Reply to ''Comment on 'Paramagnetic Meissner effect in Nb' ''

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Rice and Sigrist (RS) have proposed a d-wave mechanism to explain the paramagnetic Meissner effect (PME) observed in some inhomogeneous samples of high-T_c superconductors. However, the observation of a PME in some inhomogeneous samples of Nb (an s-wave superconductor) demonstrates that a d-wave pairing mechanism is not needed to produce the effect. Moreover, the remarkable similarity between the PME observed in these Nb and in the high-T_c samples argues that the same mechanism is operable in both types of superconductors. In this Reply, new measurements on $La_2CuO_{4+\delta}$ and on irradiated Nb are discussed, which strongly support the notion that the PME is most likely associated with layered T_c inhomogeneities. Further experiments to test this notion are proposed. We also discuss critically the three experiments proposed by RS to distinguish between two PME mechanisms unrelated to layered T_c inhomogeneities. [S0163-1829(97)02721-5]

In several papers[1] and in the previous Comment,[2] Rice and Sigrist (RS) argued that the observation of a paramagnetic Meissner effect (PME), or Wohlleben effect, in some granular samples of $Bi_2Sr_2CaCu_2O_{8+\delta}$ (BSCCO) provides strong evidence for the existence of a d-wave pairing mechanism in the high transition temperature T_c cuprates. However, a similar effect was recently reported[3] and confirmed by us[4] in some inhomogeneous disk-shaped samples of Nb in fields **H** normal to the disks. Upon polishing the surfaces of those Nb samples exhibiting the effect, the shape of the superconducting transition was altered and the PME disappeared. Thus, we[3,4] attributed the PME to surface T_c inhomogeneities, combined with inhomogeneous flux pinning effects, which were also known to be present.

We argued that the origin of the PME is likely to be the *same* in Nb (an s-wave superconductor) and BSCCO, and thus cannot be attributed to a d-wave mechanism. Some recent measurements provide additional support for a common mechanism in all superconductors exhibiting the PME to date. Although the precise mechanism is presently unknown, the phenomenon appears to be closely associated with layered T_c inhomogeneities in the samples. In their Comment,[2] RS presented three experimental tests to distinguish between two proposed mechanisms, flux compression and orbital magnetic moments (OMM's) appearing as a consequence of d-wave pairing, neither of which contains this crucial feature. In the following, we summarize these new and other experimental results, and propose additional experiments. We also critically review the three experiments proposed by RS.

The field-cooled magnetization (FCM) $M(T)$ and $M(H)$ curves obtained[3,4] for inhomogeneous Nb were *strikingly similar* to those obtained for some melt-cast, polycrystalline samples[5] of BSCCO. With cooling, the $M(T)$ showed a pronounced dip at T_c, followed by a rise to a paramagnetic (positive) value at lower temperatures T, and remained rather constant down to $T=0$. With increasing H, the low-T $M(H)$ increased from 0 to a broad maximum, and then decreased, eventually becoming diamagnetic (negative). These are the same characteristic PME behaviors of those BSCCO samples.[5]

Most BSCCO samples do not exhibit the PME. The broad transitions in those few BSCCO samples exhibiting the PME (Refs. 5–7) indicate that those samples are very *inhomogeneous*. It appears this strong T_c inhomogeneity is a necessary condition for the appearance of the PME in both Nb and BSCCO.

The PME was also observed in single crystals of $YBa_2Cu_3O_{7-\delta}$ (YBCO) (Ref. 8) and $La_2CuO_{4+\delta}$ (LCO).[9] Similar to the effect of polishing the surfaces of Nb, the PME disappeared after cleaving the single-crystal of YBCO.[8] These single-crystal results are apparently *inconsistent* with the RS model. The RS model requires the presence of π junctions arising from different lobes of the d-wave order parameter present at internal interfaces (grain boundaries), where spontaneously generated OMM's occur. Although π junctions could arise in YBCO and LCO from magnetic impurities at sites of oxygen inhomogeneities, they could only occur in the d-wave model of RS for c-axis aligned grains if the grains have substantial ab orientation variability other than at twin boundaries, which variability does not occur in single crystals. Thus, as RS agree, a d-wave mechanism is apparently not *essential* to produce the effect in high-T_c cuprates. Furthermore, it cannot explain the appearance of the PME in single-crystal YBCO and LCO.

In YBCO, the PME observed to date is quite small, rather similar in magnitude to the effect observed to date in Nb. Some samples of BSCCO have shown a much larger PME.[6,7] However, in single-crystal LCO,[9] a very large PME was also reported. The field-cooled susceptibility χ at 2 Oe and $T\rightarrow 0$ was 26% of $1/4\pi$. We note that in Ref. 9, systematic measurements were not made to determine the maximum PME χ. However, in BSCCO, the maximum PME occurs at $H\ll 2$ Oe;[7] the response is diamagnetic at 2 Oe.[5–7] Thus, it is possible that the maximum PME χ would be even larger in LCO than in BSCCO. In any event, very large PME's can be observed in high-T_c oxides under special circumstances, which are not explainable with the OMM d-wave mechanism of RS.

Very recently, neutron-diffraction measurements were reported for the *same* LCO single crystal which showed the very large PME.[10] Those measurements showed that the composition was an *inhomogeneous* layered mixture of different stage oxygen intercalation compounds, with roughly 60% of stage 2, and 20% each of stages 3 and 4, respectively.

Since La_2CuO_4 is an insulator, the T_c value of LCO depends strongly upon the oxygen stoichiometry. The observation of variable local oxygen intercalation compositions strongly supports the notion that T_c varies substantially in that material, with the primary T_c variability being layered in nature. This behavior would appear to be similar to that observed in the Nb and YBCO samples where evidence of layered T_c inhomogeneity was reported.[3,4,8] Furthermore, we note that it has been reported very recently[11] that the PME could be enhanced and even *induced* in Nb samples not previously showing it, by irradiating the top and bottom 120 nm of the disk-shaped Nb samples with Kr ions. In all of these cases, it appears the magnitude of the PME is closely correlated with the amount of layered T_c inhomogeneity.

Thus, the evidence is strong that the same mechanism which causes the PME in Nb, in single-crystal YBCO, and in single-crystal LCO, is also causing the PME in the inhomogeneous BSCCO samples. We do not find it persuasive that a separate mechanism need be proposed to account for the PME in BSCCO. Nor do we find it persuasive that the occasional observation of the PME in inhomogeneous BSCCO provides any evidence pertaining to the pairing mechanism.

In their Comment,[2] RS state that OMM's have been observed in a number of experiments involving controlled geometries (Ref. 6 of Ref. 2), and assert that these experiments confirm the existence of OMM's which appear as a consequence of their d-wave mechanism. While a Reply is not the appropriate forum for us to comment specifically on details of other experiments, we remark that each of those experiments cited has its own set of experimental problems, complicating the interpretations. Some of those experiments have already been discussed as arising from corner effects[12] or self-field effects,[13,14] and the rest of those cited experiments can have other possible interpretations, usually involving sample defects and/or trapped flux.[15,16]

RS described three experiments, which they asserted would distinguish between two different mechanisms (OMM and flux compression[17]) that had been proposed to explain the PME. They did not consider any mechanism involving layered T_c inhomogeneity. Here, we consider those proposed experiments.

(1) RS note that the magnitude of the reported PME in Nb is small, and thus may be consistent with flux compression.[17] They infer that one would never expect to find a large PME in Nb, whereas a large PME has already been observed in BSCCO. We agree that additional information could come from comparative magnitude studies. We do not know how large the effect can be in Nb, since optimal conditions for the effect are not known. However, we do know that, like in Nb, a small (or even zero) PME is usually observed in BSCCO. Again, special (unknown) sample conditions are needed before the signal can be observed. If a large PME were observed in Nb, this would provide more evidence that the effect had a common origin in Nb and the cuprates. However, if larger PME magnitudes were not found in Nb, one could not be sure that suitable samples had been prepared to maximize the effect.

(2) An anomalous, nonmonotonic microwave absorption (MWA) in a static external field was observed in some cuprate samples that showed the PME.[5] These experiments have not yet been performed on inhomogeneous Nb, and we agree that such experiments should be performed. However, we again disagree with RS regarding the likely significance of such experiments. In the work reported in Ref. 5, of the eight cuprate samples exhibiting the PME in which the field dependence of the MWA was measured, three samples exhibited the anomalous MWA and five samples did not. Clearly, there is not a robust correlation between the PME and the anomalous MWA, as one might expect if the MWA were readily understood in the context of OMM's.

In addition, the anomalous MWA was only observed within a narrow T range, approximately between 1 and 6 K below T_c,[5] which corresponds roughly to the T regime over which $\chi(T)$ is rapidly decreasing with increasing T, or approximately the width of the transition. If the anomalous MWA were found to occur in PME-exhibiting samples of Nb in the very narrow T range (roughly 0.1–0.2 K wide) over which $d\chi/dT<0$, our contention that the origin of the PME is similar in BSCCO and Nb would be further supported. However, nonobservation of the anomalous MWA in several samples of inhomogeneous Nb would not imply a different origin of the PME from that in BSCCO. Even in BSSCO samples showing the PME, the anomalous MWA is only sometimes observed just below T_c.

(3) RS assert that the direct observation of the OMM with a superconducting quantum interference device (SQUID) microscope in zero-field-cooled (ZFC) cuprate samples exhibiting the PME would constitute a proof of their proposed OMM (i.e., d-wave) mechanism for the PME. Implicit in this assumption is their belief that trapped flux could be completely eliminated by sufficient magnetic shielding. However, inhomogeneous samples *always* exhibit trapped flux, possibly generated spontaneously in the creation of vortex-antivortex pairs upon cooling through T_c. The signature of the trapped flux can be indistinguishable from OMM when observed in SQUID microscopes.[18] Moreover, good-quality single crystals of YBCO have recently been shown by Josephson junctions[19] and by a SQUID microscope[20] to have substantial trapped flux lying in the ab plane, *even* when the sample was cooled in a well-shielded, nominally zero magnetic field. A SQUID microscope placed above a ZFC sample would only measure the field component in a fixed direction, usually normal to the layers. In general, it would not accurately account for flux which lies predominantly in the ab plane (parallel to the layers), and pops out (normal to the layers) at defect sites, as in Ref. 18. The observed SQUID signals, resulting from trapped flux, could easily be mistaken for OMM's.

RS argued[1,2] that optimal samples for showing the PME consist of clusters of c-axis aligned large grains (platelets, $\approx 10\ \mu$m), which are randomly oriented but well connected within the basal plane. According to simulations, optimal PME conditions are also obtained with a high density of such c-axis aligned grains.[21] To test their hypothesis, we have measured 12 samples of $Bi_{1.8}Pb_{0.4}Sr_2Ca_2Cu_3O_{10+\delta}$

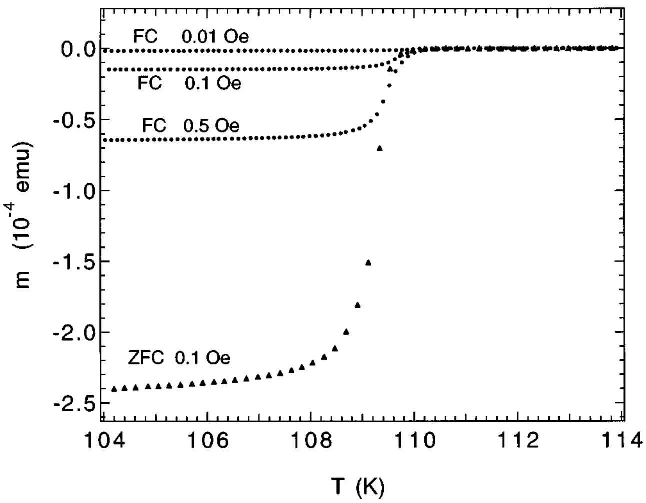

FIG. 1. Comparison of FCM and ZFCM measurements from a c-axis aligned polycrystalline sample of $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ tape.

(BSCCO-2223) which should very closely satisfy these optimal conditions. The samples are silver clad tapes containing high-purity, densely packed BSCCO-2223 polycrystals, with grains that are 1–10 μm in size, approximately c-axis oriented, and randomly oriented in the ab plane.[22] The samples typically have sharp superconducting transitions at 109.5 K, with a width of 1 K, as determined from the 10–90% zero-field-cooled magnetization (ZFCM), and have large transport current densities ($\approx 1.7\times 10^4$ A/cm^2) at 77 K in the tape plane, measured in zero field. These measurements indicate that the samples are homogeneous and of high quality. Figure 1 shows typical ZFCM and FCM measurements. The ZFCM was measured on warming in 0.1 Oe field. For the FC masurements, samples were cooled and measured on warming in fields of 0.01, 0.1, and 0.5 Oe. These are typical measuring fields at which the PME has been observed in the other materials. However, these data show the ordinary Meissner effect behavior *normally* observed in high-T_c superconductors. Of the 12 samples measured, none showed the PME. Thus, the experimental configuration optimal for the observation of the PME from the RS d-wave-generated OMM mechanism does not always lead to a PME. In addition, these results reinforce our notion that the PME is associated with T_c inhomogeneities, or broad transitions.

In the interest of clearly determining the PME mechanism, we suggest the following set of experiments: (1) Perform a careful study of the PME in single-crystal LCO with varying oxygen compositions. Correlate the effect with structural and compositional variations, including sample homogeneity. (2) Try to induce the PME in cuprate samples, such as the sample for which the magnetization data are presented in Fig. 1, which do not show the effect. This could be done (a) by ion bombardment of non-PME cuprates, (b) by making a multilayer of different T_c cuprates, or (c) by making mixtures of sintered cuprate samples, in which the different components of the mix have sharp, but different T_c values. These experiments might help to determine if the layering aspect of the T_c inhomogeneities is indeed an essential ingredient in the actual mechanism for the PME.

In short, the experiments suggested in the previous Comment[2] could provide supporting evidence that the mechanisms for the PME in inhomogeneous Nb and cuprates were the same, but could not be used to decide if they were different. We have presented substantial evidence that the actual mechanism for the PME in both Nb and the cuprates is indeed the same, and is closely associated with layered T_c inhomogeneities in the samples. We have also proposed additional experiments to help identify the precise conditions necessary for the appearance of the PME. Finally, we believe that the preponderance of evidence demonstrates that the origin of the PME, while unknown,[4,17] is *unlikely* to be related to d-wave superconductivity.

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