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Type-I superconductivity of the layered silver oxide $Ag_5Pb_2O_6$

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We report the zero-resistivity transition and the details of the magnetic transition of a layered silver oxide $Ag_5Pb_2O_6$ single crystal, which provide definitive evidence of superconductivity in this compound. In the ac susceptibility of a monocrystal, we observed large supercooling, as well as positive peaks in the real part of the susceptibility indicating the reversibility of the magnetic process. These observations reveal that $Ag_5Pb_2O_6$ is an oxide that shows type-I superconductivity. Evaluation of the superconducting parameters not only gives confirming evidence of type-I superconductivity, but also indicates that it is a dirty-limit superconductor. We also analyze supercooling to determine the upper limit of the Ginzburg-Landau parameter.

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In the last two decades, research of oxide superconductors has become one of the most actively studied fields in solid state physics.[1,2] Copper oxide high-T_c superconductors[3] discovered in 1987 made the greatest impact to the field. Sr_2RuO_4,[4] with accumulating evidence for a spin-triplet superconductor,[5] has attracted much attention. More recently, $Na_xCoO_2 \cdot yH_2O$ with a triangular lattice[6] has been widely studied because of the coexistence of superconductivity and possible geometrical frustration. We note here that the unconventional superconductors of oxides listed above have layered structures, and that it is believed a quasi-two-dimensional crystal structure is more favorable for unconventional superconductivity than three-dimensional structures. As possible candidates for unconventional superconductivity, silver oxides are particularly worth investigation, since they might have electronic structures analogous to the high-T_c cuprates. However, the silver oxide superconductors reported so far were the cubic clathrate salts Ag_7O_8X (X=NO_3, HF_2, etc.)[7] found in 1966. Curiously, no other silver oxide superconductors have been reported for nearly 40 years, let alone those with layered structures.

Here we report on superconductivity in $Ag_5Pb_2O_6$, with T_c of 52.4 mK, an eagerly awaited layered silver oxide superconductor. We also found that superconductivity of $Ag_5Pb_2O_6$ is type I. Most known type-I superconductors are pure metals and only a handful are reported among compounds and alloys; these compound type-I superconductors include $YbSb_2$,[8] $LaPd_2Ge_2$,[9] MPd_2Si_2 (M=Lu, Y, La),[10] $TaSi_2$,[11] $AuIn_2$,[12] C_xK,[13] (intercalation) and $LaRh_2Si_2$.[10]

$Ag_5Pb_2O_6$, which was reported by Byström and Evers in 1950,[14] has a rather interesting crystal structure (see the inset of Fig. 1) consisting of a silver Kagome lattice parallel to its ab plane and silver chains along the c axis.[15] This silver oxide exhibits metallic conductivity. Band calculation by Brennan and Burdett[16] shows that its conductivity mainly comes from the Ag5s orbital, and that its Fermi surface has a quasi-three-dimensional character because both the silver chain and Kagome lattice contribute to the density of states at the Fermi level. Interestingly, the resistivity behaves as $\rho = AT^2 + \rho_0$ in an unusually wide range of temperature, down to below 4 K and up to room temperature.[17] This means that an unknown strong scattering mechanism dominates over the usual electron-phonon scattering. Superconductivity of $Ag_5Pb_2O_6$ was recently suggested by the present authors.[17] We reported quite a large diamagnetic signal in the ac susceptibility measured using a cluster of single crystals below 48 mK but could not obtain zero resistivity at that time. We finally observed zero resistivity by improving experimental techniques, and present in this paper not only the observation, but also the details, of the superconducting properties of $Ag_5Pb_2O_6$.

In the experiments, we used single crystals of $Ag_5Pb_2O_6$ grown by the self-flux method, from a mixture of 5-mmol $AgNO_3$ and 1-mmol $Pb(NO_3)_2$.[17] All the measurements reported here were performed with a ^{4}He-^{3}He dilution refrigerator (Cryoconcept, Model DR-JT-S-100-10), covering the measurement temperatures as low as 16 mK. The resistivity was measured using a conventional four-probe method with an ac current of 10.4 μA rms at 163 Hz with a hexagonal-stick single crystal that fits in $0.14 \times 0.21 \times 1.15$ mm^3. We

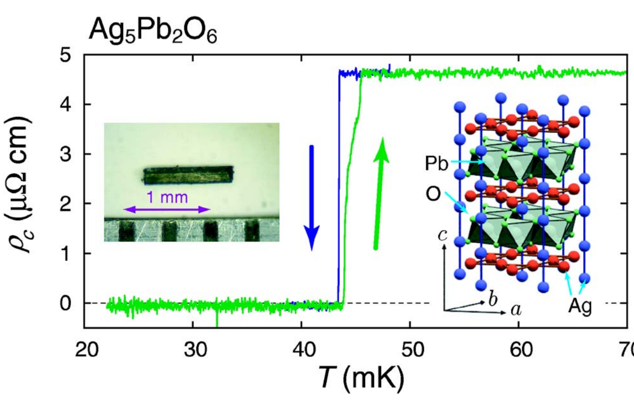

FIG. 1. (Color online) Temperature dependence of the out-of-plane resistivity ρ_c of $Ag_5Pb_2O_6$ below 70 mK. The sweep rate was approximately 0.05 mK/min. Hysteretic behavior at the transition is attributable to a residual magnetic field. The inset photo on the left shows the single crystal used for the measurements. The long axis of the stick corresponds to the c axis. The inset on the right shows the crystal structure of $Ag_5Pb_2O_6$. Red and blue spheres represent the silvers on the Kagome lattice and the chain, respectively.

used pure gallium to attach electrical wires of copper to the sample crystals. We note here that one must keep the temperature of the electrodes well below the melting point of gallium (29 °C) all the time after soldering in order to avoid the electrical contacts getting worse. We avoided using gold wires because gallium easily dissolves gold. The ac susceptibility was measured by a mutual inductance method. We fabricated a very small and highly sensitive cell by winding a 50-μm-diam copper wire on a 0.5-mm-diam polyimide tube (The Furukawa Electric Co., Ltd., PIT-S). The excitation field H_{ac} was 8.7 mOe rms at 887 Hz, which is much lower than the H_c of $Ag_5Pb_2O_6$. To reduce the influences of remnant magnetic fields such as the earth's field and the residual field in the equipment, these measurements were performed in a magnetic shield. We used a cylinder of permalloy (Hamamatsu Photonics K.K., E989-28), which has an extremely high permeability. Inside the permalloy tube, we also placed a lead cylinder with a closed bottom, to expel the remaining magnetic flux. The dc magnetic field for the measurements was applied with a small solenoidal coil of Nb-Ti superconducting wire placed inside the shield. The magnitude of the dc field H_{dc} is numerically calculated by taking into account the shielding current on lead shield's surface.[18,19]

The observed zero-resistivity transition is shown in Fig. 1. A clear zero resistivity is seen, which marks definitive evidence of the superconductivity of $Ag_5Pb_2O_6$. We note here that the result in Fig. 1 was obtained without the magnetic shield. A hysteresis at the superconducting transition and a lower T_c than that in the ac susceptibility measurement are attributable to the influence of the uncanceled residual field. We confirmed that the hysteresis indeed disappears in the measurement with the magnetic shield. We next show in Fig. 2 the real part of the ac susceptibility χ'_{ac} of a monocrystal with the magnetic shield described above. It is worth noting that we used the identical crystal for the measurements for Figs. 1 and 2 (see the left inset of Fig. 1). We also note here that the diamagnetic signal shown in Fig. 2 is as large as that of pure Al with a similar size and shape. Such results of the low-frequency susceptibility add a strong support for the bulk nature of the superconductivity in $Ag_5Pb_2O_6$. The measurements were performed under the condition $H_{dc} \| H_{ac} \| c$. The critical temperature T_c to some extent depends on samples; the highest T_c obtained is 52.4 mK, as shown in Fig. 2.

In Fig. 2, there are two strong pieces of evidence that $Ag_5Pb_2O_6$ is a type-I superconductor. One is the fact that a large supercooling is observed at the superconducting transition under magnetic fields while no supercooling is seen in zero field. This means that the superconducting transition becomes first order only when an external field is applied. Such behavior is only seen in type-I superconductors. The other is the very large positive peaks of χ'_{ac} just before the superconducting to normal transitions. These peaks are ascribable to the "differential paramagnetic effect" (DPE),[20] which represents that the field derivative of the magnetization $\partial M/\partial H$ is positive near the transition and also the magnetic process in this region is reversible. DPE should be observed in either type-I and type-II superconductors, if pinning of domain walls in the intermediate state of type-I

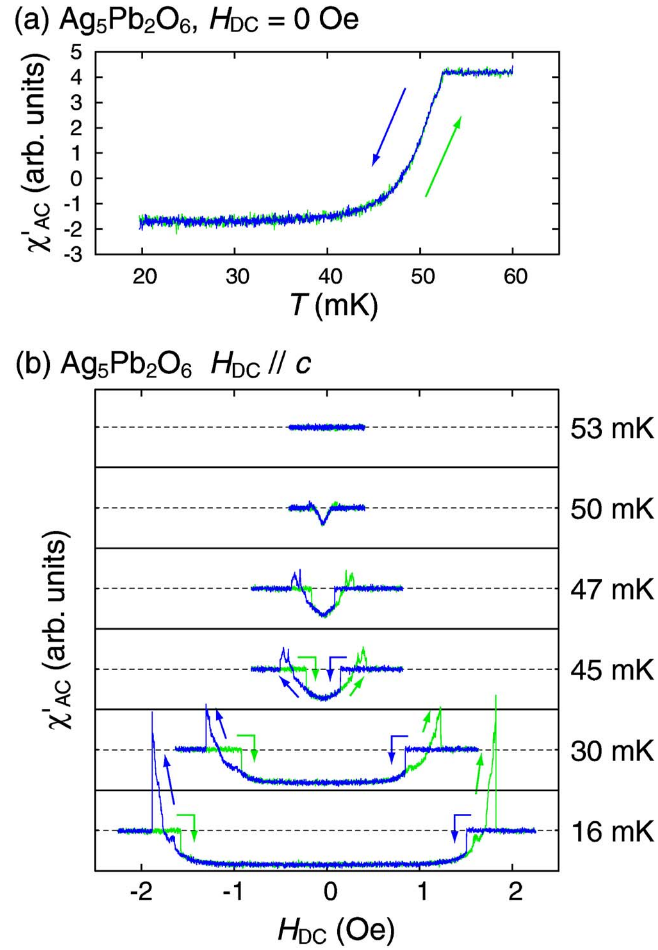

FIG. 2. (Color online) ac susceptibility of $Ag_5Pb_2O_6$. (a) The result of a temperature sweep with a sweep rate of 0.2 mK/min. The residual field H_{res} has been compensated in this sweep, yielding T_{c0}=52.4 mK. (b) The results of field sweeps at several temperatures with a sweep rate of 24–47 mOe/min. From the slight asymmetry of the data, the residual field is estimated as H_{res}=0.040 Oe. The double peaks seen in 45 and 47 mK do not seem to be intrinsic, since they are not reproducible with other crystals.

superconductors or of magnetic flux in the mixed state of type II is absent or very weak. However the observed sharp and large DPE near the transition is a hallmark of type-I superconductivity, since $\partial M/\partial H$ in type-II superconductors should be much smaller than 1 near H_{c2} and thus the height of DPE in type-II superconductors cannot exceed $|\chi'_{dia}|$, where χ'_{dia} is the diamagnetic susceptibility in the Meissner state.[21] We note that preliminary results show supercooling and DPE also for field along the *ab* plane. Such observation supports that they are intrinsic behavior.[22]

Figure 3 is the phase diagram based on the ac susceptibility of the crystal with the highest T_c. Here we identify the transition fields of the superconducting to normal transition as critical fields H_c. This should be valid despite the possibility of superheating, because the observed DPE shows that $Ag_5Pb_2O_6$ is in the intermediate state, in which superconducting and normal states coexist, and there should be no superheating at the "transition" from the intermediate state to the normal state. We also define the normal to superconduct-

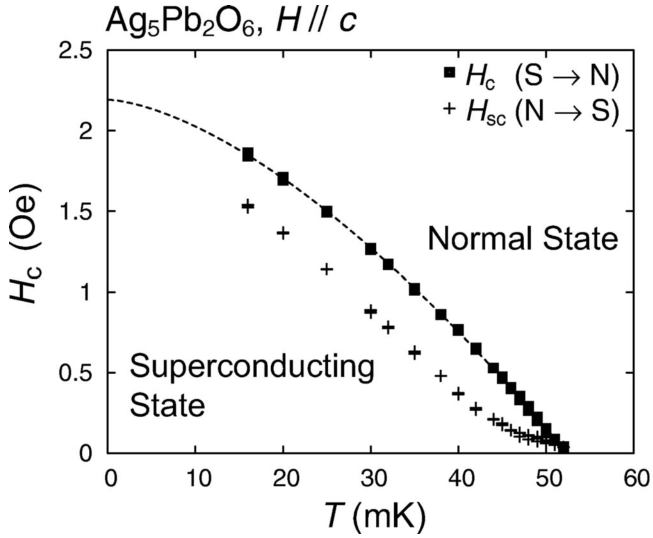

FIG. 3. Phase diagram of the superconducting phase of $Ag_5Pb_2O_6$, determined from the field-sweep data of ac susceptibility. The residual field has been subtracted in the shield $H_{res}=0.040$ Oe from the raw data. The filled squares are the superconducting to normal transition field and should be equal to H_c (see text). The crosses are the supercooling field H_{sc} corresponding to the normal to superconducting transitions. The broken line is the result of fitting with $H_c(T)=H_{c0}[1-(T/T_{c0})^{\alpha}]$.

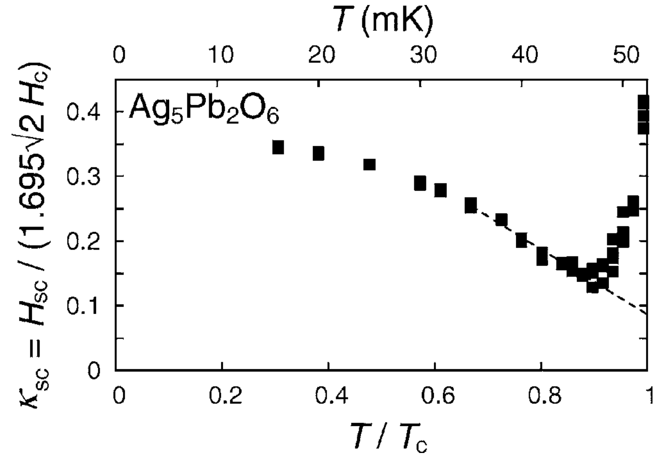

FIG. 4. The ratio $\kappa_{sc}\equiv H_{sc}/(1.695\sqrt{2}H_c)$ of $Ag_5Pb_2O_6$, which gives the upper limit of the GL parameter. The upturn of the graph near T_c is attributable to the size effect. The broken line is the result of linear fitting between $T=35$ and 47 mK, where the size effect is not significant.

ing transition fields as supercooling fields H_{sc}. This transition should be from the normal to the full Meissner states since we observed no DPE. We can fit a relation $H_c(T)=H_{c0}[1-(T/T_{c0})^{\alpha}]$ to all the H_c data down to 16 mK using H_{c0} and α as fitting parameters, while $T_{c0}=52.4$ mK is determined from the temperature sweep data in zero field. As a result, we obtained $H_{c0}=2.19$ Oe and $\alpha=1.56$. The data can also be fitted by a conventional relation with $\alpha=2$: $H_c(T)=H^*_{c0}[1-(T/T_{c0})^2]$. However, the fitting is successful only down to $T/T_c=0.7$ and the resulting parameter is $H^*_{c0}=1.80$ Oe. The origin of this discrepancy is unknown at this stage of experiments. One possible origin is the modification of critical fields due to the large coherence length and the small sample size.

Now we can evaluate some of the superconducting parameters from these results. First, the London penetration depth is obtained as $\lambda_L(0)=(m^*c^2/4\pi ne^2)^{1/2}=83$ nm. Here $n=1.0/V_M=0.51\times10^{22}$ electrons/cm^3 is the electron carrier density, where $V_M=0.195$ nm^3 is the volume of a unit cell,[23] and $m^*=(3\hbar^2\gamma_e)/(k_B^2k_F)=1.2m_e$ is the effective mass. We used here the measured electronic specific heat coefficient[17] $\gamma_e=3.42$ mJ/mol K^2=291 erg/cm^3 K^2, and the Fermi wave number $k_F=4.5$ nm^{-1} (in the *ab* plane).[24] The coherence length in clean limit, $\xi_0=(0.18\hbar v_F)/(k_BT_c)=11$ μm, where $v_F=\hbar k_F/m^*$ is the Fermi velocity, is comparable to that of tungsten[25] ($\xi_0=32$ μm, $T_c=15.4$ mK). The mean free path l is given by $l=v_F\tau$, where τ is the scattering time of electrons and has a relation $\tau^{-1}=ne^2\rho/m^*$ for the Drude model. If we use $\rho=1.5$ $\mu\Omega$ cm, the residual resistivity in the *ab* plane,[17] we obtain $l=240$ nm.

One of the important consequences of the above evaluation is that $Ag_5Pb_2O_6$ is a dirty-limit ($\xi_0\gg l$) superconductor. This is rather inevitable, since it seems practically impossible to make l longer than ξ_0. In a dirty-limit superconductor, the Ginzburg-Landau (GL) parameter κ is given by $\kappa=0.75\lambda_L(0)/l$,[26] and is 0.26 in our case. This is indeed smaller than $1/\sqrt{2}$, the border between type-I and -II superconductors, and is consistent with the type-I behavior of $Ag_5Pb_2O_6$. The dirty-limit conclusion also implies that the pairing symmetry of the superconductivity is not anisotropic, because anisotropic superconductivity should be easily suppressed even by nonmagnetic impurities.

According to the GL theory, analysis of supercooling gives the upper limit of κ. When one decreases the external field of a supercooled superconductor at constant temperature, the sample turns into the superconducting state before the field reaches the ideal supercooling field $H_{sc,ideal}$. If the sample is in vacuum, $H_{sc,ideal}$ is equal to the surface nucleation field H_{c3},[27] which has a relation $H_{c3}=1.695H_{c2}=1.695\sqrt{2}\kappa H_c$. The observed supercooling field H_{sc} satisfies an inequality

$$H_{sc}\geq H_{sc,ideal}=1.695\sqrt{2}\kappa H_c. \quad (1)$$

Thus κ must be smaller than $\kappa_{sc}\equiv H_{sc}/(1.695\sqrt{2}H_c)$.

An approach based on this has been used to determine κ of several pure metals and alloys by observing *ideal* supercooling. For example, Feder and McLachlan[28] realized ideal supercooling of indium and tin with precise experiments and obtained $\kappa_{In}=0.0620$ and $\kappa_{Sn}=0.0926$.

We calculated κ_{sc} of $Ag_5Pb_2O_6$ at each temperature as shown in Fig. 4. The steep increase of κ_{sc} at $T/T_c\gtrsim0.9$ is attributed to the size effect, which occurs when the temperature-dependent coherence length $\xi(T)\propto[T_c/(T_c-T)]^{1/2}\xi$ becomes comparable to the size of a sample. In fact, the coherence length, being $\xi\sim(\xi_0 l)^{1/2}$ in a dirty-limit superconductor,[26] becomes 1.4 μm. This is large enough to cause the size effect near T_c in a sample of 100–200 μm($\sim100\xi$). Indeed, in the experiments of Feder and McLachlan[28] a sphere of clean indium ($\xi\sim\xi_0$

$=0.20\ \mu$m) with a radius 16 μm($\sim 80\xi$) showed the size effect also at $T/T_c \gtrsim 0.9$.

Feder and McLachlan determined κ by extrapolating $\kappa(T)$ to $T=T_c$, because the influence of nucleation centers becomes negligible near T_c due to the divergence of $\xi(T)$. Following their procedure we extrapolated $\kappa_{sc}(T)$ in 35 mK$<T<$47 mK to T_c as the broken line in Fig. 4. The extrapolation gives $\kappa_{sc}|_{T=T_c}=0.085$, which should be the upper limit of κ of $Ag_5Pb_2O_6$. This estimated upper limit is smaller than the calculated value but the difference should be within a consistency. In the case of indium or tin,[28] there are also differences of a few factors among values of κ obtained by different procedures.

In conclusion, we succeeded in observing the zero-resistivity transition of a silver oxide $Ag_5Pb_2O_6$, giving definitive evidence of the long-awaited layered silver oxide superconductor since the discovery of high-T_c cuprates. The ac susceptibility reveals that $Ag_5Pb_2O_6$ is an oxide type-I superconductor. It is widely considered that type-I superconductivity is rare in compounds, although there is no fundamental reason to prohibit it. The present paper indeed demonstrates that even an oxide can be an extreme type-I superconductor. Superconducting parameters indicate that $Ag_5Pb_2O_6$ is a dirty-limit type-I superconductor and thus the pairing symmetry of $Ag_5Pb_2O_6$ should be isotropic. The report of this class of superconductor, a silver oxide superconductor with a layered structure, should motivate searches for more superconductors among similar silver oxides. A salient next target is to adjust the doping to realize the electronic states with strong electron correlations, closely analogous to that of the high-T_c cuprates, in order to seek for unconventional superconductivity.

Note added in proof. The band structure reported in Ref. 16 has been substantially revised by a recent calculation[29] and by a recent experiment of quantum oscillations.[30] Nevertheless, the value of k_F used in this paper remains consistent with the recent reports.

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[1] S. Nagata and T. Atake, J. Therm Anal. Calorim. **57**, 807 (1999).
[2] R. J. Cava, J. Am. Ceram. Soc. **83**, 5 (2000).
[3] J. G. Bednorz and K. A. Müller, Z. Phys. B: Condens. Matter **64**, 189 (1986).
[4] Y. Maeno, H. Hashimoto, K. Yoshida, S. Nishizaki, T. Fujita, J. G. Bednorz, and F. Lichtenberg, Nature (London) **372**, 532 (1994).
[5] A. P. Mackenzie and Y. Maeno, Rev. Mod. Phys. **75**, 657 (2003).
[6] K. Takada, H. Sakurai, E. Takayama-Muromachi, F. Izumi, R. A. Dilanian, and T. Sasaki, Nature (London) **422**, 53 (2003).
[7] M. B. Robin, K. Andres, T. H. Geballe, N. A. Kuebler, and D. B. McWhan, Phys. Rev. Lett. **17**, 917 (1966).
[8] Y. Yamaguchi, S. Waki, and K. Mitsugi, J. Phys. Soc. Jpn. **56**, 419 (1987).
[9] G. W. Hull, J. H. Wernick, T. H. Geballe, J. V. Waszczak, and J. E. Bernardini, Phys. Rev. B **24**, 6715 (1981).
[10] T. T. M. Palstra, G. Lu, A. A. Menovsky, G. J. Nieuwenhuys, P. H. Kes, and J. A. Mydosh, Phys. Rev. B **34**, 4566 (1986).
[11] U. Gottlieb, J. C. Lasjaunias, J. L. Tholence, O. Laborde, O. Thomas, and R. Madar, Phys. Rev. B **45**, 4803 (1986).
[12] R. J. Soulen, D. B. Utton, and J. H. Colwell, Bull. Am. Phys. Soc. **22**, 403 (1977).
[13] M. Kobayashi and I. Tsujikawa, J. Phys. Soc. Jpn. **50**, 3245 (1981).
[14] A. Byström and L. Evers, Acta Chem. Scand. (1947-1973) **4**, 613 (1950).
[15] M. Jansen, M. Bortz, and K. Heidebrecht, J. Less-Common Met. **161**, 17 (1990).
[16] T. D. Brennan and J. K. Burdett, Inorg. Chem. **33**, 4794 (1994).
[17] S. Yonezawa and Y. Maeno, Phys. Rev. B **70**, 184523 (2004).
[18] T. I. Smith, Rev. Sci. Instrum. **44**, 852 (1973).
[19] K. A. Muething, D. O. Edwards, J. D. Feder, W. J. Gully, and H. N. Scholz, Rev. Sci. Instrum. **53**, 485 (1982).
[20] R. A. Hein and R. L. Falge, Jr., Phys. Rev. **123**, 407 (1961).
[21] See for example: S. S. Banerjee *et al.*, Physica C **308**, 25 (1998).
[22] S. Yonezawa and Y. Maeno (unpublished).
[23] The value of V_M, which is a room-temperature value, is taken from Ref. 15. Strictly speaking, we should use the value at T_c. However, temperature variation of V_M should be less than a few percent.
[24] The value of k_F is quoted from Ref. 16. Since the figure is not given in that article, we estimated its value from the graph of band dispersion.
[25] J. C. Wheatley, R. T. Johnson, and W. C. Black, J. Low Temp. Phys. **1**, 641 (1969).
[26] P. G. de Gennes, *Superconductivity of Metals and Alloys* (W. A. Benjamin, New York, 1966).
[27] H. J. Fink, D. S. McLachlan, and B. Rothberg-Bibby, in *Progress in Low Temperature Physics*, edited by D. F. Brewer (North-Holland, Amsterdam, 1978), Vol. VII B, Chap. 6.
[28] J. Feder and D. S. McLachlan, Phys. Rev. **177**, 763 (1969).
[29] T. Oguchi, cond-mat/0509268, Phys. Rev. B (to be published).
[30] M. Sutherland *et al.*, cond-mat/0509547 (unpublished).