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Comment on “Electronic Structure of Insulating Salts of the-(BEDT-TTF Family Studied by Low-Temperature Specific-Heat Measurements”

Nathanael Fortune
Smith College, nfortune@smith.edu

Yu V. Sushko
NEC Corporation

COMMENTS

Comments are short papers which criticize or correct papers of other authors previously published in **Physical Review B.** *Each Comment should state clearly to which paper it refers and must be accompanied by a brief abstract. The same publication schedule as for regular articles is followed, and page proofs are sent to authors.*

Comment on "Electronic structure of insulating salts of the κ-(BEDT-TTF)$_2X$ family studied by low-temperature specific-heat measurements"

N. A. Fortune
Department of Physics, Smith College, Northampton, Massachusetts 01063

Yu. V. Sushko
Fundamental Research Laboratories, NEC Corporation, Miyukigaoka 34, Tsukuba 305, Japan
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Recently reported specific-heat measurements by Nakazawa and Kanoda between 20 and 50 K show no evidence for an expected antiferromagnetic ordering transition in the quasi-two-dimensional (2D) molecular conductor κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl [Y. Nakazawa and K. Kanoda, Phys. Rev. B **53**, R8875 (1996)]. Although the absence of an observable transition was taken as evidence for 2D short-range ordering at elevated temperatures, even a small increase in pressure from the application of the grease used to mount the sample would shift this magnetic transition below 20 K. In their paper, Nakazawa and Kanoda erroneously assume that pressure-induced effects can be ruled out by the magnetic-field independence of the low-temperature specific heat below 3 K. In this Comment, we explain why this assumption is invalid. We conclude that specific-heat measurements in the intermediate temperature range of 3–20 K are needed before the absence of a discernible magnetic and/or pressure-induced phase transitions can be asserted. [S0163-1829(97)01026-6]

In a recent paper,[1] Nakazawa and Kanoda use measurements of the low-temperature specific heat between 0.85 and 2.8 K and again between 20 and 50 K to contrast two archetypal low-dimensional molecular conductors: κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Br and κ-(BEDT-TTF)$_2$Cu[N(CN)$_2$]Cl. The Br salt is a superconductor with a zero-field, ambient pressure superconducting transition temperature $T_c^0 = 11.6$ K (Ref. 2) while the Cl salt is a weakly ferromagnetic insulator with a zero-field, ambient pressure magnetic transition temperature $T_{WF}^0 \approx 22$ K.[13] The temperature at which this transition occurs depends on the applied magnetic field and pressure: applying a magnetic field enhances T_{WF} by ≈ 2 K/T (Ref. 3) while applying hydrostatic pressure suppresses T_{WF} by ≈ 20 K/kbar.[4] Because of the enhancement with magnetic field, this magnetic transition is seen at ≈ 23 K in susceptibility measurements in a 1-T field[5] but between 25 and 30 K by high-field NMR in a 3.7-T field.[5] In Ref. 1, T_{WF} is referred to as a 26–27 K antiferromagnetic transition.

Surprisingly, Nakazawa and Kanoda find no evidence for this magnetic transition between 20 and 50 K in their zero-field specific-heat data for the Cl salt,[1] concluding that its absence implies a "two-dimensional short-range magnetic order far above the three-dimensional ordering temperature typical of a high-T_c cuprate." In Ref. 1, Nakazawa and Kanoda acknowledge that pressure effects caused by the application of grease could suppress this transition but argue that these effects can be ruled out by the magnetic-field independence of the low-temperature specific heat below 3 K. In this Comment, we explain why this argument is invalid and what additional data are needed before the absence of a discernible magnetic transition can be asserted.

In the absence of magnetic field, γ—the electronic coefficient of the specific heat—is zero for both materials, indicating the presence of a gap at the Fermi level at low temperatures. For the Br salt, this zero-field gap is due to superconductivity at 11.6 K.[2] For the Cl salt, this zero-field gap is attributed[1] to the insulating state found below T_{WF} at ambient pressure, although the data for the Br salt demonstrate that the bulk superconducting state found in the Cl salt at 13 K for pressures $\geqslant 300$ bar (Refs. 6–9) would produce identical results. Not mentioned in Ref. 1 is that at this and even higher pressures (400–500 bar) a reentrant magnetic transition occurs between 5 and 6 K for sufficiently slowly cooled samples.[4,10–12] Since this reentrant phase is an insulator, it too is consistent with the zero-field data presented in Ref. 1.

As acknowledged in Ref. 1, the suppression of T_{WF} due to the creation of a pressure-induced ground state must be considered for the Cl salt, since thick coatings of the Apiezon *N* grease used to mount the samples to the calorimeters[1,13,14] have already been observed to induce superconductivity in this salt.[15,16] In the case of the thin layer of grease used in Ref. 1, the magnitude of the induced increase in pressure is unknown.

In an attempt to distinguish between ambient and pressure-induced ground states, Nakazawa and Kanoda compare the magnetic-field dependence of the specific heat below 2.8 K for the Br and Cl salts. Their data demonstrate that in the presence of magnetic field, γ becomes nonzero for the Br salt but remains unchanged for the Cl salt. Nakazawa and Kanoda argue that ''the fact that gamma value [for the Cl salt] is not affected by such large fields means that there is no fraction of pressure-induced superconductivity in this measurement''[1] and hence that the possibility of an inadvertent application of pressure can be dismissed. In fact, the specific-heat data reported in Ref. 1 do not demonstrate the absence of pressure-induced superconductivity at zero field in the Cl salt. The data in Ref. 1 only demonstrate that the low-field and high-field ground states both have gaps at the Fermi level.

It is true that applying a magnetic field leads to a transition in the Br salt from a low-field superconducting ground state to a high-field normal-metallic ground state with a nonzero value for γ.[17] And indeed, the partial suppression of superconductivity in the Br salt by an 8-T magnetic field is readily apparent in Fig. 2 of Ref. 1. This change in the measured value of γ is not, however, a signature of superconductivity at zero field. It is merely an indication that applying a magnetic field induces a change from a zero-field ground state with a gap at the Fermi level to a high-field ground state without a gap.

In the case of the Cl salt, no change in the measured value of γ would be seen even if the sample were pressurized. Depending on the exact pressure and cooling conditions, the zero-field ground state will be a magnetic insulator, a superconductor, or a reentrant magnetic insulator, but for all three possibilities, $\gamma=0$. For both the superconducting and reentrant states, the high-field ground state of the Cl salt is an insulator.[18,19] We conclude that the absence of a change in γ from zero with the application of a magnetic field does not demonstrate the absence of a zero-field pressure-induced superconducting state.

In summary, the data presented in Ref. 1 are insufficient to prove the absence of a discernible antiferromagnetic phase transition. What is missing in Ref. 1 are measurements of the specific heat between 3 and 20 K that directly demonstrate the absence of any observable magnetic transitions in the Cl salt under the conditions previously used to measure the zero-field specific heat between 20 and 50 K. We wish to emphasize that even at pressures too weak to induce bulk superconductivity, the magnetic ordering transition T_{WF} can still be suppressed below 20 K.[4] This means even a direct proof of the absence of bulk superconductivity would not be sufficient to prove the absence of a pressure-induced suppression of T_{WF} below 20 K.

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