Superconductivity in Granular Systems Built from Well-Defined Rhombohedral Bi Clusters: Evidence for Bi-Surface Superconductivity

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Granular systems built from well-defined Bi clusters with rhombohedral bulk structure show, in contrast to bulk Bi, the occurrence of superconductivity. The experimental facts of a strong size dependence of T_c and an influence of the surrounding matrix or adsorbed gas on normal-state resistivity $\rho(0)$ and T_c can be satisfactorily explained by assuming the occurrence of surface superconductivity due to a strongly increased density of states $N(\epsilon_F)$ at the cluster surface.

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The rapidly developing field of cluster physics bridges the traditionally separated fields of atomic (molecular) physics on one side and that of solid-state physics on the other one. New interesting physical properties may be found in such clusters in comparison with those of the bulk material. The electronic properties of metal clusters, for example, are expected to be different from those of the corresponding bulk materials mainly due to the following reasons: (i) The crystallographic structure of the clusters may be different from that of the bulk material;[1] (ii) there is a large fraction of surface atoms N_s; (iii) so-called quantum-size effects (QSE) will appear below a temperature T_0 when the average splitting ΔE between electronic levels[2] becomes larger than kT_0.

The superconducting properties of metal clusters have been of interest for many years.[3] Zeller and Giaever,[4] for example, studied *isolated,* superconducting Sn clusters, embedded in an oxide barrier. They found an *increase* in the superconducting transition temperature T_c with decreasing cluster size, exceeding T_c of bulk Sn for $L \lesssim 4$ nm. Surface effects have been proposed to be responsible for the T_c enhancement.[5] QSE, which should result in a disappearance of superconductivity at very small L,[6] have not been seen in these experiments. If superconductivity in granular systems, built from metal clusters, is studied by transport measurements *above* the percolation threshold, the clusters form a *connected* percolation network of infinite (sample) size. In this case only structural or surface effects will have an influence on the superconducting transition. Such surface effects can be of either phononic or electronic nature. In the former case a lattice softening is expected,[5,7] which according to McMillan's theory[8] leads to an increase in the electron-phonon coupling constant and consequently a T_c enhancement in agreement with experimental data.[9] Surface effects of electronic nature, on the other hand, may be caused by a change in the band structure at the surface and consequently a change in the electronic density of states $N(\epsilon_F)$ at the Fermi surface. Such effects will be exceptionally large for metals with a very peculiar band structure, for example, for the semimetal Bi: Transport properties of *non*superconducting thin films of crystalline Bi, measured as a function of film thickness d ($d \gtrsim 20$ nm), indicate a dramatic increase in $N(\epsilon_F)$ with decreasing d.[10]

We have studied the superconducting properties of granular films built from well-defined crystalline (rhombohedral) Bi clusters far above the percolation threshold. These granular films have been prepared by a new method,[11] namely, by the *in-beam* preparation of metal clusters of well-defined size L followed by a deposition together with a matrix atomic beam on a substrate at low temperatures. We find that these granular films are superconducting. This is the first time that superconductivity is found in small metal clusters while the bulk material with the same structure is *not* superconducting. Furthermore, the superconducting transition temperature T_c strongly depends on cluster size L (surface fraction), with $T_c \lesssim 2$ K for $\bar{L} \gtrsim 20$ nm, and T_c as well as the normal-state conductivity σ are strongly influenced by the surrounding matrix or adsorbed gas on the cluster surface. These experimental facts can be satisfactorily explained if we assume the occurrence of Bi surface superconductivity. It is attributed to a strongly enhanced density of states $N(\epsilon_F)$ at the cluster surface.

Samples were obtained as described in detail in a previous paper.[11] Bi clusters of well-defined size L were prepared *in beam* in a so-called cluster source.[12] In this way, Bi clusters of mean size $\bar{L}$ between 2.5 and 40 nm, with a typical half-width of the cluster size distribution of ~ 1.5 nm, can be produced. The mean cluster size and the cluster size distribution were measured by transmission electron microscopy with the help of a carbon-foil "catcher," held at 300 K, which was brought for a short time ($\lesssim 0.5$ s) into the cluster beam. Bi clusters were deposited either together with a matrix (M) atomic beam (M=Kr, Xe, Ge) or at a partial pressure of $\simeq 10^{-6}$ mbar of O_2 or H_2 onto a cold ($\simeq 40$ K) sapphire substrate mounted on the cold finger of a variable-temperature ($2 \leq T \leq 300$ K) helium cryostat. The residual vapor pressure in the cryostat was $\simeq 5 \times 10^{-8}$ mbar; typical film thickness were $\simeq 150$ nm. The dc

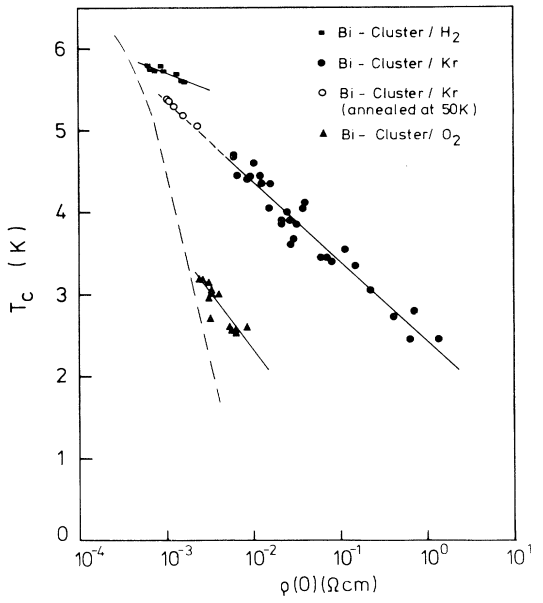

FIG. 1. Superconducting transition temperature T_c vs normal-state resistivity $\rho(0)$ for granular films built from Bi clusters (mean size $\bar{L}\simeq 0.38$ nm) embedded in Kr or with H_2 (O_2) gas adsorbed on the cluster surface. The solid lines are only a guide to the eye. The dashed line is the T_c vs $\rho(0)$ dependence observed for amorphous Bi/Kr (Ref. 13).

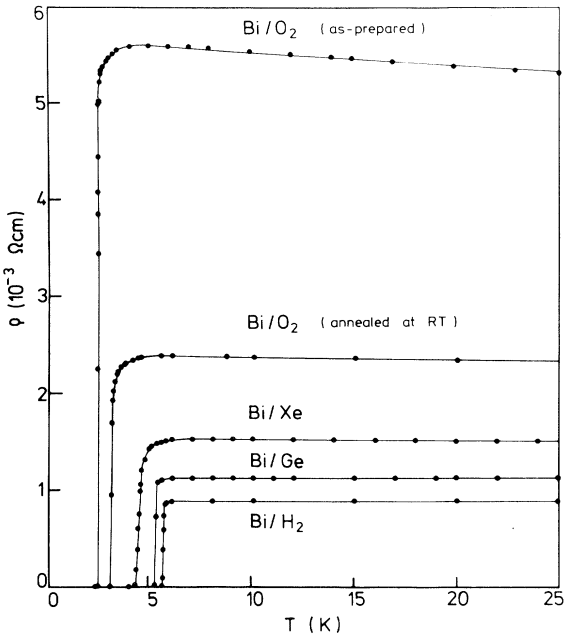

FIG. 2. Temperature dependence of the resistivity of granular films built from Bi clusters (mean size $\bar{L}\simeq 0.38$ nm) embedded in different matrices (Xe, Ge) or with H_2 (O_2) gas adsorbed on the cluster surface.

conductivity of the films was measured by a four-terminal technique in the temperature range $2 \leq T \leq 300$ K.

First experiments were performed with Bi clusters of size $L\simeq 4$ nm embedded in a Kr matrix. All samples Bi_xKr_{1-x} with a composition $x > x_c$, where $x_c = 0.34$ is the percolation threshold,[11] exhibit a superconducting transition at T_c. The value of T_c decreases with increasing x or increasing normal-state resistivity $\rho(0)$, extrapolated to $T = 0$ K, as shown in Fig. 1. This decrease in T_c is rather weak compared to that observed in amorphous Bi/Kr composites (see dashed curve in Fig. 1). This fact indicates that effects of weak localization and/or electron-electron interaction, responsible for the T_c decrease in amorphous Bi/Kr,[13] are rather small in the Bi-cluster/Kr system, as expected from theoretical arguments.[14]

Additional experiments with Bi clusters of mean size $L\simeq 4$ nm, using other matrices (Xe, Ge) or adsorbed gas (O_2,H_2) on the Bi-cluster surface during cluster deposition, revealed a strong dependence of $\rho(0)$ and T_c on the surrounding matrix or adsorbed gas, as can be seen in Fig. 2: The lowest $\rho(0)$ and highest T_c were observed for Bi clusters with H_2 adsorbed on the cluster surface, while O_2 adsorption results in the highest $\rho(0)$ and lowest T_c values. Annealing of the latter system at room temperature and successive cooling down to $\simeq 2$ K showed a decrease in $\rho(0)$ and increase in T_c (see Fig. 2). Further studies with O_2 and H_2, where the amount of adsorbed gas has been varied, showed, similar to the Bi-cluster/Kr system, a decrease of T_c with increasing $\rho(0)$ (see Fig. 1). The T_c-$\rho(0)$ curves, however, are definitely different for the three systems studied.

In order to understand the origin of the occurrence of superconductivity in the above given systems of Bi clusters with mean size $\bar{L}\simeq 4$ nm, we have varied the Bi-cluster size L. All these experiments were performed using Kr as a matrix gas and at a composition far above the percolation threshold (metal volume fraction $\simeq 0.9$). Figure 3(a) shows the surprising result that T_c linearly decreases with increasing mean cluster size $\bar{L}$ and superconductivity finally disappears ($T_c \lesssim 2$ K) for $\bar{L} \gtrsim 20$ nm. The L dependence of the normal-state conductivity $\sigma(0)$, on the other hand, shows a significant minimum at $\bar{L}\simeq 5$ nm with an almost linear increase in $\sigma(0)$ at large L and a rapid increase at small L [see Fig. 3(b)].

It is a well-known fact that bulk, rhombohedral Bi is not superconducting ($T_c \lesssim 50$ mK), whereas there exist many different crystallographic phases of Bi which are superconducting in the bulk phase: high-pressure phases of Bi called Bi II, III and V with $T_c = 3.9$, 7.2, and 8.5 K,[15-17] respectively, fcc Bi with $T_c \lesssim 4$ K,[18] "amorphous" Bi with $T_c \simeq 6$ K,[19] and Pb- or K-doped $BaBiO_3$.[20] For this reason it is necessary to determine the structure of our Bi clusters. Since we cannot perform *in situ* x-ray-diffraction experiments on our Bi-cluster films,

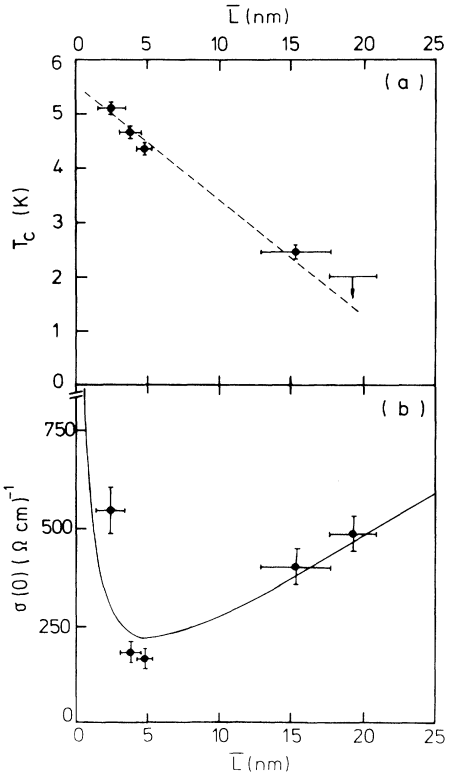

FIG. 3. (a) Bi-cluster-size dependence of superconducting transition temperature T_c and (b) normal-state conductivity $\sigma(0)$ for Bi-clusters embedded in a Kr matrix (metal volume fraction $\simeq 0.9$). The solid line in (b) is a simulation of $\sigma(0)$ as described in the text.

we had to heat the films to room temperature (RT) and remove them from the cryostat. Such a procedure obviously was not possible for the films using Kr or Xe as a matrix gas. However, it also failed for the Bi/Ge system due to the occurrence of cracks in the film during the temperature cycling. The only system which could be annealed to RT for x-ray-diffraction analysis and cooled down again in order to check if the annealed films were still superconducting was the system Bi/O_2. The x-ray diffractogram of Bi clusters of mean size $\bar{L} \simeq 4$ nm with O_2 adsorbed on the cluster surface can be seen in Fig. 4. Comparison with the diffraction peaks of rhombohedral Bi (see dashed vertical lines in Fig. 4) clearly shows that the Bi clusters have the rhombohedral structure with essentially the same lattice parameters as those of bulk Bi. The width of the diffraction peaks is that which one would expect for clusters with size $L \simeq 4$ nm. Our finding is in good agreement with that of Yokozeki and Stein who measured the structure of Bi clusters of similar size, obtained by a supersonic jet expansion, *in beam* by electron diffraction.[1] As already mentioned above, these RT-annealed Bi/O_2 films are still superconducting when cooled down again to low temperatures (see Fig. 2).

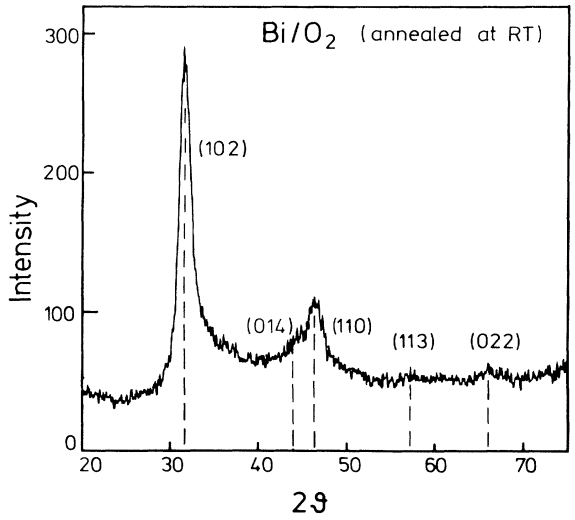

FIG. 4. X-ray-diffraction pattern of granular film built from Bi clusters (mean size $\bar{L} \simeq 0.38$ nm) with O_2 gas adsorbed on the cluster surface. The dashed vertical lines give the diffraction peak positions of rhombohedral bulk Bi.

Thus, we are now confronted with the experimental finding of superconducting, rhombohedral Bi clusters for $\bar{L} \lesssim 20$ nm. We explain this finding together with the additional experimental facts (linear decrease of T_c with cluster size L, strong influence of surrounding matrix or surface-adsorbed gas on T_c) by the occurrence of *surface superconductivity* due to a strongly enhanced density of states $N(\epsilon_F)$ at the Bi-cluster surface. A strong increase in $N(\epsilon_F)$ for very thin crystalline (rhombohedral) Bi films has already been postulated by Komnik *et al.*[10] (see above); however, no observation of superconductivity was reported in this work.

Assuming such a surface superconductivity, we can explain *all* of our experimental findings in the following way: (i) The surface density of states is influenced by the surrounding matrix or surface-adsorbed gas. For example, O_2 adsorption leads to a reduction in $N(\epsilon_F)$ (O_2 acts as an electron "acceptor") while H_2 adsorption increases $N(\epsilon_F)$ (H_2 acts as an electron "donor"). Consequently, $\sigma(0)$ and T_c are decreased (increased) by O_2 (H_2) adsorption. This explanation is further supported by the fact that the T_c values for the systems Bi/H_2, Bi/Kr, and Bi/O_2 with the highest metal volume fraction [highest T_c and $\sigma(0)$ values] lie on the T_c-$\rho(0)$ curve of amorphous Bi/Kr (see Fig. 1). In the latter case it was shown by Hall-coefficient measurements that the decrease of T_c is mainly caused by a decrease in the density of states.[13] (ii) The surface/volume ratio decreases with increasing cluster size L. Thus T_c will decrease with increasing L due to the proximity effect, if we make the reasonable assumption that the cluster core, similar to bulk Bi, is *not* superconducting.

This "two-phase" model [superconducting surface lay-

er with large $N(\epsilon_F)$ and consequently large $\sigma(0)$, and "semimetallic" core with small $N(\epsilon_F)$ and small $\sigma(0)$, similar to bulk Bi] even allows us to explain the observed L dependence of $\sigma(0)$ as shown in Fig. 3(b). Using such a simple model, the effective conductivity is roughly given by $\sigma_{\text{eff}}=\sigma_s 2d/L+\sigma_c(L-2d)/L$, where σ_s and σ_c are the normal-state conductivity of the surface layer and core, respectively, and d is the surface-layer thickness. σ_c depends on the cluster core size if we assume that the elastic mean free path l_e within the core is given by the core size, i.e., if we assume $\sigma_c \propto L-2d$. The solid line in Fig. 3(b) is a simulation for $\sigma_{\text{eff}}(L)$ with $\sigma_c \simeq 25$ $\Omega^{-1}\text{cm}^{-1}$ for $l_e=1$ nm and $\sigma_s d/(1\text{ nm}) \simeq 300$ Ω^{-1} cm^{-1}. If we assume a surface-layer thickness of 0.3 nm we get a surface conductivity of $\sigma_s \simeq 10^3$ $\Omega^{-1}\text{cm}^{-1}$, which is a factor of about 5 smaller than that of amorphous Bi.[21] The cluster core conductivity σ_c, on the other hand, seems to be about 1 order of magnitude higher than the value one would expect for bulk Bi with l_e given by the cluster core diameter $[\sigma(0)_{\text{bulk Bi}}=3\times10^4$ $\Omega^{-1}\text{cm}^{-1}$ for $l_e \simeq 8$ μm (Ref. 22)]. Our "two-phase" model certainly is a simplification. A continuous decrease in $N(\epsilon_F)$ going from the surface to the core may be more appropriate.

Thus we come to the conclusion that the assumption of surface superconductivity due to a strongly increased density of states $N(\epsilon_F)$ at the cluster surface can explain all of our experimental findings with respect to T_c, and also give a satisfactory explanation for the observed cluster-size dependence of the normal-state conductivity σ. The occurrence of surface superconductivity in Bi clusters due to a strongly enhanced $N(\epsilon_F)$ at the cluster surface certainly is a special case due to the peculiar band structure of bulk Bi. Other surface effects, e.g., surface phonons, usually responsible for the T_c enhancement in metal clusters[5,7] seem to play a minor or even negligible role in the case of Bi clusters. However, we have to confess that explanations other than surface superconductivity in principle could be possible, such as, for example, a change in the atomic structure of Bi in small clusters compared to that in bulk Bi. For that reason we suggest that photoelectron spectroscopic studies be performed on bulk Bi surfaces, in order to confirm our proposal of strongly enhanced density of states at the Bi surface.

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