# Influence of cluster size on the normal- and superconducting-state properties of granular Bi films

C. Vossloh, M. Holdenried, and H. Micklitz
*II.Physikalisches Institut, Universität zu Köln, Zülpicherstrasse 77, D-50937 Köln, Germany*
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The Hall coefficient $R_H$ and the magnetic-field dependence of the superconducting transition temperature $T_c$ of granular films built from well defined Bi clusters has been measured as a function of Bi cluster size $L$ ($3.5 \leqslant L \leqslant 10$ nm) in magnetic fields up to 8 T and at temperatures $T > 1.8$ K. From these experimental results we can conclude that with decreasing $L$ the original rhombohedral bulk structure of the Bi clusters becomes more and more distorted (increasing number of defects), until at $L = L^* \approx 4.0$ nm the structure changes into the ''amorphous'' Bi structure. For $L = L^*$ the Bi conduction electrons become almost localized and $(dB_{c2}/dT)_{T_c}$ has an unusually large value of $-16.7$ T/K. The good agreement between the $L$ dependencies of normal and superconducting properties indicates that the electronic structure of the Bi clusters changes with $L$, but is rather homogeneous for a given $L$. [S0163-1829(98)02042-6]

## I. INTRODUCTION

Rhombohedral bulk Bi is a semimetal which is *not* superconducting down to $T = 50$ mK. In contrast to this, granular Bi films prepared from rhombohedral Bi clusters with well-defined size $L$ show superconductivity with a cluster size dependent superconducting transition temperature $T_c$ (e.g., $T_c = 4.3$ K for a mean cluster size $L \approx 5$ nm and $T_c < 2$ K for $L \approx 20$ nm).[1] We have explained the appearance of superconductivity in granular Bi on the basis of the following model:[1] Bi clusters have a surface layer with a strongly increased density of states $N(E_F)$ at the Fermi energy[2] which leads to ''surface superconductivity;'' the cluster core remains ''semimetallic'' (similar to bulk Bi), i.e., is *not* superconducting. This model essentially can explain all experimental facts known at that time. However, further experimental data definitely are necessary in order to decide if the above given model is indeed correct. It is for this reason that we have performed additional experiments on granular Bi films, namely, measurements of the Hall constant $R_H$ and the change of $T_c$ with applied external magnetic field $B$, i.e., of $(dB_{c2}/dT)_{T_c}$. Such experiments give information on the conduction electron density $n_e$ as well as on $N(E_F)$. The measurement of both $R_H$ and $(dB_{c2}/dT)_{T_c}$ as a function of Bi cluster size $L$, therefore, will allow us to examine in more detail how the electronic structure of Bi clusters changes with $L$. First preliminary results already have been published elsewhere.[3]

## II. EXPERIMENTAL SETUP

Experiments were performed with a so-called inert-gas aggregation cluster source[4,5] which was attached to a He cryostat. Two different He cryostats have been used: the Hall effect experiments have been performed in a $^4$He cryostat (cryostat $A$) with superconducting split-coil magnet allowing experiments in magnetic fields up to 4.5 T for temperatures $T > 1.8$ K; the measurements of $(dB_{c2}/dT)_{T_c}$ were mostly done in a $^3$He cryostat (cryostat $B$) with a superconducting split-coil magnet for magnetic fields $B < 8$ T and $T > 0.45$ K; both cryostats allowed a variable $B$-direction with respect to the film surface (see below).

Granular films of Bi clusters embedded in an insulating Kr matrix were obtained by the co-deposition of Bi clusters emerging from the cluster source and the Kr gas atoms onto a cold ($\approx 40$ K) sapphire substrate attached to the coldfinger of the He cryostat. Both deposition rates were controlled by quartz balances. Typical deposition rates for the cluster beam were 0.1 nm/s and typical film thicknesses were 100–150 nm. All films had a Bi cluster volume fraction of $\approx 80\%$, i.e., had a composition far above the percolation threshold.[5] Bi cluster size distribution was determined with the help of a thin carbon foil catcher, brought for a short time in the cluster beam, and analyzed *ex situ* by transmission electron microscopy. Typical cluster size distributions had a width $\Delta L$ (FWHM) of $(\Delta L/L) \approx 0.25$.[6]

Sample geometry and arrangement of the Au electrodes on the sapphire substrate were the same as described in Ref. 7. Electrical transport measurements were done in both cryostats *in situ* by lowering the sample holder into the bore of the superconducting split-coil magnet. Magnetic field direction for Hall effect measurements in cryostat ($A$) was perpendicular to the film surface and the current direction. Magnetic field direction for $(dB_{c2}/dT)_{T_c}$ measurements could be changed from perpendicular to parallel to the film surface by rotating the He cryostat inset within the bore of the superconducting magnet. In this way the magnetic field dependence of $T_c$ could be measured in the so-called ''force-free'' configuration, i.e. with $B$ and current directions being parallel to each other (see below). Transverse and longitudinal voltages were measured by a dc method for two opposite current and field directions, respectively. In this way misalignment voltages and thermomagnetic effects have been eliminated. The Hall voltage $U_H$ obtained from these four measurements always showed a linear behavior with increasing magnetic field up to 4.5 T allowing the determination of $R_H$ from the slope of $U_H$ vs $B$.

## III. EXPERIMENTAL RESULTS

The Bi cluster size dependence ($3.5 \leqslant L \leqslant 10.0$ nm) of the normal state conductivity $\sigma$, measured at $T \approx 10$ K, is shown

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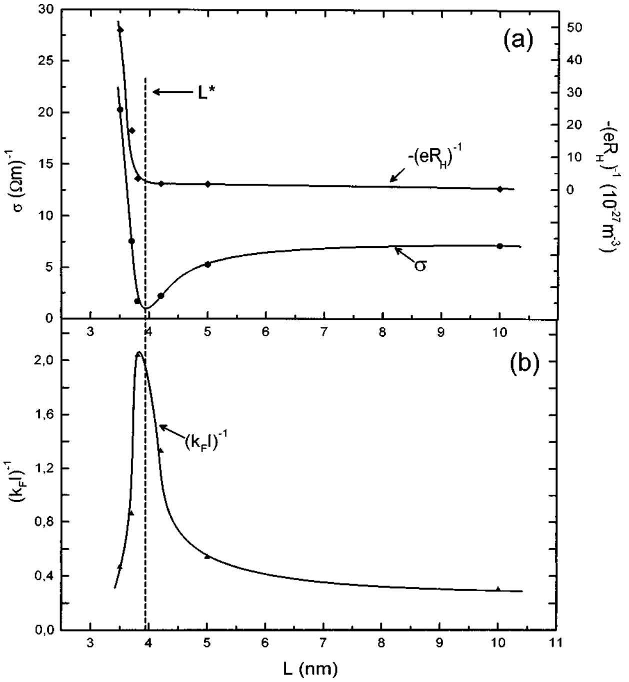


FIG. 1. (a) Normal state conductivity $\sigma$ and conduction electron density $n_e = -(eR_H)^{-1}$, $R_H$ = Hall constant, and (b) $(k_F l)^{-1}$ as obtained from $\sigma$ and $R_H$ within the Fermi gas model of granular Bi films as a function of Bi mean cluster size $L$. The solid lines through the data points are only guides to the eyes. The dashed vertical line indicates the critical cluster size $L^*$ (see text).

in Fig. 1(a). One can see a decrease in $\sigma$ with decreasing $L$ until $\sigma$ reaches a pronounced minimum at $L^* \approx 4.0$ nm. Further decreasing $L$ leads to a rapid increase in $\sigma$ towards the known value for amorphous Bi $[(\sigma)_{\mathrm{Bi,amorph}} \approx 70\ (\Omega\ \mathrm{m})^{-1}$ (Ref. 8)]. These data are in good agreement with those published before for $2.5 \leqslant L \leqslant 20$ nm.[1] On the basis of those $\sigma$ data we had developed the above mentioned ''two-component''-model of the Bi cluster structure. As we will see below this model has to put into question on the basis of the following new experimental data $[R_H$ and $(dB_{c2}/dT)_{T_c}]$.

The Bi cluster size dependence ($3.5 \leqslant L \leqslant 10.0$ nm) of the electron density $n_e \propto R_H^{-1}$ as obtained from the measured $R_H$ values is shown in Fig. 1(a). Here we see a continuous increase of $n_e$ for $L > L^*$ and the same rapid increase in $n_e$ for $L < L^*$ as we observe for $\sigma$ [see Fig. 1(a)]. This clearly shows that the increase in $\sigma$ for $L < L^*$ is caused by a rapid increase in $n_e$ towards the value for amorphous Bi.[8]

We have now additionally plotted in Fig. 1(b) the quantity $(k_F l)^{-1}$ ($k_F$ = Fermi wave vector, $l$ = mean free path) as calculated from $\sigma$ and $R_H$ using the free electron gas model. This quantity, which is a measure for the ''localization'' of the conduction electrons, will appear again in the discussion of the superconducting properties, namely $(dB_{c2}/dT)_{T_c}$ (see below). One sees a rapid increase in $(k_F l)^{-1}$ with decreasing $L$ for $L < 5$ nm until $(k_F l)^{-1}$ reaches a maximal value of $(k_F l)^{-1} \approx 2$ for $L \approx L^*$. Such a high $(k_F l)^{-1}$-value indicates that the conduction electrons are almost localized at this Bi cluster size $L^*$. There is a sharp drop in $(k_F l)^{-1}$ for $L < L^*$ due to the strong increase in $n_e$ and finally $(k_F l)^{-1}$ approaches the value for amorphous Bi.[8]

Next we will show the influence of an external magnetic

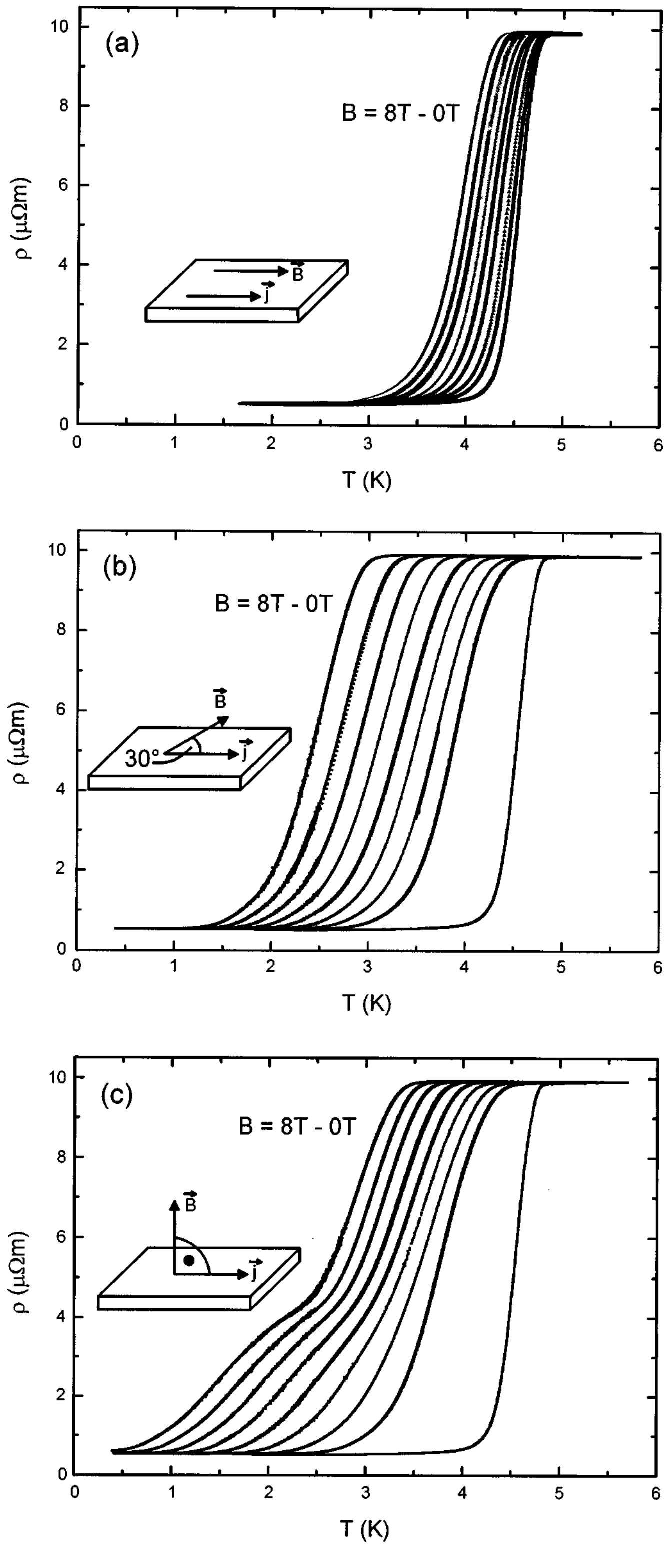


FIG. 2. Resistivity versus temperature for granular Bi film with $L \approx 4.5$ nm as a function of external magnetic field $B$. The insets show the different directions of $B$ relative to the current direction and the film plane, respectively.

field on the superconducting transition occurring at $T_c$. As already mentioned in Sec. II, the direction of magnetic field $B$ relative to the film plane could be changed. Figure 2 shows the resistivity curves for a granular Bi film with $L \approx 4.5$ nm as a function of magnetic field strength for three different

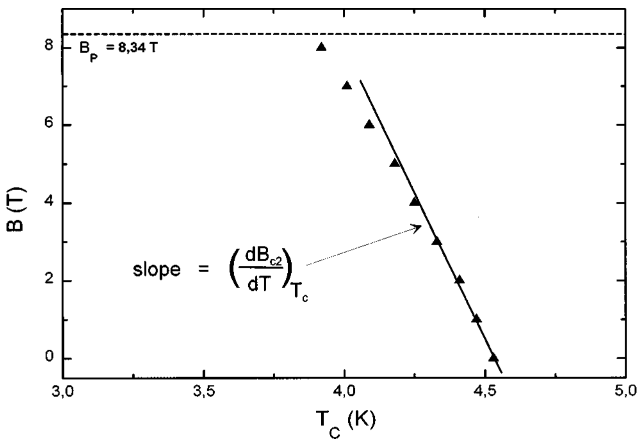


FIG. 3. Magnetic field dependence of superconducting transition temperature $T_c$ of granular Bi film as obtained from Fig. 2(a). The solid line through the data points is a least-squares fit [straight line with slope $(dB_{c2}/dT)_{T_c}$]. The horizontal dashed line gives the paramagnetic (Clogston) limit $B_p$ (see text).

field directions. As expected, the shift of the $\rho(T)$-curves is increasing with increasing angle $\alpha$ between current and field directions. This is due to the fact that for $\alpha \neq 0$ flux line movement caused by the Lorentz and Magnus force acting on the flux lines leads to a longitudinal voltage, i.e., gives rise to resistivity. The interesting thermodynamic quantity $dT_c/dB$ or $(dB_{c2}/dT)_{T_c}$ can be determined from the ''force-free'' ($\alpha = 0$) configuration only. We have plotted in Fig. 3 the magnetic field dependence of $T_c$ as obtained from the resistivity curves in Fig. 2(a) using the midpoint of the transition curve as definition of $T_c$. From such plots one gets the initial slope $(dB_{c2}/dT)_{T_c}$. In this way $(dB_{c2}/dT)_{T_c}$ has been determined for different cluster sizes $L$. The result is shown in Fig. 4. One can see a maximum in $-(dB_{c2}/dT)_{T_c}$ for $L \approx L^*$, similar to that observed for $(k_F l)^{-1}$ [see dashed curve in Fig. 4 taken from Fig. 1(b)]. The value of $-(dB_{c2}/dT)_{T_c}$ for $L \approx L^*$ is more than one order of magnitude higher than that observed for example in ''amorphous''

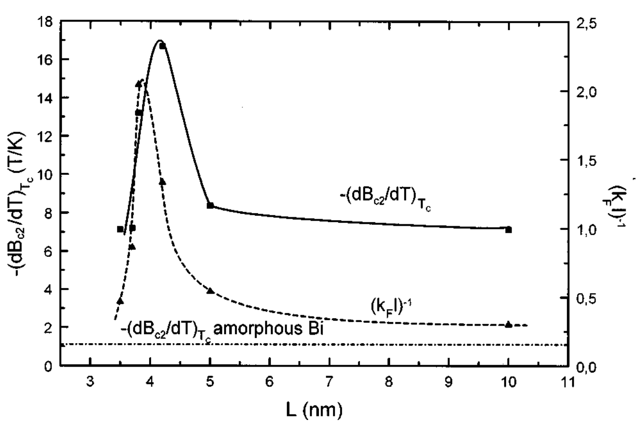


FIG. 4. Values of $(dB_{c2}/dT)_{T_c}$ for granular Bi films as a function of Bi mean cluster size $L$. The solid line through the data points is a guide to the eyes. The dashed curve shows the $(k_F l)^{-1}$ values from Fig. 1(b) for comparison. The $(dB_{c2}/dT)_{T_c}$ value for amorphous Bi (from Ref. 8) is given by the dashed-dotted horizontal line.

Bi [$(dB_{c2}/dT)_{T_c} = -1.12$ T/K (Ref. 8)]. In the following we want to discuss this result together with the $\sigma$ and $R_H$ data.

## IV. DISCUSSION

Considering the $L$ dependencies of $\sigma$, $R_H$ and $(k_F l)^{-1}$, as shown in Fig. 1, we can develop the following model on the changing crystallographic and electronic structure of the Bi clusters with decreasing cluster size $L$. For large $L$ ($L > 5$ nm) we essentially have Bi clusters with the rhombohedral bulk structure. This finding is in agreement with *in-beam* electron diffraction experiments by Yokozeki and Stein[9] on Bi clusters with size $6 \leq L \leq 9.5$ nm prepared in a gas aggregation cluster source. For $L^* < L < 5$ nm the mean free path $l$ within the Bi clusters becomes strongly reduced (seen in the reduction of $\sigma$), while the conduction electron density $n_e$ continuously increases. This indicates that the number of defects in the rhombohedral structure strongly increases, i.e., that this structure becomes highly distorted. Such a distortion shifts $E_F$ relative to the Bi conduction band edge and increases $n_e$ as well as $N(E_F)$ (see below). At $L \approx L^*$, something like a ''critical'' Bi cluster size, there occurs a crystallographic ''phase transition'' from a heavily distorted rhombohedral to the ''amorphous'' Bi structure. The latter structure is known[8] to have a strongly increased $n_e$ and $N(E_F)$ compared to that of rhombohedral Bi [e.g., $n_e(\text{amorphous})/n_e(\text{rhombohedral}) \approx 5 \times 10^5$ (Refs. 8,10)]. Both $\sigma$ and $R_H$ for $L = 3$ nm already are close to the corresponding values for ''amorphous'' Bi. It should be mentioned that the x-ray scattering experiments performed on a granular Bi/$O_2$ film with a Bi cluster size $L \approx 3.8$ nm which revealed the rhombohedral structure of these clusters[1] essentially are in agreement with this model.

The $L$-dependence of $(k_F l)^{-1}$, as obtained from $\sigma$ and $R_H$ data using the Fermi gas model shows a pronounced maximum for $L = L^*$ with $(k_F l)^{-1} \approx 2$ [see Fig. 1(b)]. This means that the crystallographic ''phase transition'' just occurs when the Bi conduction electrons are almost localized. Therefore it would be tempting to interpret the crystallographic ''phase transition'' as being triggered by the disappearance of metallic binding at $L^*$. However, we are not aware of any other system wherein a ''localization-delocalization'' transition causes a crystallographic phase transition. For that reason the opposite probably will be true: the ''localization-delocalization'' transition at $L^*$ is induced by the crystallographic ''phase transition'' which occurs when the number of defects within the rhombohedral structure exceeds a critical value. Next we have to discuss the $L$-dependence of $(dB_{c2}/dT)_{T_c}$. Using Ginzburg-Landau-Abrikosov-Gorkov theory we can connect $(dB_{c2}/dT)_{T_c}$ with the normal state (residual) resistivity $\rho$ and the Sommerfeld constant $\gamma$ via the following equation which is valid in the dirty limit:[11,12]

$$(dB_{c2}/dT)_{T_c} = -(12e/\pi^3 k_B)\gamma\rho \propto N(E_F)\rho. \quad (1)$$

This means that within the Fermi gas model $(dB_{c2}/dT)_{T_c} \propto m^* \cdot (k_F l)^{-1}$, with $m^*$ being the effective ''dressed'' electron mass including electron-phonon interaction. Assuming that $m^*$ does not depend on $L$, the $L$-dependencies of both

$(dB_{c2}/dT)_{T_c}$ and $(k_F l)^{-1}$ should be the same. This is exactly what we observe, especially with respect to their maximum for $L \approx L^*$ (see Fig. 4).

Now we want to make a comment about the absolute value of $(dB_{c2}/dT)_{T_c}$, especially about the unusual large value of $(dB_{c2}/dT)_{T_c} = -16.7$ T/K for $L = 4.2$ nm$\approx L^*$. This value is much higher than those found for the Chevrel phases,[13] once the classical extreme type II-superconductors, and it is as high as those observed for some of the high temperature superconductors (HTS) on the basis of the cuprates and for superconducting heavy fermion systems. We do not know any other superconducting compound which has a similar high $(dB_{c2}/dT)_{T_c}$ value. The high $(dB_{c2}/dT)_{T_c}$ values for the just mentioned three systems are understandable considering Eq. (1): for heavy fermion systems $\gamma$ (or the effective mass $m^*$) is extremely large, in HTS compounds $k_F$ is small due to their small carrier density, and for Bi clusters of size $L \approx L^*$ we have both, a relative small $k_F$ [again due to the small number of conduction electrons $(n_e/n_{\mathrm{Bi}} \approx 0.1)$] and a small mean free path (within the free electron gas model $l \approx 0.15$ nm for $L = L^*$).

The upper critical magnetic field $B_{c2}$ can be extrapolated from $(dB_{c2}/dT)_{T_c}$ using the so-called Werthamer-Helfand-Hohenberg (WHH) theory.[11] In the limit of negligible spin paramagnetism as well as spin-orbit scattering, i.e., for pure orbital pair-breaking, $B_{c2}(0)$ is given by $[B_{c2}(0)]_{\mathrm{WHH}} = -0.693(dB_{c2}/dT)_{T_c}$ which results in $[B_{c2}(0)]_{\mathrm{WHH}} \approx 50$ T for Bi clusters of size $L^*$. This $B_{c2}(0)$ value is quite reasonable: the superconducting coherence length $\xi$ calculated from $B_{c2}(0)$ is $\xi \approx 2.5$ nm, a value which is somewhat smaller than the Bi cluster size $L^*$.

In addition to $[B_{c2}(0)]_{\mathrm{WHH}}$ there exists another critical field, namely, the so-called paramagnetic or Clogston limit $B_p$: at this magnetic field the paramagnetic energy of the electron spins becomes equal to the superconducting condensation energy and a transition from the superconducting to the normal state occurs.[14] In the case of weak spin-orbit coupling this transition is of first order[15] while it becomes continuous for strong spin-orbit coupling. In the first case this critical field is given by $B_p = 1.84 T_c$. Since usually $B_p > [B_{c2}(0)]_{\mathrm{WHH}}$ such a transition has only to be observed in ultrathin films with $B$ being parallel to the film.[16,17] However, for Bi clusters of size $L^*$ with $T_c = 4.6$ K we have $B_p = 8.5$ T which is *much lower* than $[B_{c2}(0)]_{\mathrm{WHH}} = 50$ T and thus in principle the observation of such a transition should be possible. The highest magnetic field we could apply was $B = 8$ T which is just a little below $B_p$. The measured $T_c$ reduction at this field is only about 10% with no indication of a transition to the normal state (see Fig. 4, the dashed horizontal line gives $B_p$). In order to explain this we have to take into account the known strong spin-orbit scattering occurring in Bi [spin-orbit scattering time $\tau_{\mathrm{so}} \approx 5 \times 10^{-13}$ s (Ref. 18)]. This $\tau_{\mathrm{so}}$ corresponds to a spin-orbit coupling parameter[11] $\lambda_{\mathrm{so}} = 2\hbar/3\pi\tau_{\mathrm{so}} k_B T_c \approx 0.8$ and gives an enhancement of $B_p$ by a factor of 1.2,[18] i.e., an increase of $B_p$ to about 10 T which definitely is higher than the highest field we could apply. In this connection we should mention that recent electron tunneling experiments on Al clusters in external magnetic fields revealed that the superconducting gap collapses at much higher fields than theoretical expected and thus indicated the presence of significant spin-orbit scattering whose origin is not fully understood.[19]

Finally we want to make a comment with respect to the model of the crystallographic and electronic structure of the Bi clusters which we have proposed in our previous paper.[1] The new experimental finding, namely, that the $L$-dependencies of the $(k_F l)^{-1}$ values as obtained from the *normal* state properties, i.e., from $\sigma$ and $R_H$, and that of the *superconducting* state property $(dB_{c2}/dT)_{T_c}$ are very similar (see Fig. 4) has a severe consequence: it means that an *inhomogeneous* cluster model (semimetallic, nonsuperconducting cluster core and metallic, superconducting cluster surface layer) probably is not correct. In such an inhomogeneous two-component model it is very unlikely that the $L$-dependencies of normal- and superconducting-state properties are the same. This is simply due to the fact that in the above given two-phase model the effective Hall coefficient is determined by the Hall coefficients of both components[20] while $(dB_{c2}/dT)_{T_c}$ is determined by the electronic properties of the superconducting surface layer only. We thus have to conclude that the electronic structure of the Bi clusters is $L$-dependent (as described above) but rather *homogeneous* for a given $L$.

## V. CONCLUSION

The measurement of the Hall coefficient $R_H$ and the change of the superconducting transition temperature $T_c$ with external magnetic field $B$, i.e., of $(dB_{c2}/dT)_{T_c}$, allows us to draw some definite conclusion about the change of the crystallographic and electronic structure of Bi clusters with cluster size $L$. The observed transition from a distorted rhombohedral bulk to the ‘‘amorphous’’ Bi structure for $L < L^* \approx 4.0$ nm may be a special feature of Bi clusters. However, we cannot exclude that a similar transition may also occur for other metal clusters below a critical value of $L$. This indicates that one has to be careful to draw any conclusion on the change of electronic structure of small metal clusters with changing size $L$ unless additional informations on the crystallographic structure are available. The extreme large value of $(dB_{c2}/dT)_{T_c}$ we observe for Bi clusters of size $L^*$ shows that the superconducting properties of granular systems can be quite unusual and different from those of the corresponding crystalline or amorphous bulk materials.

## ACKNOWLEDGMENTS

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