with decreasing T, was discovered within the SC state below 0.35 K [35,36]. $CeCoIn_5$ satisfies the requirements for the formation of FFLO state because the Pauli effect overcomes the orbital effect at $H_{\rm c2}$ and it is in the very clean regime; $\xi \ll \ell$. On the basis of these arguments, the possibility of a high-field FFLO state has been evoked [35,36]. However, there still is no corroborated evidence for the FFLO state, because of other possible origins for a second-order transition, such as some sort of magnetic transition in the heavy fermion system. Therefore, a more detailed experimental investigation of the vortex state is required in order to shed light on this subject.

In the FFLO state, pair-breaking arising from the Pauli effect is reduced by forming a new pairing state ($\mathbf{k}\uparrow$, $-\mathbf{k}+\mathbf{q}\downarrow$) with $|\mathbf{q}| \sim 2\mu_{\rm B}H/\hbar v_{\rm F}$ ($v_{\rm F}$ is the Fermi velocity) between exchange-split parts of the Fermi surface, instead of ($\mathbf{k}\uparrow$, $-\mathbf{k}\downarrow$)-pairing in ordinary superconductors. As a result, a new SC state with different order parameter appears in the vicinity of the upper critical field [6,37–40]. The most fascinating aspects of the FFLO state are that Cooper pairs develop a spatially modulated order parameter and spin polarization with a wavelength of the order of $2\pi/|\mathbf{q}|$ and that the SC order parameter has planar nodes aligned perpendicular to the applied field. In particular, as pointed out in ref. [40], the flux lines are divided into segments with distance $\sim 2\pi/|\mathbf{q}|$ (see figure 4 in this paper). Therefore, in order to establish the existence of a possible FFLO state, it is particularly important to elucidate the structure of the flux line lattice (FLL), which in turn is intimately related to the electronic structure. The ultrasound velocity measurements may be suited for this purpose because they provide direct information on the FLL structure.

Figure 3 depicts the transverse sound velocity $v_{\rm t}$ in the vortex state at $H = 10.5$ T as a function of temperature in two different configurations with respect to the polarization vector $\mathbf{u}$, the sound propagation vector $\mathbf{k}$, and $\mathbf{H}$. We distinguish between the Lorentz force mode ($\mathbf{u}\perp\mathbf{H}$) where the sound wave couples to the vortices through the induced Lorentz force and the non-Lorentz mode ($\mathbf{u}\|\mathbf{H}$) where the sound wave couples only to the crystal lattice. The sound velocity in the Lorentz mode, in which flux motion is parallel to the *ab*-plane, is strongly enhanced compared to that in the non-Lorentz mode. This indicates that the transverse ultrasound strongly couples to the FLL in the Lorentz mode. The difference between the sound velocity in the Lorentz mode and in the non-Lorentz mode can be regarded as being the contribution of the FLL to the sound velocity. In the Lorentz mode, the ultrasound velocity increases rapidly with decreasing T below $T_{\rm c}$, indicating the hardening of the FLL. At $T^* \simeq 0.25$ K, marked by arrow, $v_{\rm t}$ in the Lorentz mode changes its slope with a distinct cusp. This cusp temperature coincides well with the second-order transition line below $H_{\rm c2}^{\|}$ reported in the specific heat measurements, as shown in figure 4.

The dashed line in the Lorentz mode is $v_{\rm t}$ extrapolated from $T > T^*$. Below T^*, $v_{\rm t}$ becomes lower than that extrapolated above T^*, indicating the softening of the FLL. The softening of the FLL is consistent with the phenomena expected in the FFLO phase. In the flux line above T^*, the ultrasound can propagate easily along the line. On the other hand, below T^*, the formation of the planar node prevents the propagation of the ultrasound by reducing the tilt modulus of the flux line. This situation resembles the flux lines in high-$T_{\rm c}$ cuprates, in which the 2D pancake vortices are weakly coupled by the Josephson effect [41,42]. On the basis of these results, we conclude that the second-order phase transition is characterized by a structural transition of the FLL. The present results definitely rule out the possibility that some kind of magnetic transition is at the origin of the transition. This can be seen by looking at $v_{\rm t}$ in the non-Lorentz mode, which shows no anomaly at T^*. We can also rule out the possibility of the so-called peak effect as an origin of the ultrasound anomaly at T^* because (1) peak effect was not observed at T^* [27] and (2) the FLL should exhibit the hardening if the peak effect occurs [43,44], opposite to the present results.

The correlation length d of the FLL along H estimated by the collective pinning theory and by the ultrasound measurements below T^* is approximately 80 nm [5]. This length is of the same magnitude as the modulation length expected in the FFLO phase, $d = 2\pi/|\mathbf{q}| = (m_e/m^*)(\hbar k_{\rm F}/eB) \sim 40$ nm, where $k_{\rm F}$ is the Fermi

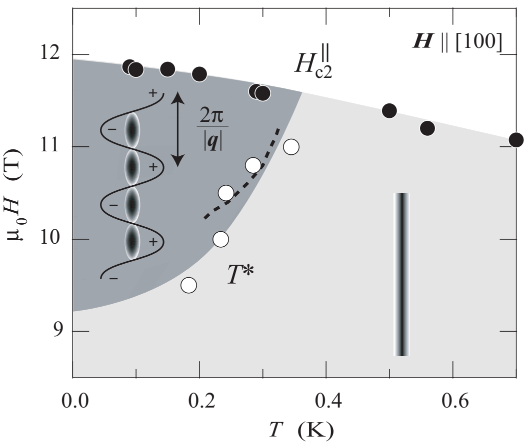

Figure 4. Experimental H–T phase diagram for $CeCoIn_5$ below 0.7 K for $\mathbf{H}\|[1\ 0\ 0]$. The transition temperature T^*, indicated by open circles, was obtained from ultrasonic measurements as indicated by the arrows in figure 1. The solid circles are the upper critical field $H_{c2}^{\|}$ determined by the ultrasonic experiments. The dotted line is the second-order transition line determined by the heat capacity reported in ref. [26]. The schematic figures are sketches of a flux line above and below the transition.

wave number. Thus we find a distinct anomaly of the sound velocity, the nature and magnitude of which provide strong evidence for a vortex state with modulated order parameter as predicted for the FFLO phase.

5. Summary

In summary, two distinct SC phases with different symmetries, the phase transition between them, and the presence of point nodes highlight the unconventional superconductivity in $PrOs_4Sb_{12}$. Ultrasound velocity measurements of $CeCoIn_5$ reveal an unusual structural transformation of the FLL at the second-order phase transition within the SC state. The results are a strong indication that the high field superconducting state is the FFLO phase, in which the order parameter is spatially modulated and has planar nodes aligned perpendicularly to the FLL.

Acknowledgments

I would like to thank K Izawa, T Watanabe, Y Kasahara, Y Nakajima, T Sakakibara, C J van der Beek, M Nohara, T Hanaguri, H Takagi, J Goryo, K Maki, P Thalmeier, S Osaki, H Sugawara, H Sato, H Shishido, R Settai and Y Onuki for collaboration of this work.

References

[1] R Joynt and L Taillefer, *Rev. Mod. Phys.* **74**, 235 (2002)
[2] C Petrovic, *Europhys. Lett,* **53**, 354 (2001)
[3] E D Bauer, *et al*, *Phys. Rev.* **B65**, 100506(R) (2002)
[4] K Izawa *et al*, *Phys. Rev. Lett.* **90**, 117001 (2003)
[5] T Watanabe *et al*, *Phys. Rev.* **B70**, 020506 (2004)
[6] P Fulde and R A Ferrel, *Phys. Rev.* **A135**, 550 (1964)
[7] K Izawa *et al*, *Phys. Rev. Lett.* **86**, 2653 (2001)
[8] Y Aoki *et al*, *Phys. Rev. Lett.* **91**, 067003 (2003)
[9] E E M Chia *et al*, *Phys. Rev. Lett.* **91**, 24700 (2003)
[10] G E Volovik, *JETP Lett.* **58**, 469 (1993)
[11] I Vekhter *et al*, *Phys. Rev.* **B59**, R9023 (1999)
[12] H Won and K Maki, cond-mat/0004105
[13] P Miranovic *et al*, *Phys. Rev.* **B68**, 052501 (2003)
[14] H Kusunose, *J. Phys. Soc. Jpn.* **73**, 2512 (2004)
[15] M Udagawa *et al*, *Phys. Rev.* **B70**, 184515 (2004)
[16] K Izawa *et al*, *Phys. Rev. Lett.* **87**, 057002 (2001)
[17] H Aubin *et al*, *Phys. Rev. Lett.* **78**, 2624 (1997)
[18] K Izawa *et al*, *Phys. Rev. Lett.* **88**, 027002 (2002)
[19] K Izawa *et al*, *Phys. Rev. Lett.* **89**, 137006 (2002)
[20] T Watanabe *et al*, *Phys. Rev.* **B70**, 184502 (2004)
[21] A D Huxley *et al*, *Phys. Rev. Lett.* **93**, 187005 (2004)
[22] J Goryo, *Phys. Rev.* **B67**, 184511 (2003)
[23] R Movshovich *et al*, *Phys. Rev. Lett.* **86**, 5152 (2001)
[24] Y Nakajima *et al*, *J. Phys. Soc. Jpn.* **73**, 5 (2004)
[25] R Bel *et al*, *Phys. Rev. Lett.* **92**, 217002 (2004)
[26] A Bianchi *et al*, *Phys. Rev. Lett.* **89**, 137002 (2002)
[27] T Tayama *et al*, *Phys. Rev.* **B65**, 180504 (2002)
[28] H Adachi and R Ikeda, *Phys. Rev.* **B68**, 184510 (2003)
[29] K Kakuyanagi *et al*, *Phys. Rev. Lett.* **94**, 047602 (2005)
[30] K Kumagai *et al*, *Phys. Rev.* **B63**, 144502 (2001)
[31] K Kakuyanagi *et al*, *Phys. Rev.* **B65**, 060503 (2002)
[32] K Kakuyanagi *et al*, *Phys. Rev. Lett.* **90**, 197003 (2003)
[33] Y Matsuda *et al*, *Phys. Rev.* **B49**, 4380 (1994)
[34] Y Matsuda *et al*, *Phys. Rev.* **B40**, 5176 (1989)
[35] A Bianchi *et al*, *Phys. Rev. Lett.* **91**, 187004 (2003)
[36] H A Radovan *et al*, *Nature (London)* **425**, 51 (2003)
[37] H Shimahara, *Phys. Rev.* **B50**, 12760 (1994)
[38] U Klein, D Rainer and H Shimahara, *J. Low Temp. Phys.* **118**, 91 (2000)
[39] L W Gruenberg and L Gunther, *Phys. Rev. Lett.* **16**, 996 (1996)
[40] M Tachiki *et al*, *Z. Phys.* **B100**, 369 (1996)
[41] Y Matsuda *et al*, *Phys. Rev. Lett.* **75**, 4512 (1995)
[42] Y Matsuda *et al*, *Phys. Rev. Lett.* **78**, 1972 (1997)
[43] B Wolf *et al*, *J. Low Temp. Phys.* **107**, 421 (1997)
[44] M B Gaifullin *et al*, *Phys. Rev. Lett.* **84**, 2945 (2000)