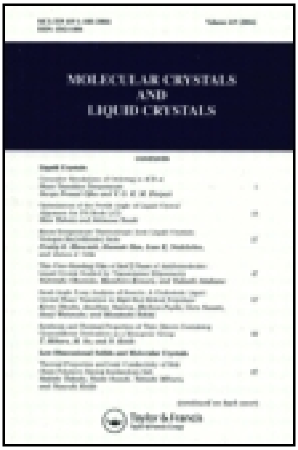

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Pressure Dependence of the Metal-Insulator and Superconducting Phase Transitions in $(TMTSF)_2$ Reo_4

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PRESSURE DEPENDENCE OF THE METAL-INSULATOR AND SUPERCONDUCTING PHASE TRANSITIONS IN $(TMTSF)_2ReO_4$

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Measurements of the pressure and temperature dependence of the a-axis resistivity of $(TMTSF)_2ReO_4$ are presented. The metal-insulator transition seen in this material at the remarkably high temperature of $\sim$180 K at ambient pressure and which is associated with an ordering of the ReO_4^- anions is suppressed under pressure. For pressures above $\sim$9.5 kbar we observe a superconducting transition near 1.3 K. There is a narrow intermediate pressure regime about 2.5 kbar in width in which both superconductivity and effects of anion ordering are observed. In this regime (i) a superconducting transition is seen near 1.3 K even though ρ just above the transition can be up to 10–100 times greater than ρ(300 K), and (ii) there is an extraordinarily large hysteresis in ρ below $\sim$ 100 K with the possibility of varying the resistance of the low temperature state by several orders of magnitude by appropriate temperature cycling. These results establish the first order character of the transition. We suggest that at high pressures the anions remain frozen in a metastable disordered state to low temperatures.

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INTRODUCTION

Whereas the salts of TMTSF of the form $(TMTSF)_2X$ where X is an octahedral anion ($X= PF_6$, AsF_6, SbF_6, TaF_6) all show a metal-insulator (M-I) transition below ∿20 K at ambient pressure[1] the salts containing anions of lower symmetry show more disparate behaviour. In particular the salts $(TMTSF)_2ReO_4$ and $(TMTSF)_2BF_4$ containing the tetrahedral anions, ReO_4 and BF_4, exhibit M-I transitions at the much higher temperatures of ∿180 K and 40 K respectively[1,2] while $(TMTSF)_2ClO_4$ remains metallic and becomes superconducting below 1.2 K at ambient pressure[2] In contrast although there is a phase transition in $(TMTSF)_2NO_3$ which contains the planar nitrate anion at ∿40 K at 1 bar it is signatured by only a weak anomaly in the a-axis resistivity[1] It was suggested that these relatively high temperature transitions might be associated with an ordering of the anions which are disordered at high temperatures between two symmetry related positions[1-3] and this has subsequently been found with the determination of the low temperature superstructure in several cases[3]. For the $(TMTSF)_2X$ materials in which the band filling is fixed by charge transfer from the singly charged anions the conduction band is half-filled. Thus a doubling of the unit cell along the a direction, the high conductivity axis, corresponds to the creation of a potential $V_{2\underline{k}_F}$ (where $\underline{k}_F$ is the Fermi wave-vector) which will strongly couple with the conduction electrons, opening an energy gap at $\pm \underline{k}_F$.

Under sufficient pressure the M-I transition in the octahedral anion complexes is suppressed and all these materials show superconductivity[4-7]. The M-I transition in these materials is associated with an antiferromagnetic transition rather than the Peierls instability which is more commonly observed in quasi-one dimensional metals[8]. In this paper we show that the order-disorder transition in $(TMTSF)_2ReO_4$ is quenched under pressure and a superconducting transition is seen near 1 K. In an intermediate range of pressure both effects of anion ordering and a partial superconducting transition are observed revealing the coexistence of these two phenomena.

RESULTS

Details of the experimental configuration have previously been described[7]. The resistivity was measured along the high conductivity a axis for temperatures down to 1.2 K using a low-frequency lock-in technique with currents below 10 μA. Contacts

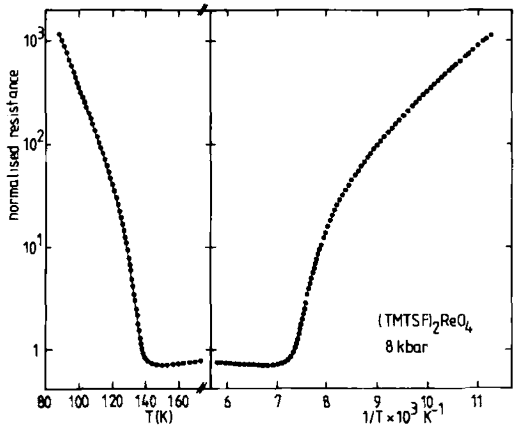

FIGURE 1 a-axis resistivity of $(TMTSF)_2ReO_4$ at 8 kbar plotted on a logarithmic scale versus (a) temperature and (b) inverse temperature. Only the warming curve is shown.

were made with silver paint using the normal 4 in-line contact arrangement. Isopentane was used as the pressure transmitting fluid with a freezing point in the range 140-220 K for the various pressures studied. Both a single-stage Maraging steel bomb and a two-stage Be-Cu pressure bomb for magnetic field studies were used in a He^4 cryostat.

The M-I transition temperature in $(TMTSF)_2ReO_4$ falls rapidly under pressure at ∿8 K/kbar from its value of ∿180 K at ambient pressure. A typical resistivity versus temperature curve measured for pressures up to some critical pressure, P_c, of ∿ 9.5 kbar is shown in figure 1a corresponding to 8 kbar. T_{M-I} defined from the derivative of the curve is about 130 K at this pressure. For pressures below P_c the resistivity is activated at low temperatures, as shown in figure 1b, with large activation energies. We find $\Delta \rightarrow 1200$ K at 1 bar and falls under pressure to about half this value at P_c[9]. Whereas at ambient pressure the hysteresis for the M-I transition is is measured to be very small [3,10], we observe a hysteresis in conductivity at all pressures which increases with increasing pressure as shown on the P-T phase diagram given in figure 2. For pressures above ∿12 kbar we observe no effect of anion ordering on the resistivity. Figure 3 shows a resistivity curve at 12.5 kbar: $(TMTSF)_2ReO_4$ remains metallic to low

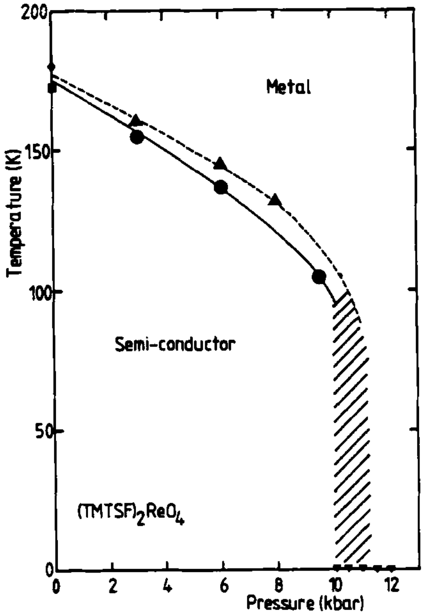

FIGURE 2 Phase diagram of $(TMTSF)_2ReO_4$ Triangles and circles correspond to T_{M-I} derived from warming and cooling curves respectively. Inverted triangles show observation of superconductivity.

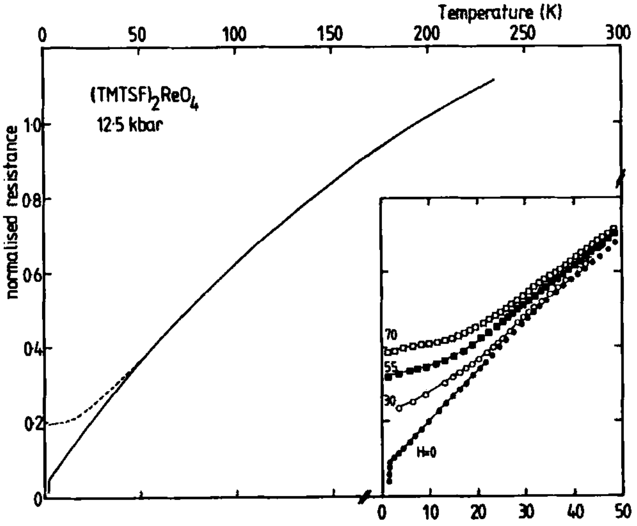

FIGURE 3 a-axis resistivity of $(TMTSF)_2ReO_4$ at 12.5 kbar normalised with respect to ρ(200 K). The broken line corresponds to the application of a magnetic field of 70 kG applied along some arbitrary direction perpendicular to the a axis. The inset shows curves corresponding to several different fields.

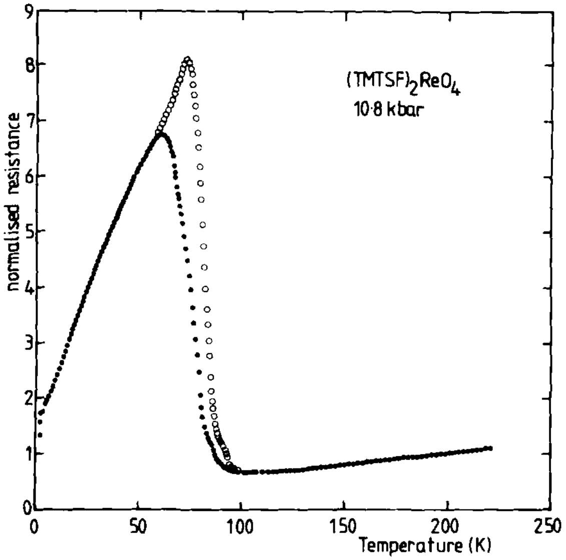

FIGURE 4 Normalised a axis resistivity of $(TMTSF)_2ReO_4$ at 10.8 kbar. The cooling and warming curves are shown as solid circles and open circles respectively.

temperatures and there is a superconducting transition near 1.2 K, which as shown in the figure is suppressed with the application of a transverse magnetic field. As is observed in other $(TMTSF)_2X$ materials there is a large magnetoresistance and a strong temperature dependence of ρ to temperatures as low as T_c[4,6,7].

The shaded region in the phase diagram in figure 2 corresponds to a narrow pressure regime (9.5< P <∿12 kbar) where we observe both large hysteretic anomalies in the resistivity for temperatures between 50 and 100 K and indications of a superconducting transition near 1 K. In this intermediate pressure region the resistivity abruptly increases as the temperature is decreased below ∿100 K and peaks at a value that can be some several orders of magnitude larger than the room temperature resistivity, below which ρ falls. Typical curves are shown in figures 4 and 5 for pressures of 10.8 and 10.5 kbar respectively. As the pressure is decreased below ∿ 12 kbar the anomaly becomes more marked developing from a plateau in resistivity near 80 K at 12 kbar through a well-defined peak as shown in figure 4 to broader features as shown

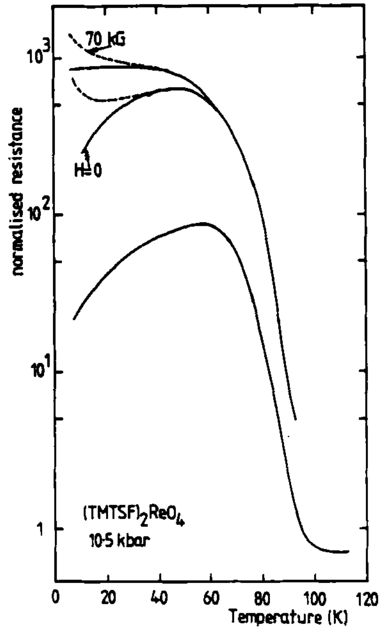

FIGURE 5 Several a-axis resistivity cooling curves for $(TMTSF)_2ReO_4$ for the same sample at a fixed pressure of 10.5 kbar, obtained by temperature cycling. The broken curves show the effect of a transverse magnetic field of 70 kG.

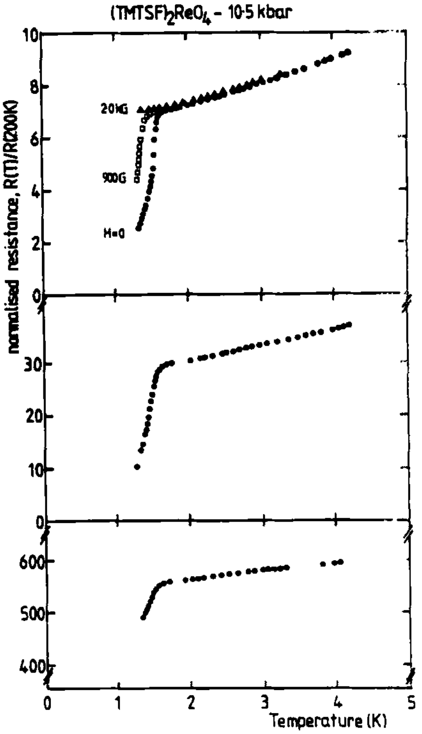

FIGURE 6 Several a-axis resistivity curves for $(TMTSF)_2ReO_4$ at 10.5 kbar for temperatures below 4 K, corresponding to cooling curves similar to those shown in figure 5 for the same sample. The top part of the figure shows curves for an applied magnetic field of 0.9 and 2.0 kG.

in figure 5. Figure 4 shows that there is a marked hysteresis with on warming a further increase in resistance above the cooling peak. For a single temperature cycle hysteresis is seen over a range of temperature ∿ 30 K wide but the cooling and warming curves are identical at low temperatures and temperatures well above the transition,suggesting the system is frozen in some metastable state at low temperatures. Figure 5 shows several cooling curves measured on the same sample at the same fixed pressure. The resistivity can be increased by a factor of more than 100 at low temperatures depending on temperature cycling and the rate of cooling (and warming) through the transition region. By stabilising the temperature somewhere in the transition region (∿50-80 K) we observe a gradual increase in resistance with time. These measurements clearly indicate the low temperature state is a metastable state: we estimate this state develops over a time scale of tens of minutes near 70 K. The corresponding warming curves to those in figure 5 follow the cooling curves at low temperatures up to ∿ 50 K where the resistivity continues to increase beyond that measured on cooling and shows a sharp peak before falling[9]. Finally note there is a large transverse magnetoresistance in the high resistance low temperature state as indicated in figure 5.

Figure 6 shows the behaviour at temperatures below 4 K at 10.5 kbar for several cooling curves similar to those shown in figure 5 for the same sample. We observe a superconducting transition near 1.2 K with a critical field of ∿ 2 kG for a field applied in some direction perpendicular to a, with a resistance just above the transition some 8 times larger than that at 200 K. We find that even when the resistance at low temperatures is increased by temperature cycling to a value of up to 500 times the room temperature resistance,a partial superconducting transition is observed but which is depressed slightly in temperature. Note that these experiments were limited to temperatures above ∿ 1 K.

DISCUSSION

The possibility of increasing the resistance of the low temperature state in $(TMTSF)_2ReO_4$ by several orders of magnitude through temperature cycling and controlling the rate of change of temperature in the pressure range, 9.5 kbar < P < 12 kbar, clearly shows the low temperature state is a metastable state and indicates the metal-insulator transition in this compound is of first-order character. We emphasize that we observe considerable hysteresis even at much lower pressures. We propose that these effects are related to ordering of the ReO_4 anions and suggest that at high pressures the ReO_4 anions remain frozen in a disordered state at low temperatures, so that there is no effect on the resistivity apart from a possible temperature independent resistivity associated with scattering of the electrons from the disordered array of charged anions.

A detailed low temperature structure has not yet been made for $(TMTSF)_2ReO_4$ but from room temperature structures of this material and members of the isostructural family $(TMTTF)_2X$[10–12], it appears that there are generally two possible orientations of the non-centrosymmetric anions in these materials. Clearly there will exist some energy barrier for an anion to swap between these two symmetry related orientations. There will also be some effective interaction energy between the anions determining the transition temperature. When the barrier to rotation of the anion molecules becomes larger than the k_BT_{O-D} (where T_{O-D} is the ordering temperature) the disordered state is frozen-in. We suggest this occurs with increasing pressure either by increases in the barrier energy or by lowering of the effective anion-anion interaction. We then propose, for example, that the different behaviours of $(TMTSF)_2ClO_4$ and $(TMTTF)_2ClO_4$,containing the same anion,but with the former showing no order-disorder transition and the latter an order-disorder transition near 70 K[3] at 1 bar which is rapidly suppressed under pressure[13] can be rationalised in this model. The low temperature state in $(TMTSF)_2ClO_4$ is a metastable state: the intrinsic ordering temperature of the anions may well be relatively high.

We find similar behaviour to that we have described here corresponding to ordering of the anions in $(TMTSF)_2ReO_4$,in the materials $(TMTSF)_2BF_4$[9] and $(TMTTF)_2SCN$[14] under pressure but with different critical pressures. By considering all the members of the $(TMTSF)_2X$ and $(TMTTF)_2X$ families showing order-disorder transitions we suggest that the transition is driven by the electrostatic interactions between the anions[9] and we speculate that the potential seen by the electrons may result from a distortion of the organic molecular stack. In this way it may be possible to reconcile the very large electronic energy gap ($\Delta \sim 1000$ K) with the much lower order-disorder transition temperature observed in $(TMTSF)_2ReO_4$. The potential associated with this large gap would be created at the transition by a reorganisation of the molecular chain, which is not inconsistent with the first-order nature of this transition.

We briefly mention a few points with regard to the above model which we discuss in more detail in ref 9. Firstly considering the anion-anion interaction a simple-minded model shows that the direct electrostatic interaction between anions is sufficiently large to be able to account for the observed T_{O-D} in the salts containing low-symmetry anions[7]. However for the tetrahedral anion complexes the Madelung energy of the anion array depends sensitively on the orientation of the anions with respect to the lattice and for the observed anion orientation in $(TMTTF)_2BF_4$[11] and $(TMTSF)_2ReO_4$[10] the Madelung energy, assuming the centre of gravity of each anion is unchanged in the ordered state would be minimised for an ordered anion structure with periodicity a along the chain axis: such a potential would not couple to the conduction electrons. However we suggest that in the ordered state the centre of gravity of the anions are displaced transversely (with a component along the c direction) alternately along the anion chain in the a direction, so creating a potential with periodicity $2k_F$. Such a distortion reduces the elctrostatic energy of the anion array[9]. We cite as possible evidence for this proposed distortion firstly the detailed structure made on $(TMTTF)_2BF_4$ above the ordering temperature which shows very large thermal factors for only two out of the four F atoms on each anion[11]. Thus the two remaining F atoms are static and the anion rotates not about its centre of gravity but about an edge of the tetrahedron. Secondly room temperature measurements on $(TMTSF)_2ReO_4$ and $(TMTSF)_2ClO_4$ reveal one short O-Se contact for each anion[15] which we interpret as indicating a tendency towards a transverse displacement of the anion. Thirdly the metal-insulator transition in $(TMTTF)_2SCN$, which under pressure behaves similarly to $(TMTSF)_2ReO_4$ and which we propose is associated with an ordering of the SCN anions[14]. Taking into account the known orientation of the anions at room temperature [12] the order-disorder transition must involve a displacement of the centre of gravity of the charge on this dipolar species in some transverse direction and the large electrostatic energy so gained would easily be sufficient to account for the observed ordering temperature. Again estimates of the sideways displacement of the BF_4 anions in $(TMTTF)_2BF_4$ suggest the energy gained is considerable when compared with k_BT_{O-D}[9]. Clearly detailed measurements of the low temperature ordered anion structure are required to check this hypothesis.

There is some evidence that at the metal-insulator transition in $(TMTSF)_2ReO_4$ the reorganisation of the crystal structure involves more than ordering of the anions. Firstly there is a significant jump in the a lattice parameter at T_{O-D}[16] and secondly the measured volume increase and the rate of fall of T_{O-D} with pressure presented above give, using the

Clausius-Clapeyron relation, an entropy change significantly larger than that expected for the anion ordering ($\sim 4\ln 2\ k_B$ per anion as against $\ln 2\ k_B$ per anion)[9]. A similar large entropy change has been measured at the order-disorder transition in $(TMTTF)_2ClO_4$ from specific heat measurements[17]. These measurements may thus suggest a possible distortion of the molecular stack itself.

Finally note that x-ray measurements on $(TMTSF)_2ReO_4$ show that the transition is three-dimensional in the sense that the precursor x-ray scattering observed above the transition temperature is isotropic[3]. If the transition were driven by the entropy of the quasi one-dimensional electron gas one might expect to see typical one-dimensional precursor x-ray diffuse scattering. We thus conclude from the above discussion that the order-disorder transition in the $(TMTSF)_2X$ and $(TMTTF)_2X$ families is driven by the anion entropy. Further discussion of this model is given in ref 9.

The second important aspect of these results is to show the coexistence of superconductivity and anion ordering in a narrow range of pressure where the semiconducting gap introduced by the ordering is not too large. It has previously been suggested that these two phenomena might be incompatible one with another and a correlation between the presence of anion ordering and the absence of superconductivity has been proposed[3]. Our results appear to be in contradiction with this hypothesis. Moreover there is recent experimental and theoretical evidence for the possible coexistence of superconductivity and other instabilities such as charge density and spin density waves[18-20].

CONCLUSION

We have shown that the very high temperature metal-insulator transition in $(TMTSF)_2ReO_4$ is suppressed with the application of a relatively small pressure, where it gives way to a metastable metallic state with a superconducting transition near 1 K. It has been shown that the superconducting state coexists with anion ordering in a narrow intermediate pressure regime.

The first-order character of the transition has clearly been established. Very large hysteretic phenomena are observed for pressures intermediate between those in which a well defined metal-insulator transition is seen at relatively high temperatures and those at higher pressures in which a metallic state is found. These results suggest the low temperature state in the high pressure phase is metastable and the anions remain frozen in a disordered state at low temperatures.

An important aspect of these results is in the interpretation of the properties of other $(TMTSF)_2X$ and $(TMTTF)_2X$ materials and the understanding of their various properties [9].

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REFERENCES

1. K. Bechgaard, C.S. Jacobsen, K. Mortensen, H.J. Pedersen and N. Thorup, Solid State Commmun., 33, 1119 (1980).
2. K. Bechgaard, K. Carneiro, F.B. Rasmussen, M. Olsen, G. Rindorf, C.S. Jacobsen, H.J. Pedersen and J.C. Scott, J. Am. Chem. Soc., 103, 2442 (1981).
3. J.P. Pouget, R. Moret, R. Comés, K. Bechgaard, J.M. Fabre and L. Giral, this conference.
4. D. Jérome, A. Mazaud, M. Ribault and K. Bechgaard, J. Physique Lett., 41, L95 (1980).
5. M. Ribault, J.P. Pouget, D. Jérome and K. Bechgaard, C.R. Acad. Sci., Paris, 291, B145 (1980).
6. S.S.P. Parkin, M. Ribault, D. Jérome and K. Bechgaard, J. Phys. C:Solid State Phys., 14, L445 (1981).
7. S.S.P. Parkin, M. Ribault, D. Jérome and K. Bechgaard, J. Phys. C:Solid State Phys., in press.
8. K. Mortensen, Y. Tomkiewicz, T.D. Schultz and E.M. Engler, Phys. Rev. Lett., 46, 1234 (1981).
9. S.S.P. Parkin, F. Creuzet, D. Jérome and K. Bechgaard, to be submitted.
10. C.S. Jacobsen, H.J. Pedersen, K. Mortensen, G. Rindorf, N. Thorup, J.B. Torrance and K. Bechgaard, to be submitted.
11. J.L. Galigné, B. Liautard, S. Peytavin, G. Brun, M. Maurin, J.M. Fabre, E. Toreilles and L. Giral, Acta. Cryst., B35, 1129 (1979).
12. J.L. Galigné, B. Liautard, S. Peytavin, G. Brun, M. Maurin, J.M. Fabre, E. Toreilles and L. Giral, Acta. Cryst., B35, 2609 (1979).
13. S.S.P. Parkin, F. Creuzet, D. Jérome, K. Bechgaard and J. M. Fabre, to be submitted.
14. S.S.P. Parkin and C. Coulon, to be submitted.

15. N. Thorup, G. Rindorf and H. Soling, Physica Scripta, in press.
16. D.R.P. Guy, E.A. Marseglia, S.S.P. Parkin, R.H. Friend and K. Bechgaard, J. Phys. C:Solid State Phys., to be submitted and this conference.
17. C. Coulon, P. Delhaes, S. Flandrois, R. Lagnier, E. Bonjour and J.M. Fabre, J. Physique, submitted.
18. K. Machida, J. Phys. Soc. Japan, 50, 2195 (1981).
19. R. Sooryakumar and M.V. Klein, Phys. Rev. Lett., 45, 660 (1980).
20. C.A. Balseiro and L.M. Falicov, Phys. Rev. Lett., 45, 662 (1980).