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Violation of Kohler's Rule in the Magnetoresistance near the Lower Charge-Density-Wave Instability in $NbSe_3$

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This paper reports the measurements of resistance (R) and magnetoresistance of $NbSe_3$ near the critical pressure ($P_c = 7.5$ kbar), where the lower charge-density-wave (CDW) phase is on the verge of destruction. For $P = 7.6$ kbar, the temperature dependence of dR/dT exhibits a weak anomaly at $T^* = 15$ K and the superconducting transition is observed at $T_c = 2.8$ K. From the observation of a large magnetoresistance due to an imperfect nesting of Fermi surface, we show that the weak anomaly is closely related to the lower CDW phase. Moreover, an excess conductance and violation of Kohler's rule are found below $\sim T^*$. The origins of the excess conductance and the violation of Kohler's rule are discussed in terms of charge fluctuation associated with the lower CDW state.

KEYWORDS: $NbSe_3$, charge-density-wave, superconductivity, critical pressure, magnetoreistance, Kohler's rule
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1. Introduction

A physical system that crosses the boundary between crystalline ordered and itinerant phases changes its properties in a fundamental way. It may, for example, melt or freeze. This macroscopic change is driven by microscopic fluctuation. When the temperature of the system approaches zero, all thermal fluctuations die out. This prohibits phase transitions in classical systems at zero temperature. In a quantum system, however, fluctuations are present even at zero temperature, so-called quantum fluctuations. These quantum fluctuations may be strong enough to drive a transition from one phase to another, bringing about a macroscopic change.

In this paper, we focus on the pressure–temperature (P–T) phase diagram in a typical quasi-one dimensional conductor $NbSe_3$,[1–3)] in which there is remarkable competition of the superconducting (SC) and the lower charge-density-wave (T_2-CDW) states at a critical pressure of $P_c = 7.5$ kbar (see Fig. 1).[4,5)] This competition has been understood in terms of the Fermi surface (FS) nesting[4–6)] and the quantum fluctuations are ignored. The quantum fluctuations, however, may play an important role for the competition near P_c. Because the SC state is the itinerant off-diagonal long-range order (ODLRO) by Bose condensation of the Cooper pairs, while the CDW is the diagonal long-range order (DRLO) with structural ordering with electrons and the competition occurs

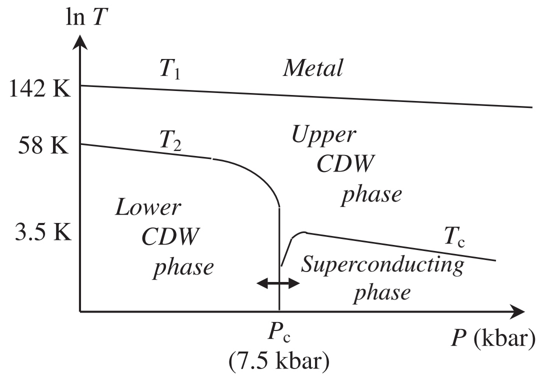

Fig. 1. Schematic pressure–temperature phase diagram of $NbSe_3$. Near $P_c = 7.5$ kbar, the lower CDW phase competes with the superconducting phase at low temperatures.

at low temperatures down to ~ 3 K. We are also interested in the lower CDW phase near P_c where the exotic phase behavior due to the quantum fluctuations of the lower CDW phase is expected at low temperatures. Actually, Snow *et al.*[7)] recently observed the quantum melting of a CDW state tuned by a pressure at low temperatures. In this paper, we report the experimental results of the resistance (R) and magnetoresistance (MR) of $NbSe_3$ near P_c.

2. Experimental

Single crystals of $NbSe_3$ were grown by chemical vapor transport. The crystals gave residual resistance ratio $R(300\,K)/R(4.2\,K)$ in the range 50–60. The R and MR were measured by a usual four probe dc method, where current and magnetic field are parallel to the b- and c-axes, respectively. The pressure was generated by use of a WC piston and a copper–beryllium cylinder with the internal diameter of 8 mmϕ. Transmitting liquid was 1 : 1 mixture of Fluorinert FC70 and FC77. The pressure was applied at room temperature and kept constant during the measurements in cooling and heating processes. Pressures were estimated from NH_4F I–II transition and the pressure dependence of T_1

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and T_2 in $NbSe_3$ based on a previous result.[5)]

It is known that the lower CDW phase is accompanied with a large magnetoresistance (LMR) just below T_2 when magnetic field is applied parallel to the *c*-axis.[8–11)] The origin of the LMR has been explained by considering the normal carriers on the small pockets created by the imperfect nesting of the FS.[10–12)] As a unique method to detect the lower CDW phase near P_c, we took advantage of the occurrence of the LMR. The LMR appears as long as the lower CDW phase exists, while the LMR disappears as soon as the lower CDW phase is suppressed totally, showing that the observation of the LMR is useful for probing the lower CDW phase near P_c.[10,11)]

3. Results

Figure 2 shows the temperature (T) dependence of the R (left-hand scale, dot) and dR/dT (right hand scale, squares) for $P = 7.6$ kbar. With decreasing temperature, R decreases monotonically and the superconducting transition takes place at $T_c = 2.8$ K. There is no anomaly associated with the lower CDW transition. These results agree well with previous results.[4,5)] Besides these conventional phenomena, we find that the T-dependence of dR/dT exhibits a weak anomaly at $T^* = 15$ K. The slope of dR/dT below T^* is gentler than that above T^*. The origin of the weak anomaly is unclear. Near P_c, one expects the presence of the lower CDW phase. In order to know whether the weak anomaly is related to the lower CDW transition or not, we measured the resistance under magnetic fields for $P = 7.6$ kbar.

Figure 3(a) shows the T-dependence of the resistance in magnetic fields ranging from 0 to 17 T under a pressure of 7.2 kbar. The lower CDW transition is observed at $T_2 = 22$ K under zero magnetic field. The magnetic field enhances the resistance anomaly due to the lower CDW formation. However, the value of T_2 is almost independent of the magnetic fields. The origin of the field-induced enhancement of the lower CDW resistance anomaly has been explained by normal carriers on the small pockets created by the imperfect nesting of the FS, leading to the occurrence of the LMR.[10–12)] On the other hand, a small increment of resistance is observed above T_2. Here the magnitude of

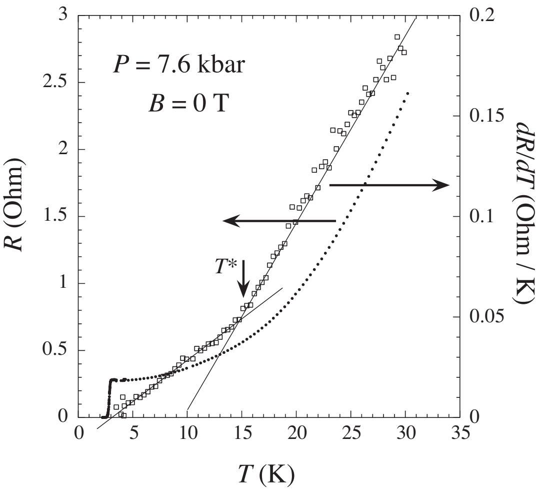

Fig. 2. Temperature dependence of R (left-hand scale, dots) and dR/dT (right-hand scale, squares) for $P = 7.6$ kbar.

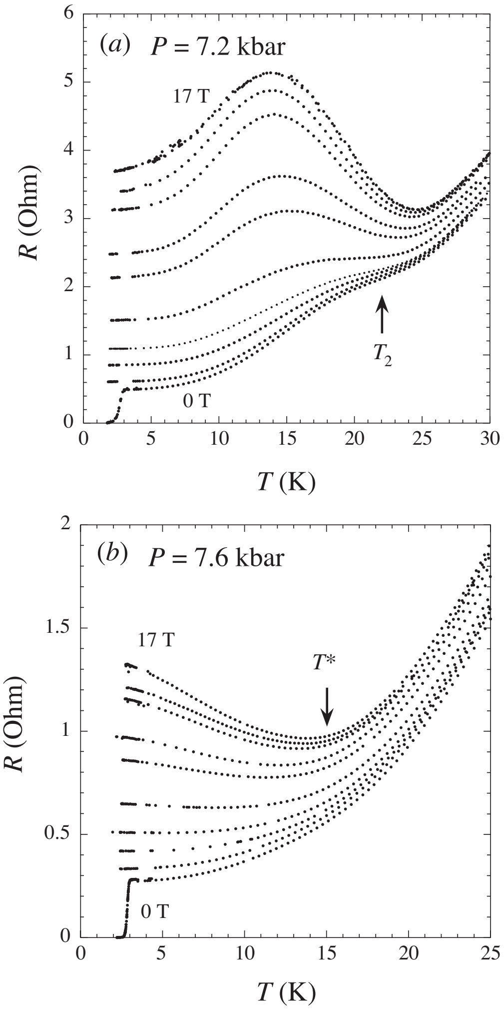

Fig. 3. Temperature dependence of R in magnetic fields ranging from 0 to 17 T. The magnetic fields are 0, 0.5, 1, 1.5, 2.5, 5, 7, 12, 14.5, and 17 T in order of increasing resistance for (a) $P = 7.2$ kbar and (b) $P = 7.6$ kbar.

MR is negligibly small at ambient pressure because of the nearly perfect nesting of FS for the upper CDW phase.[13)] However, applying pressure causes a pressure-induced imperfect nesting of FS, leading to the appearance of MR which is called the pressure-induced MR (PIMR).[10,11)] These observations agree well with our previous results.[10,11)]

In addition, we find the superconducting phase transition at $T_c = 2.7$ K. This result does not agree with previous results by Ido *et al.*[5)] It is known that the superconductivity of $NbSe_3$ is very sensitive to the pressure inhomogeneity below P_c. However, the observed resistive transition is very sharp and very reproducible. In addition, a recent high pressure study[14)] by cubic anvil device shows that the superconductivity coexists with the upper CDW phase near critical pressure for the upper CDW phase. These observations may suggest that the coexistence of superconductivity and the lower CDW phase is intrinsic.

Figure 3(b) shows the T-dependence of the resistance in magnetic fields ranging from 0 to 17 T under a pressure of 7.6 kbar. We observe metallic behavior ($dR/dT > 0$) below 2.5 T while upturn around below T^* above 2.5 T. The striking feature below T^* is reminiscent of the field-induced enhancement of the lower CDW resistance anomaly as seen in Fig. 3(a).

In Fig. 3, the SC transitions vanish above 0.5 T. These observations are consistent with a previous result.[15] The small upper critical magnetic field, H_{c2}, has been explained by the effective mass model for H_{c2}.[16]

Figure 4(a) shows the T-dependence of MR, $\Delta\rho/\rho_0$, under the pressure of 7.2 kbar. The LMR is clearly observed around below T_2, while relatively small PIMR above T_2. The occurrences of the LMR and PIMR agree well with previous results.[10,11] Figure 4(b) shows the T-dependence of MR, $\Delta\rho/\rho_0$, under the pressure of 7.6 kbar. The T-dependence of MR for 7.6 kbar is very similar to that for 7.2 kbar. MR gradually increases with decreasing temperature and then it rises sharply around T^*. For $P = 7.6$ kbar, the value of MR at 3 K are about 400% and much larger than that of the PIMR appearing above 15 K.[10,11] These results suggest that the weak anomaly at T^* in dR/dT is closely related to the lower CDW phase transition.

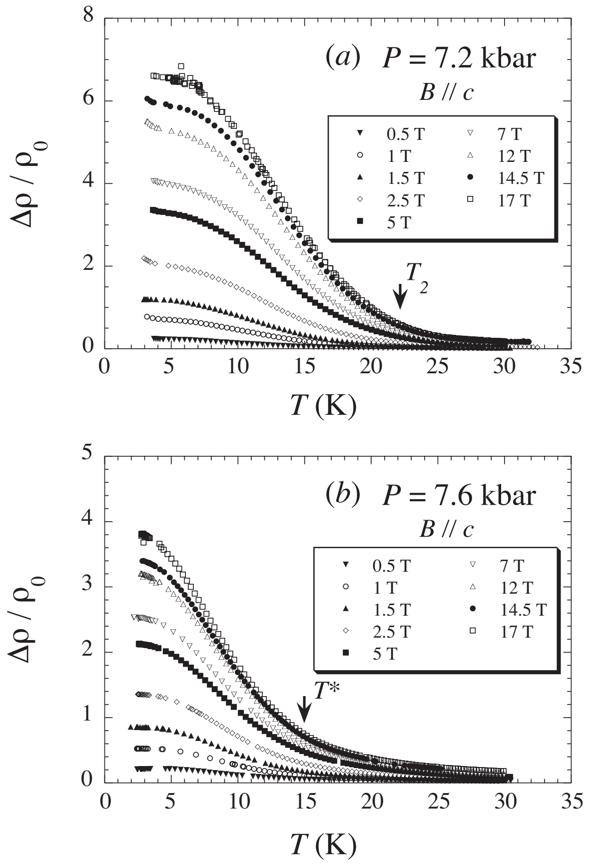

Fig. 4. Temperature dependence of magnetoresistance under pressure of (a) $P = 7.2$ kbar and (b) $P = 7.6$ kbar.

4. Discussion

The LMR can be explained by semiclassical transport theory.[10,11] According to the semiclassical transport theory, Kohler's rule holds if there is a single species of charge carrier and the scattering time is the same at all points on the FS.[17] Kohler's rule is given by

$$\frac{\Delta\rho}{\rho_0} = F(\omega_c\tau) = f\left(\frac{B}{R(0,T)}\right). \quad (1)$$

The corresponding plots are known as Kohler plots. Here ω_c is the cyclotron frequency, τ is the scattering time, and $R(0,T)$ is the zero-field resistance. If Kohler's rule holds, all of MR curves would collapse onto a single curve. Let us check whether the MR for 7.2 and 7.6 kbar obey Kohler's rule or not.

Figure 5(a) shows the MR data for $P = 7.2$ kbar in the form of Kohler plots. In this case, we see that MR curves collapse onto an upper and a lower curves for $T < T_2/2$ and $T > T_2$, respectively. This implies Kohler's rule holds for $T < T_2/2$ and $T > T_2$. Note that here the T-dependence of the lower CDW gap is very little. On the other hand, the violation of Kohler's rule is clearly observed for $T_2/2 < T < T_2$ where the magnitude of the lower CDW gap varies significantly. These observations are consistent with the T-dependence of the lower CDW gap.

Next, we consider the MR data in the form of Kohler plots for $P = 7.6$ kbar. Figure 5(b) shows the most surprising and striking results of the present work. We find Kohler's rule holds for temperatures $T > T^*$ and does not below $T < T^*$. Comparing with the result observed at $P = 7.2$ kbar [see

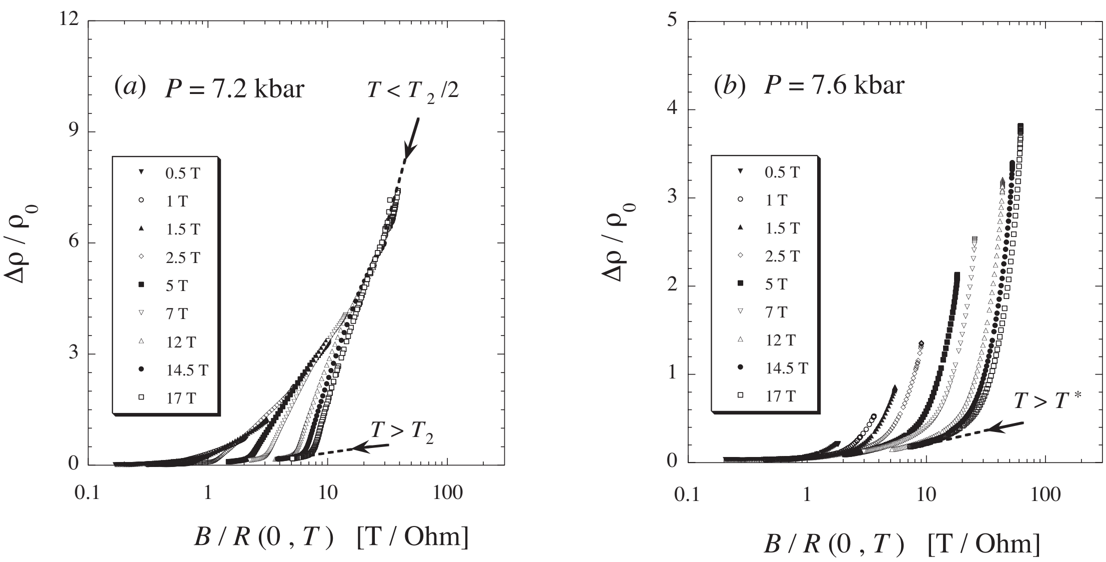

Fig. 5. Magnetoresistance data for (a) $P = 7.2$ kbar and (b) $P = 7.6$ kbar in the form of Kohler plots.

Fig. 5(a)], it might be natural to assume that T^* corresponds to the lower CDW transition temperature at $P = 7.6$ kbar. However, MR does not follow Kolher's rule even at 3 K despite the T-dependence of the lower CDW gap is considered to be very little for temperatures $T < T^*/2 \sim 7.5$ K, indicating that T^* does not necessarily correspond to the lower CDW transition temperature where the 3D long-range order is formed.

To consider the origin of the violation of Kohler's rule, we carefully analyze the T-dependence of R and dR/dT. Let us consider the T-dependence of R in the absence of the weak anomaly at T^* in dR/dT. If there is no anomaly at T^* in dR/dT, the T-dependence of dR/dT is expected to be a straight line which is obtained by extrapolating the dR/dT above T^* (see Fig. 2). Integrating the straight line with respect to T, we can calculate the T-dependence of R in the absence of the weak anomaly at T^* as seen in Fig. 6. From the analysis, we find that the weak anomaly of dR/dT at T^* yields an excess conductance below T^*. This behavior is contrary to the case of a usual CDW transition.[1–3] The excess conductance around below T^* cannot be readily explained in the case of a pinned static CDW state.

One may think that the excess conductance is caused by the sliding motion of the lower CDW state. But we can observe the excess conductance in the ohmic regime. So it is unlikely that the excess conductance is attributed to the sliding CDW state. Then we consider that a charge fluctuation associated with the lower CDW state as the possible origin of the excess conductance. Because the CDW domains may be very mobile in the so-called fluctuation regime,[18] leading to the lack of the depinning electric threshold field. It is, therefore, not surprising that the $R(T)$ behaves as if there were no CDW fluctuation. Our observed excess conductance is reminiscent of a metallic phase in TTF-TCNQ (tetrathiafulvalene-tetracyanoquinodimethane) with a strongly temperature-dependent conductivity due to the fluctuating CDW.[19,20] In the fluctuation regime of $NbSe_3$, a pseudo gap will open.[18] Then the electronic structure changes and the charge fluctuation along the chain direction will bear enhancement of anisotropy of scattering time. Moreover, the pseudo gap will develop with decreasing temperature as similar to the CDW gap.[21] These will lead to the violation of the Kohler's rule. Therefore, we conclude that the excess conductance and the violation of the Kohler's rule are due to the charge fluctuation associated with the lower CDW state.

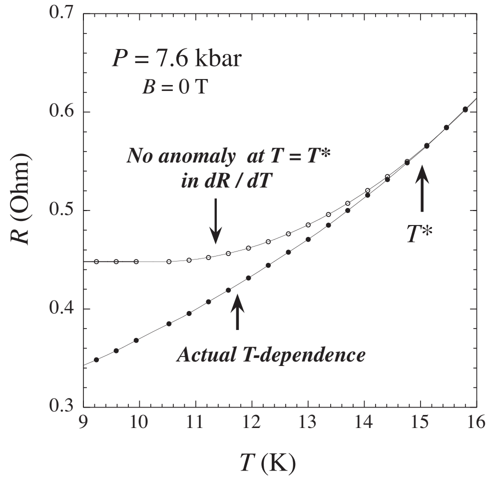

Fig. 6. Temperature dependence of resistance in the absence (calculation, open circles) and presence (experiment, solid circles) of the weak anomaly at T^*.

The violation of Kohler's rule at low temperatures shows that the lower CDW transition temperature T_2 is below 3 K at least, or will go to absolute zero at P_c, where the thermal fluctuations frozen out, while the quantum fluctuations prevail. This observation suggests importance of a quantum mechanical nature in the lower CDW phase near P_c, which is not considered by the mean-field theory by Yamaji.[6] Recently, Snow *et al.*[7] revealed in a CDW system $1T$-$TiSe_2$ that the CDW softens and exhibits enhanced fluctuations when the collapse of the CDW state occurs near a critical pressure at low temperatures. Destruction of the lower CDW phase in $NbSe_3$ has been explained in terms of collapse of the conventional FS nesting.[4–6] The lower CDW state near P_c, however, may be very similar to the quantum melting of the CDW state in $1T$-$TiSe_2$.[7]

5. Conclusions

We have performed the measurements of R and MR near P_c ($= 7.5$ kbar) where the lower CDW phase is on the verge of destruction. For $P = 7.6$ kbar, we find the weak anomaly at $T^* = 15$ K in the T-dependence of dR/dT and the superconducting transition takes place at $T_c = 2.8$ K. From the measurements of the LMR, we show that the weak anomaly is closely related to the lower CDW phase. Moreover, the excess conductance and the violation of Kohler's rule are found below T^*. Based on the above findings, we claim the presence of the charge fluctuation related to the lower CDW phase below T^* near P_c. The experimental results reported here demonstrate the exotic phase behavior due to the quantum fluctuations of the lower CDW phase near P_c, which is not predicted by the mean-field theory by Yamaji.[6]

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1) P. Monceau, N. P. Ong, A. M. Portis, A. Meershant and J. Rouxel: Phys. Rev. Lett. **37** (1976) 602.
2) J. A. Wilson: Phys. Rev. B **19** (1979) 6456.
3) F. Devreux: J. Phys. (Paris) **43** (1982) 1489.
4) A. Briggs, P. Monceau, M. Nunez-Regueiro, J. Peyrard, M. Ribaut and J. Richard: J. Phys. C **13** (1980) 2117.
5) M. Ido, Y. Okayama, T. Ijiri and Y. Okajima: J. Phys. Soc. Jpn. **59** (1990) 1341.
6) K. Yamaji: J. Phys. Soc. Jpn. **51** (1982) 2728.
7) C. S. Snow, J. F. Karpus, S. L. Cooper, T. E. Kidd and T.-C. Chiang: Phys. Rev. Lett. **91** (2003) 136402.
8) R. V. Coleman, G. Eiserman, M. P. Everson, A. Johnson and L. M. Falicov: Phys. Rev. Lett. **55** (1985) 863.
9) R. V. Coleman, M. P. Eiserman, H.-A. Lu, A. Johnson and L. M. Falicov: Phys. Rev. B **41** (1990) 460.
10) S. Yasuzuka, Y. Okajima, S. Tanda, K. Yamaya, N. Takeshita and N. Môri: Phys. Rev. B **60** (1999) 4406.

11) S. Yasuzuka, Y. Okajima, S. Tanda, N. Takeshita, N. Môri and K. Yamaya: J. Phys. Soc. Jpn. **69** (2000) 3470.
12) V. Kiryukhin, D. Casa, B. Keimer, J. P. Hill, M. J. Higgs and Bhattaacharya: Phys. Rev. B **57** (1998) 1332.
13) N. Shima: J. Phys. Soc. Jpn. **51** (1982) 11.
14) S. Yasuzuka, K. Murata, T. Fujimoto, M. Shimotori and K. Yamaya: J. Phys. Soc. Jpn. **74** (2005) 1782.
15) P. Monceau and J. Richard: Physica B **108** (1981) 1237.
16) L. A. Turkevitch and G. A. Klemm: Phys. Rev. B **19** (1979) 2520.
17) A. B. Pippard: *Magnetoresistance in Metals* (Cambridge University Press, Cambridge, 1989).
18) G. Grüner: in *Density Waves in Solids*, ed. D. Pines (Addison-Wesley, Reading, MA, 1994).
19) M. J. Cohen, L. B. Coleman, A. F. Garito and A. J. Heeger: Phys. Rev. B **10** (1974) 1298.
20) A. Andrieux, H. J. Schulz, D. Jerome and K. Bechgaard: Phys. Rev. Lett. **43** (1979) 227.
21) H. Haifeng and Z. Dianlin: Phys. Rev. Lett. **82** (1999) 811.