Spherical agglomeration of superconducting and normal microparticles with and without applied electric field

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It was reported by Tao *et al*. [Phys. Rev. Lett. **83**, 5575 (1999); Physica C **377**, 357 (2002); Phys. Rev. B **68**, 144505 (2003); Physica C **398**, 78 (2003)] that in the presence of a strong electric field superconducting microparticles assemble into balls of macroscopic dimensions. Such a finding has potentially important implications for the understanding of the fundamental physics of superconductors. However, we report here the results of experimental studies showing that (i) ball formation also occurs in the absence of an applied electric field, (ii) the phenomenon also occurs at temperatures above the superconducting transition temperature, and (iii) it can also occur for nonsuperconducting materials. Possible origins of the phenomenon are discussed.

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I. INTRODUCTION

It has been reported by Tao and coworkers that superconducting microparticles in a strong electric field assemble into compact balls of macroscopic dimensions (diameter fraction of a mm).[1–4] These balls are robust and survive collisions with the electrodes at high speeds. Tao *et al*. attributed the ball formation to a new kind of "surface tension" of superconducting particles in the presence of a strong electric field.[1] They found that this phenomenon occurs for both high-T_c cuprate superconductors[1] and for low-T_c conventional superconductors.[2,4] Furthermore they reported that the balls become fragile and break apart easily both when the electric field is turned off and/or when the temperature is raised above the superconducting transition temperature.

If valid, these findings would have enormous implications for the understanding of the fundamental physics of superconductors. The conventional theory of superconductivity[5] predicts that the response of superconductors to applied electrostatic fields is the same as that of normal metals:[6] electric fields should be screened within a distance on the order of angstroms (Thomas-Fermi length) of the surface, and thus would not be expected[1] to give rise to phenomena such as the spherical aggregation reported by Tao. One of the present authors has proposed[7] that the phenomenon reported by Tao is evidence of the inadequacy of the conventional theory of superconductivity,[8] and is a consequence of the same physics that leads to the Meissner effect within the unconventional theory of "hole superconductivity,"[9] namely expulsion of negative charge from the interior of the superconductor to the surface. Quite generally, if this aggregation indeed took place only in the superconducting state and only under a strong applied electric field, it would call for an explanation beyond the generally accepted physics of superconductors.

However, we report in this paper that the spherical aggregation is a more widespread phenomenon than previously reported. We find that it can occur both in the presence and in the absence of an electric field, and both in the superconducting state as well as above the superconducting transition temperature, and also in nonsuperconducting materials. These findings undermine the claims that the Tao experiments cast doubt on the conventional theory of superconductivity[8] and are evidence in favor of an alternative theory.[7] While the phenomenon appears to be strongest in materials that are high-temperature superconductors, we have not found clear evidence that it is stronger in the superconducting versus the nonsuperconducting state.

II. AGGLOMERATION IN AN ELECTRIC FIELD

We started by attempting to reproduce Tao's experimental results. In addition to Tao's papers, one unpublished report exists that independently supported some of Tao's findings.[10]

We used BSCCO and $YBa_2Cu_3O_{7-\delta}$ disks provided by Colorado Superconductor. The BSCCO disks were reportedly a mixture of the 2223 and the 2212 phases, with critical temperature above 100 K. Both types of disks exhibited a strong Meissner effect at liquid nitrogen temperatures. We ground the disks with a Dremel (952 aluminum oxide grinding stone) and sorted particles by sizes using sieves. Figure 1 shows typical shapes of particles obtained for various sizes. We used only the resulting microparticles that passed through a 32-μm sieve. In another set of experiments, we used $Bi_2Sr_2CaCu_2O_{8+x}$, $x = 0.15$–0.20) powder provided by Sigma-Aldrich, hereafter termed "σ powder,"with nominal grain size $\leqslant 5\mu$m.

We constructed a cell measuring 15 mm × 70 mm horizontally and 13 mm vertically from plastic plates of thickness 1 mm, and attached thin (<1 mm) metal plates either on the inside or outside walls. This formed a parallel plate capacitor with electrodes separated by 12 mm to 16 mm depending on the configuration. We used both Al and stainless steel metal plates and observed the same behavior, indicating that magnetism was not playing a role. The metal plates were connected to a DC voltage source that could deliver up to 20 kV (i.e., maximum electric field inside the capacitor approximately 1700 V/mm). This is well above the lower critical field E_{c1} required for ball formation reported by Tao of order 500–800 V/mm.[1–4]

We poured liquid nitrogen into the capacitor, added BSCCO or YBCO powder (typically between 60 mg and 150 mg) and observed the behavior when the voltage source was connected to the capacitor plates by recording with a high-speed camera that yielded 1000 frames per second.

When we put both metal plates on the inside of the plastic plates we got interesting action starting at a few thousand volts,

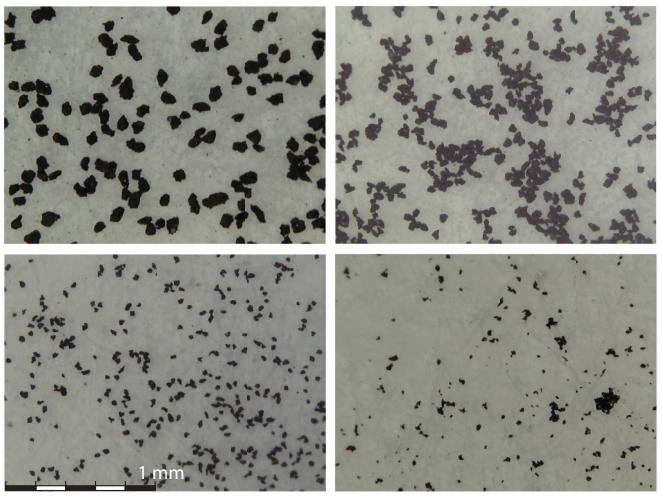

FIG. 1. (Color online) Typical microparticles of various sizes obtained by grinding superconducting disks and passing through sieves. The range of diameters of the four panels are 53 μm to 75 μm, 32 μm to 53 μm, 25 μm to 32 μm, and less than 32 μm for the upper left, upper right, lower left, and lower right panels. Note the irregular shapes of the particles.

as described below. When both metal plates were outside of the plastic plates to form insulating electrodes we found no action whatsoever, even for voltages up to 20 kV. When one of the metal plates was on the inside and one on the outside we found some very limited action. We conclude that the effect is *not* driven by a large electric field, as postulated by Tao,[1–4] since it requires *charge* being able to circulate from the conducting electrodes to the superconducting microparticles.

The action we found in the capacitor can be summarized as follows. On increasing the voltage, at several thousand volts, powder starts to move. Sometimes it suddenly flies to the electrodes. Then, balls form and start bouncing between the electrodes, as described by Tao. In addition, as described by Tao, in all runs clinging of powder to the electrodes occurs. The voltage where these processes occur is variable; depending for example on the amount of powder and its distribution between the electrodes, it was typically in the range between 6 kV and 14 kV. While Tao usually found only one ball in his 4 mm $\times$ 5 mm chamber, in our setup we typically found a large number of balls of varying size. Often, the balls aligned in a linear fashion and bounced back and forth against each other and against the electrodes. Figure 2 shows as an example a row of eight balls in five snapshots separated by 10 frames each [i.e., 10 ms (the camera records 1000 frames per second)] in a run where the potential difference between top and bottom electrodes was 9 kV. The distance between top and bottom electrodes (black horizontal lines) is 1 cm, so these balls range from approximately 0.45 mm to 0.70 mm in diameter. Note that a ball of 0.5 mm diameter would be composed of at least 4000 microparticles in close proximity. The balls are bouncing up and down and there is no apparent deformation when they bounce. Here they move between collisions at a speed of approximately 6 cm/s and the acceleration involved in a collision is of order 10 m/s^2. This linear arrangement was stable for approximately 2 s, corresponding to each particle traveling the equivalent of 12 times the distance between the electrodes and undergoing about 200 collisions with the neighboring particles. At the end of that period a ninth particle squeezed into the row and the same arrangement continued until shedding from the layer coating the upper electrode occurred.

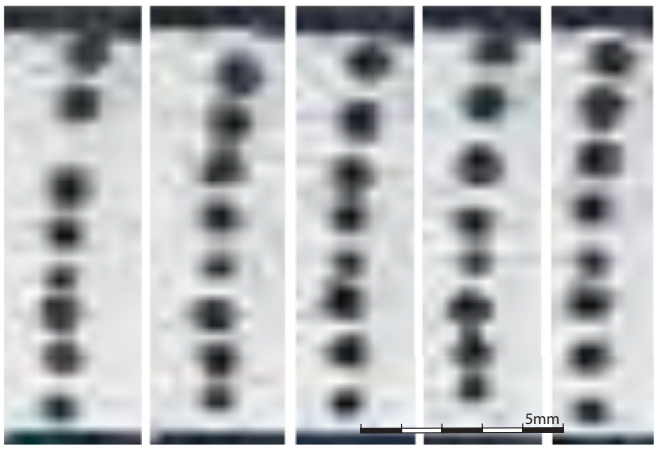

FIG. 2. (Color online) Balls bouncing up and down between electrodes, frames shown are consecutive separated by 10 ms. The vertical size of the figure corresponds to 1 cm in real life. Each ball is composed of several thousand micrograins.

The fact that ball formation only occurred when the electrodes were conducting indicates that the phenomenon is not due to the presence of an electric field as argued by Tao, rather it appears to be *facilitated* by the presence of free charge. We hypothesize two processes: in the first process, microparticles pick up positive and negative charges from the electrodes, after which they are repelled from the electrodes and return to the bulk of the chamber. Microparticles of opposite sign attract each other due to the long-range Coulomb force. When they come in contact, they share their charge. One might expect that they would then separate; the fact that they stay together indicates that another force sets in that keeps them together. In the second process, ball formation occurs at the electrodes themselves, where a thick layer of micrograins accumulates, with micrograins in close proximity to each other. Occasionally, pieces of the layer detach themselves in the form of balls that return to the bulk of the chamber. Again, the balls are held together by a force that acts between micrograins in close proximity.

III. AGGLOMERATION IN THE ABSENCE OF AN ELECTRIC FIELD

We next tested the possibility of sphere formation in the absence of applied electric field and electric charges, by gently shaking a container with superconducting powder horizontally in liquid N_2. We poured 60 mg of BSCCO or YBCO powder in a container of diameter 80 mm containing approximately 5 mm height of N_2, and kept the container cold by submerging it in a container of larger diameter with substantially higher levels of N_2. In all cases the micrograins in the powders had diameter smaller than 32 μm. Indeed, it was found after fine tuning the procedure that it was very easy to make balls of the same sizes as produced in the capacitor. Figure 3 shows one example. After forming, the balls retain their integrity upon strong shaking of the container. When the agitation became

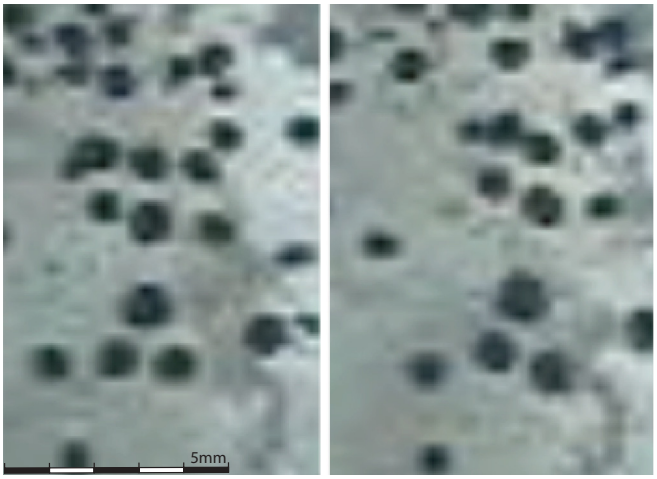

FIG. 3. (Color online) BSCCO balls formed by shaking a container with micrograins, no electric field applied. The scale is the same as in Fig. 1. The two images are separated by 30 ms and the motion is due to motion of the nitrogen caused by shaking.

sufficiently rapid and erratic the spheres would break apart back into powder. The balls could be reformed by returning to regular shaking. In addition, we verified that placing these balls inside the capacitor and applying a voltage between the plates leads to the same motion as described earlier for the case where balls were created in the capacitor when voltage was applied.

IV. TEMPERATURE AND MATERIAL DEPENDENCE

Having established that ball formation in high-temperature superconductors is independent of the presence or absence of an applied electric field, we proceeded to investigate the temperature dependence of the effect and to test the behavior of various different materials. Tao *et al*. had reported that in high-temperature superconductors, in low-temperature elemental superconductors, and in magnesium diboride (MgB_2), balls don't form above T_c and that balls that formed below T_c become fragile and are easily destroyed as soon as the temperature rises above T_c. In the following, we will present results for various materials in liquid N_2 (temperature 77.4 K) and liquid Ar (temperature 87.3 K), as well as in water at room temperature and in ethanol and methanol at temperatures in the range 150–180 K.

A. Materials used

We used the following materials:

(i) σ powder was pressed into a pellet of density approximately 3.5 g/cm^3. It was heated to 850° C and kept at that temperature in air for 40 hours, then cooled slowly to room temperature in another 40 hours. After this process the pellet did not exhibit a Meissner effect either in N_2 or in Ar. In addition, its transition temperature was measured resistively and found to have onset at $T = 73$°K, confirming the observed absence of Meissner effects. The pellet was then ground and the resulting powder passed through a 32-μm sieve. The resulting powder collected in a dry tube and gently shaken had density 1.6 g/cm^3.

(ii) A YBCO disk from Colorado Superconductors was broken into three pieces. One piece of the disk was left intact. This piece exhibited a strong Meissner effect in N_2 and a weaker Meissner effect in Ar. Another piece was brought to 800° C for 90 minutes and then quenched to 77 K in liquid N_2. According to the literature,[11,12] this procedure removes oxygen and leads to an underdoped sample, with $\delta \sim 0.65$ and T_c less than 30 K. We did not measure the T_c of this sample but verified that it exhibited no Meissner effect in N_2. The sample was conducting at room temperature. We ground and sieved these samples the same way as described for sample (i). The third piece was heated to 1050° C for 120 minutes and then cooled suddenly to 77 K. The resulting sample was now insulating, indicating that more oxygen had been removed by this process, as expected, and of course exhibited no Meissner effect. Also this sample turned to a green color. We ground this sample in the usual way, which turned out to be considerably more difficult than in the other cases as this sample was considerably harder.

(iii) MgB_2 powder obtained from Alfa Aesar, with transition temperature expected to be 39 K. Again the powder was passed through a 32-μm sieve.

(iv) Pb powder, ground from a bulk piece and passed through a 32-μm sieve.

(v) Zn powder passed through a 32-μm sieve.

(vi) BSCCO powder ground from disks as described in Sec. II and passed through a 32-μm sieve.

B. Results

We found that ball formation occurs both below and above T_c, and that balls that formed below T_c do not become fragile above T_c. Indeed, balls formed at low temperature remain robust even when they are brought to room temperature.

Figure 4 shows ball formation for the annealed σ powder [see (i) in previous subsection] in N_2 and Ar, both in the

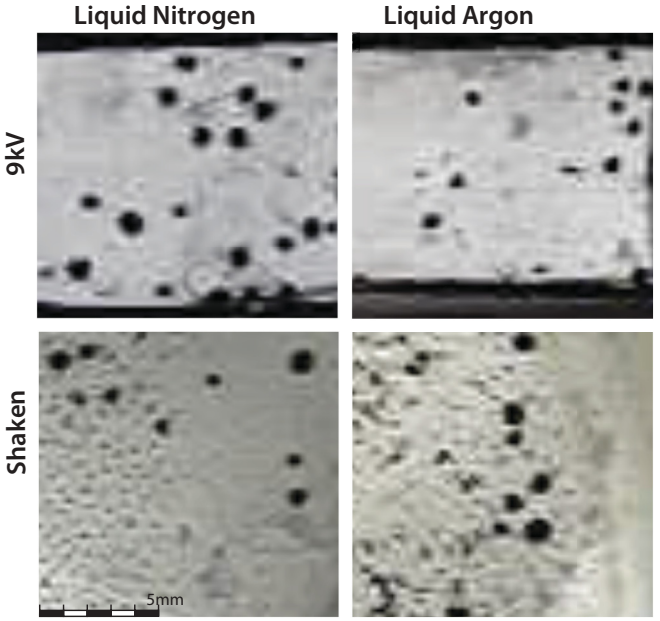

FIG. 4. (Color online) BSCCO σ powder annealed at 850°C inside the capacitor with voltage 9 kV (upper panels) and obtained by shaking in the absence of electric field (lower panels).

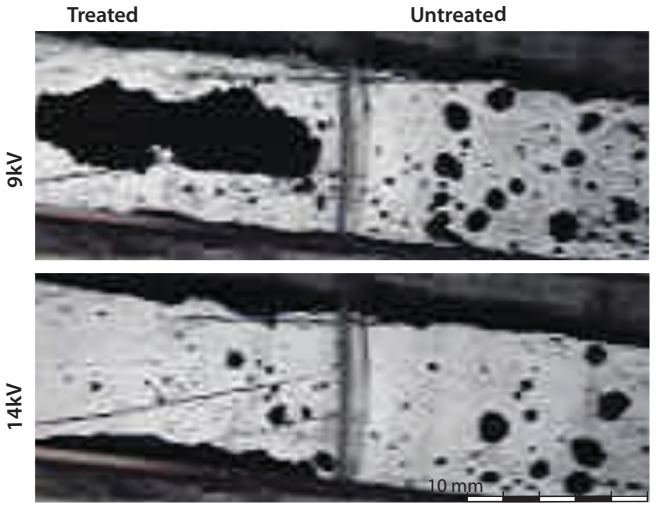

FIG. 5. (Color online) YBCO heat treated to 800°C (left panels) and untreated (right panels) in capacitor in liquid nitrogen. Voltage between capacitor plates is 9 kV in upper panels and 14 kV in lower panels.

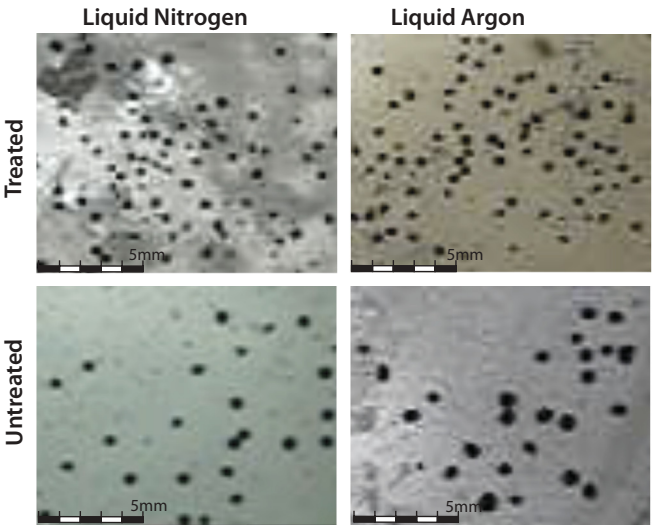

FIG. 6. (Color online) YBCO balls obtained by shaking in container with nitrogen and argon, no electric field. Upper panels: sample heat treated to 800°C; lower panels: untreated sample.

capacitor with an electric field (upper panels) and obtained by shaking without an electric field (lower panels). Since the critical temperature for this sample was 73 K, all cases correspond to temperatures higher than T_c. It can be seen that the balls look very similar in all cases.

Figure 5 shows results for YBCO heat treated to 800°C (left panels) [see (ii) in previous subsection for description of heat treatment] and untreated (right panels) in the capacitor in N_2. Initially (upper panels) we brought the voltage between capacitor plates to 9 kV. The untreated powder (which exhibits a Meissner effect) forms balls under this voltage, while the heat-treated powder did not. When we then raised the voltage to 14 kV, the heated powder also formed balls as seen in Fig. 5. There was also powder clinging to the electrodes both below and above T_c, as the right and left sides of Fig. 5 illustrate.

We also investigated ball formation under shaking in these samples, both in N_2 and Ar, and show representative images in Fig. 6. Again no discernible difference is seen among the four different cases.

Next we turned to the conventional temperature superconductors MgB_2 ($T_c = 39$ K), Pb ($T_c = 7.2$ K), and Zn ($T_c = 0.875$ K), samples (iii), (iv), and (v). It was found that balls still formed under shaking, however, the agglomeration process took several more minutes and the resulting balls for Pb and Zn were considerably smaller than in the other cases, of diameter less than 0.3 mm. We show a snapshot of the balls formed in Fig. 7. We also show in Fig. 7 balls obtained from insulating YBCO (green phase) [see Sec. IV A (ii)].

We also attempted to form balls by the same shaking procedure in water at room temperature. No tendency to agglomeration was found despite repeated attempts. Figure 8 shows examples of snapshots obtained during the shaking process for BSCCO micrograins (size less than 32 μm as always) obtained from grinding the BSCCO disk with transition temperature above 100 K. No tendency to agglomeration whatsoever was found despite repeated attempts, as Fig. 8 illustrates. We repeated these experiments in ethanol and methanol close to their solidification temperature (159 K and 175 K) and found behavior similar to that shown in Fig. 8, with no tendency to ball formation.

V. NATURE OF THE BALLS FORMED

The balls formed by shaking or in the capacitor remain stable when the liquid evaporates and the container heats to room temperature, provided the heating proceeds slowly enough to prevent violent boiling. In this section we discuss some properties of the balls obtained for the case of high-temperature superconductors (BSCCO and YBCO).

In a typical run we obtain a distribution of ball sizes. Figure 9 shows an example. The maximum ball size found was of order 2 mm diameter, both in the cases where balls

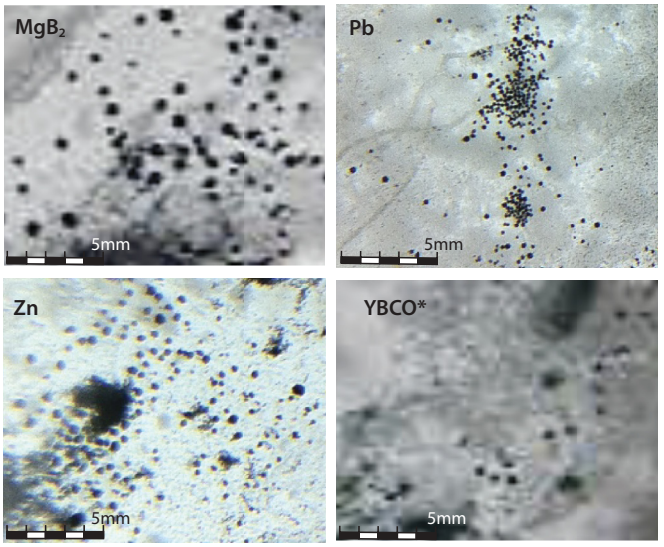

FIG. 7. (Color online) Balls obtained by shaking powders in liquid nitrogen: MgB_2, Pb, Zn, and underdoped YBCO (green phase).

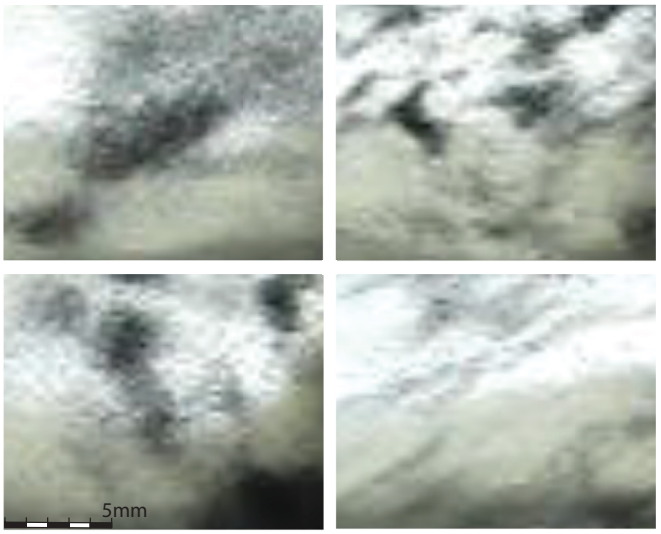

FIG. 8. (Color online) Shaking of BSCCO micrograins in water at room temperature does not result in agglomeration and ball formation; the powder remains highly dispersed. The four panels show snapshots separated by several minutes of shaking each.

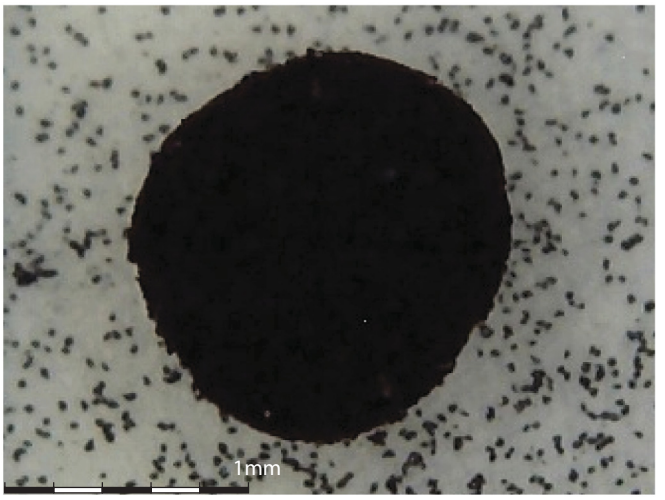

FIG. 10. (Color online) A typical BSCCO large ball of diameter approximately 1.5 mm formed by microparticles smaller than 32 μm, surrounded by microparticles that passed through a 32-μm sieve but did not pass through a 25-μm sieve. The microparticles forming the ball are of this size and smaller.

were formed by shaking as well as in the capacitor. Figure 10 shows a typical large ball, of diameter 1.5 mm, surrounded by microparticles of diameters between 25 μm and 32 μm. All microparticles used in forming these and other balls passed through a 32-μm sieve, as discussed in Sec. II, hence none are larger than those shown in Fig. 10. However, most of the microparticles forming the balls are substantially smaller than those shown in Fig. 10 surrounding the ball, as illustrated in Fig. 11 where we show a ball of 1 mm diameter in various stages of decomposition.

It appears that the presence of small microparticles is essential to the process of ball formation. We attempted to form balls composed of microparticles of large sizes only, and found that balls didn't form when the minimum size of the microparticles was 32 μm or larger. We did succeed after shaking gently for several minutes to form balls with microparticles restricted to the range 25 μm to 32 μm. Figure 12 shows examples of such balls obtained. Note that the surface of a ball here is rougher than that of the larger ball shown in Fig. 10, where the powder contained also a large number of microparticles smaller than 25 μm. In addition to being more difficult to form, the balls formed when the micrograin size was restricted to larger than 25 μm were found to be substantially more fragile than those that included smaller micrograins.

We measured the density of the balls at room temperature for BSCCO (sample (vi) in Sec. IV A) in various runs, and

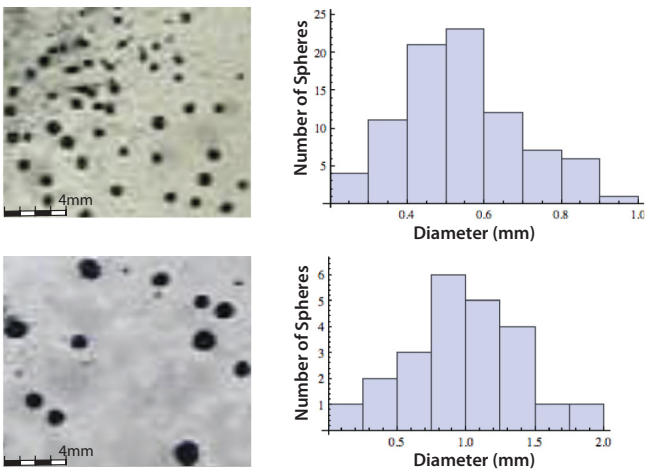

FIG. 9. (Color online) Two examples of balls formed by shaking BSCCO in nitrogen. The smaller balls (top figure) formed first after about two minutes of shaking, the bottom figure showing bigger balls is a snapshot taken after approximately two more minutes of shaking. The right side of the figures shows histograms of the ball sizes for both cases.

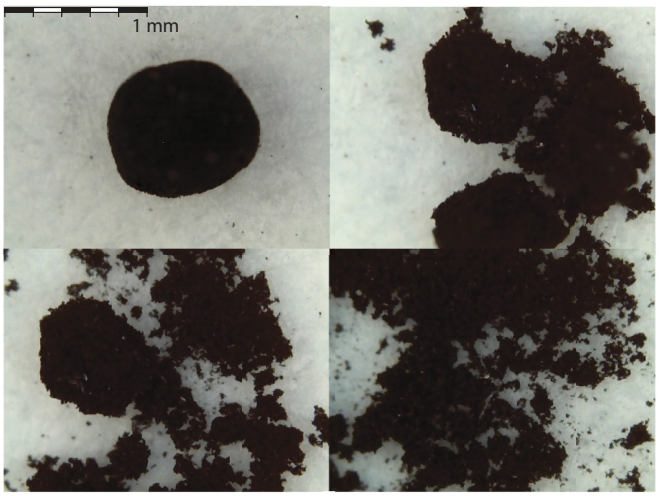

FIG. 11. (Color online) A typical BSCCO ball of diameter approximately 1 mm in varius stages of decomposition.

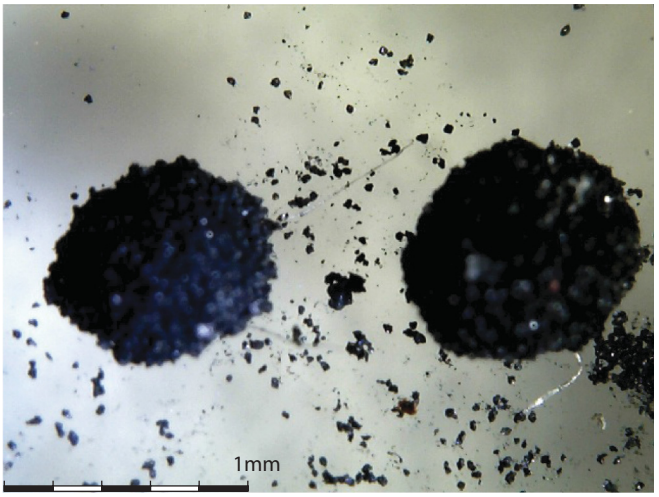

FIG. 12. (Color online) Two balls formed from agglomeration of particles of sizes between 25 μm and 32 μm only.

found that it ranged between 1.2 g/cm^3 and 1.6 g/cm^3. In contrast, the dry powder of microparticles of diameter <32 μm used in forming the balls, when put in a glass tube and gently shaken, reached a density between 1.8 g/cm^3 and 2 g/cm^3, and the disks from where the powders were obtained had density between 3.3 g/cm^3 and 3.6 g/cm^3. This indicates that the balls are quite loosely assembled and have significant voids between micrograins. There was no apparent difference in the density of balls formed by shaking and in the capacitor.

Nevertheless, the balls are remarkably stable, both in liquid nitrogen and in air at room temperature. We found that at room temperature balls that formed either by shaking or in the capacitor could be dropped from a height of at least 10 cm without breaking. The measured terminal velocity was of order 80 cm/s. In the capacitor, we found that balls bouncing back at forth at speeds of order 10 cm/s were stable, and in the shaking experiments balls moving at that speed were also stable.

VI. NONSUPERCONDUCTING MATERIALS

In the previous sections we have found that superconducting material microparticles aggregate into spheres in liquid nitrogen and argon both in the presence and in the absence of electric fields, as well as below and above their superconducting transition temperatures. The question then arises, can spherical aggregation also occur with nonsuperconducting particles?

The answer is yes. Figure 13 shows results for five different substances, as well as for superconducting BSCCO, obtained following the same shaking procedure described earlier. For all materials the size of microparticles used was considerably smaller than 32 μm. Of these materials we found that only for Al_2O_3 there seemed to be no tendency for spherical aggregation. For the other materials aggregation was found and the spheres obtained were of diameter up to $\sim$1 mm. While it took different amounts of time to get aggregation, the balls formed appeared to be very similar to those found in superconducting materials, as Fig. 13 illustrates.

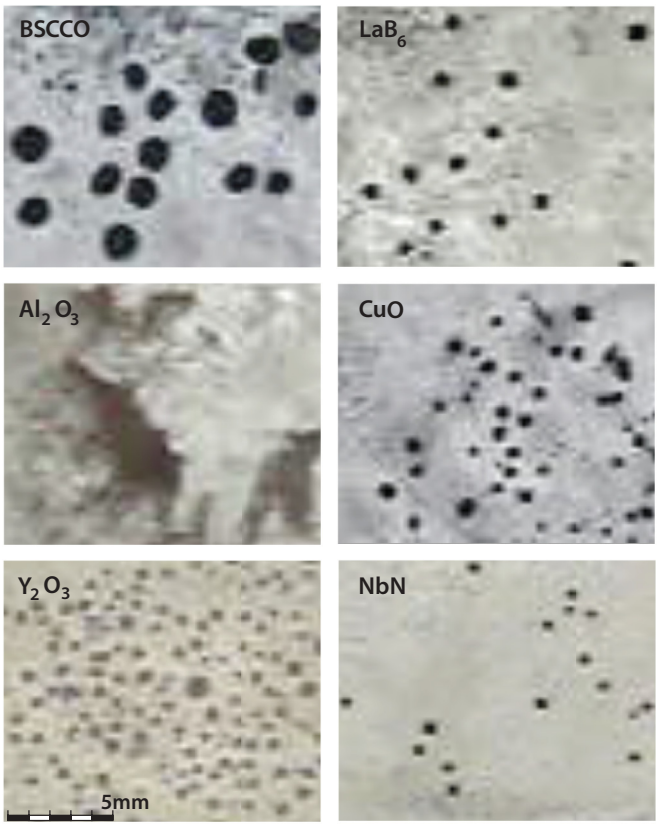

FIG. 13. (Color online) Spherical aggregation of various substances obtained by shaking of microparticles in liquid nitrogen.

VII. PHYSICS OF SPHERICAL AGGLOMERATION

Spherical agglomeration of both superconducting and nonsuperconducting particles has been previously reported,[1,13] however the explanations for the agglomeration[1,14] are incapable of explaining the phenomenon presently shown. Prior explanation of the aggregation of superconducting microparticles argued that the presence of an external electric field created a new type of surface tension in superconducting particles, which caused them to aggregate into spheres. However, we have shown in this paper that these same microparticles will aggregate even in the absence of an electric field, which discredits this argument. Agglomeration of nonsuperconducting microparticles has previously been attributed to bridging, which requires the use of two fluids as well as the microparticles. In the experiment here only N_2 (or Ar) is present in liquid form and it has been shown that water from the atmosphere cannot act as a bridging agent significantly below it's melting point[15] and the nitrogen was kept from boiling so there was also no gas-liquid surface to facilitate bridging. Agglomeration of nonsuperconducting microparticles has been reported in the absence of a bridging agent for submicron particles,[16] and attributed to attractive Van Der Waals forces between the particles. The aggregation reported here of particles considerably larger than submicron cannot be explained by these traditional methods indicating a process that produces spherical agglomeration in a wide variety of microparticles at liquid nitrogen and argon temperatures.

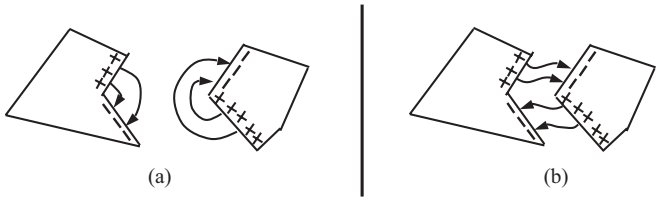

FIG. 14. Schematic depiction of charged planes of neighboring microparticles and surrounding electric field lines for (a) microparticles far apart and (b) microparticles closer together.

We conjecture that the forces giving rise to agglomeration in the cases considered here are predominantly electrostatic. The agglomeration appeared to be strongest for materials that are also high-temperature superconductors. These materials (including MgB_2) have as a common feature the presence of *planes* with a large charge imbalance. The high-T_c cuprate materials have negatively charged CuO_2 planes with two excess electrons per unit cell and compensating positively charged planes in between. MgB_2 has negatively charged B^- planes and positively charged Mg^{++} planes. For irregularly shaped microparticles there are likely to be sections where either a negatively or a positively charged plane is closest to the surface, and as a consequence electric field lines going from the negatively to the positively charged surface of a microparticle. It would then be energetically advantageous to join the electric field lines of neighboring microparticles as in the arrangement shown in Fig. 14 and bring the microparticles close together. This physics is related to the fact that quite generally a crystal will have different work functions for surfaces parallel to different crystal planes, and hence an electric potential difference between different surfaces and electric fields around them. We conjecture that the layered high-temperature superconducting materials have larger differences between work functions for different crystal planes than other materials.

As a rough estimate of the energetics involved, consider two surfaces of neighboring microparticles facing each other, of area $A = (10\ \mu\text{m})^2$ at a distance (determined by the surface roughness) of $d = 1\ \mu$m, with a potential difference of 5 V. The electrostatic energy associated with this is $U = CV^2/2 \sim 10^{-14} J$, with $C = \epsilon_0 A/d$. If these are grains of density $\rho = 3\ \text{g/cm}^3$ and volume $V = (10\ \mu\text{m})^3$ moving at speed $v = 10$ cm/s, their kinetic energy is $K = 1/2\rho V v^2 \sim 10^{-14} J$ (i.e., of the same order). This is consistent with the fact that we observe the balls to be stable in liquid nitrogen for speeds of that order and become unstable for larger speeds. For microparticles of larger volume and mass, the kinetic energy increases proportionally to the volume while the potential energy gained in joining microparticles will increase not faster than the surface area, hence the speed at which they break apart should become smaller, consistent with our observations.

The hypothesis that the forces causing agglomeration are electrostatic is also consistent with the fact that we did not find agglomeration in water (Fig. 8). Water has negative OH^- and positive H^+ (or H_3O^+) ions in solution and these ions should screen the electric fields near the surface of microparticles and inhibit the aggregation process. The microparticles themselves can also create further ionization of water in addition to the self-ionization so that no aggregation should occur even with a high concentration of microparticles. The same physics presumably inhibited aggregation in the solutions with ethanol and methanol.

VIII. SUMMARY AND CONCLUSION

In this paper we reported results showing that: (i) in a capacitor, ball formation is induced by application of a high voltage between the plates if the electrodes are conducting but not if they are insulating, (ii) aggregation of microparticles into balls occurs also in the absence of an applied electric field, (iii) balls formed below T_c remain robust when the temperature is raised above T_c, (iv) balls form both below and above T_c in liquid N_2 and liquid Ar for a variety of cuprate superconductors, (v) MgB_2, Pb, and Zn agglomerate into spheres at temperatures well above their respective T_c, (vi) insulating YBCO also agglomerates into spheres in liquid nitrogen, and (vii) microparticles of several different nonsuperconducting materials suspended in liquid nitrogen also aggregate into spheres of mm dimensions upon shaking.

Our findings show significant differences with the findings reported by Tao *et al.*[1–4] Tao *et al.* reported that (i) an electric field drives formation of superconducting balls, (ii) the balls become fragile if the electric field is turned off, (iii) there is a lower critical electric field E_{c1}, which is frequency dependent, below which balls don't form, (iv) the radius of balls decreases when the electric field increases, (v) in a large electric field, powder that clings to the electrodes below T_c will fly off above T_c, (vi) balls of BSCCO formed in nitrogen break apart when liquid argon is added to increase the temperature, (vii) balls don't form above the superconducting transition temperatures, (viii) balls formed at liquid nitrogen temperature become fragile at room temperature, (ix) granular particles making the balls are closely packed, and (x) the surface of the grains needs to be conducting for balls to form. Each one of these findings is in disagreement with our findings.

Additionally, Tao *et al.* reported that the radius of the balls is a function of the ac frequency of the electric field, that the radius of MgB_2 balls goes linearly to zero as the temperature approaches T_c from below, and that balls break up when a strong magnetic field is applied. We have not tested these findings directly but conclude in view of our other findings that they are unlikely to be correct.

In their study of ball formation in low-frequency ac electric fields,[3] Tao *et al.* reported that the lower critical field for ball formation, E_{c1}, decreased strongly as the frequency decreased and jumped almost discontinuously to a high value at zero frequency (see Figs. 6, 7, and 8 of Ref. 3). For example, for $NdBa_2Cu_3O_x$, E_{c1} decreased smoothly from about 1200 V/mm for frequency 500 Hz to 117 V/mm for 10Hz, and jumped to 760 V/mm for a dc field. Our interpretation of these observations is that the ac field causes "shaking" of the powder in a way similar to our shaking experiments. For higher frequency a larger electric field is needed so that the displacement of the microparticles is sufficient to cause agglomeration, and for very low frequencies the amplitude of the electric field required approaches zero, consistent with our observation that agglomeration occurs also in the absence of electric fields.

Our findings indicate that spherical aggregation of microparticles (both conducting and insulating) suspended in liquid nitrogen and liquid argon is a very general phenomenon. We did not find clear evidence that ball formation is helped by the presence of superconductivity in the sample as predicted theoretically.[7] We did generally find that the easiest and fastest ball formation, particularly of large balls, occurred for microparticles of high-T_c superconductors (BSCCO and YBCO). We hypothesized that a strong tendency to ball formation results from the existence of charged planes in the structures. Whether or not there are subtle changes in the tendency to ball formation depending on whether the system is in the superconducting or normal state remains an open question.

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