

# Formation and growth of lead dendrites in $\text{PbF}_2$ during direct current flow

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A crystallographically oriented growth of long, acicular Pb dendrites has been observed in a sample of the ionic conductor  $\text{PbF}_2$  during the flow of a direct current through it. The growth occurs along  $\langle 100 \rangle$  directions.

The compound  $\text{PbF}_2$  is optically transparent (its electron band gap is about 6 eV) and has a high fluorine-ion conductivity [it goes into a superionic state at  $T \sim 400^\circ\text{C}$  (Ref. 1)]. It has two crystalline modifications: a cubic high-temperature modification (fluorite, stable at  $T > 330^\circ\text{C}$ ) and an orthorhombic low-temperature modification (stable at  $T < 330^\circ\text{C}$ ). Conventional growth from the melt ( $T \sim 880^\circ\text{C}$ ) results in the cubic phase. During a subsequent cooling (at atmospheric pressure), however, kinetic factors prevent a transition to the orthorhombic modification, and a metastable cubic modification persists even at room temperature. The passage of a direct electric current results in the decomposition of  $\text{PbF}_2$ , with a precipitation of lead at the cathode.

In the present experiments we used samples of the cubic modification of  $\text{PbF}_2$ , both undoped and doped with Tb (0.1 at.%). The ionic conductivity of the undoped  $\text{PbF}_2$  at room temperature is  $\sigma = 2.5 \times 10^{-8}$  S/cm, while doped samples have  $\sigma = 8 \times 10^{-7}$  S/cm. Crystallographically oriented samples were cut into rectangular parallelepipeds with dimensions of  $3 \times 4 \times 6$  mm, optically polished, and washed with alcohol. As the electrode material we used silver paste, graphite, and gold. We found no differences in the results for the different electrode materials. The cathode had an area of  $0.1 \times 0.1$  mm and was placed at the center of the upper face. The anode occupied the entire face of the sample ( $4 \times 6$  mm) opposite the cathode.

When a current was passed through the doped samples at room temperature, we observed a crystallographically oriented growth of quasilinear Pb dendrites in the interior of the sample. Figure 1 shows one of these dendrites. They have a linear structure and three growth directions. These directions were reproducible in all the samples studied. They correspond to three equivalent  $\langle 100 \rangle$  directions. The small "twigs" are also oriented along these directions. In some of the samples, the "thinnest" dendrites had a typical transverse radius of about  $1 \mu\text{m}$ . (An estimate based on the charge passed,  $Q \sim 10^{-4}$  C, and the length of the "trunk," about 6 mm, leads to the conclusion that the growth occurred at a voltage of 300 V over a time of 3 s. When the length of the twigs around the trunk of the dendrite is taken into account, this estimate may be reduced significantly.) The samples with dendrites strongly absorb microwave power when they are placed in a cavity (these measurements were carried out at a frequency of 9300 MHz). At  $T < 120$  K, the absorption decreases rapidly (roughly in

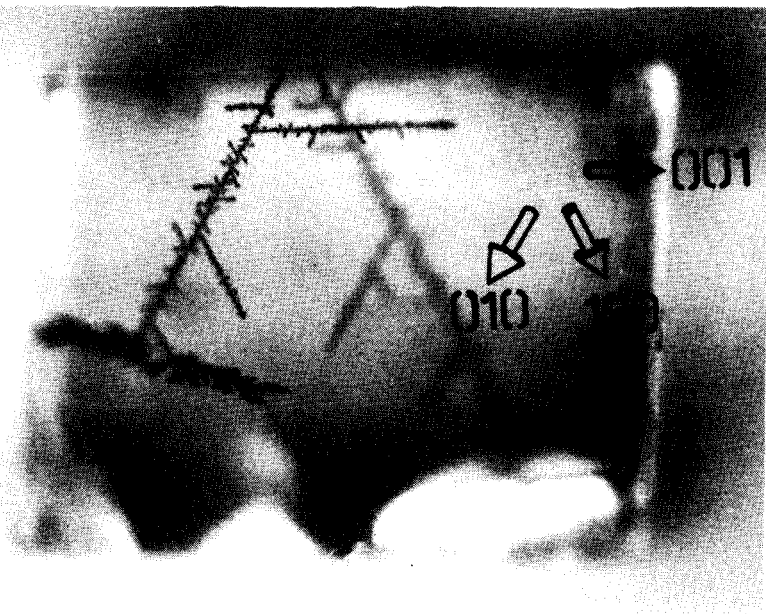


FIG. 1. Lead dendrite in a doped sample. One branch of the dendrite, which grew downward from the cathode (from right to left) ran into a plane wall between two single-crystal blocks (lower left corner). The subsequent growth of this branch occurred in this plane isotropically (as in the case of surface dendrites in undoped sample). In nonblock single crystals, this "isotropic" growth was not observed. The point cathode is at the middle of the upper face. The plane of the photograph is parallel to the  $[111]$  plane of the sample.

proportion to  $T^3$ ), and it becomes difficult to measure at  $T < 50$  K. Estimates of the resistance per unit length of the resulting "microconductors" based on the microwave absorption yield about  $60 \Omega/\text{cm}$  at 300 K. This figure corresponds to a conductivity on the order of  $10^5$  S/cm. This figure is close to the conductivity of pure lead. The rapid increase in conductivity (or the decrease in the microwave losses) with decreasing  $T$  is evidence that the Pb crystallites are of high quality.

In the undoped samples, in contrast with the doped samples, we did not observe a growth of dendrites in the interior at  $T=300$  K. We instead observed an isotropic growth of Pb dendrites at the surface of the sample, away from the point clamp cathode. The inset in Fig. 2 shows the typical shape of such a dendrite on the  $[11\bar{2}]$  surface. The shape of these dendrites, which is sharply different from that of the interior dendrites, is characteristic of an isotropic 2D fractal growth. This shape is similar to the shapes of the metal "leaves" found in Ref. 2 during 2D growth of Zn on the surface of a solution and is characteristic of 2D fractal growth. To determine the fractal dimensionality, we fed an image of the dendrite (see the inset in Fig. 2) into a computer by means of a scanner, with a resolution of  $430 \times 430$  pixels. We calculated the area ( $S$ ) occupied by the dendrite within a square of side  $R$ , as a function of  $R$ . According to Ref. 3, the  $S(R)$  dependence should be

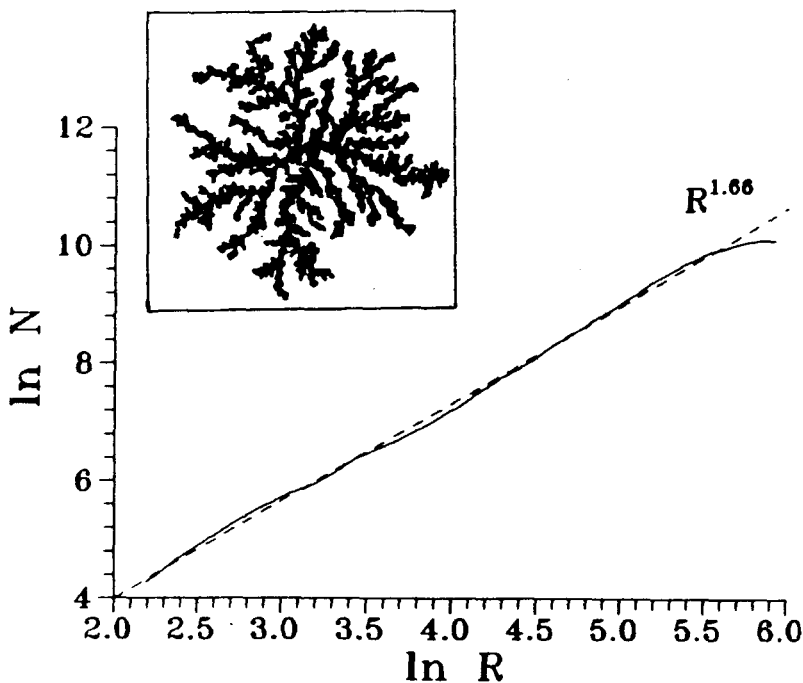


FIG. 2. Determination of the fractal dimension of a surface dendrite (shown in the inset) which grew on an undoped sample at  $T=300$  K. Solid line—Number of pixels of computer image occupied by the dendrite versus the size of the region examined; dashed line—theoretical.

$$S \sim R^D,$$

where  $D$  is the fractal dimensionality of the dendrite. Figure 2 shows our results on  $\ln S$  as a function of  $\ln R$ . The value which we found,  $D=1.66 \pm 0.05$ , agrees well with the Witten-Sander model.<sup>4</sup> We plan to carry out a more detailed study of the growth of these surface dendrites (the dependence on the temperature, the applied voltage, the charge passed, etc.).

One possible reason for this marked difference in the nature of the growth of the dendrites in the doped and undoped samples might be a large difference between their resistivities. We accordingly carried out some additional experiments on the undoped samples at  $120^\circ\text{C}$ , at which the conductivity of these samples is equal to that of the doped samples at room temperature. We again found a predominant growth of dendrites at the surface, but some dendrites growing inside the sample also appeared after a prolonged current flow. The directions of the dendrite growth in the interior in this case corresponded to the [100], [010], and [001] directions.

*Discussion of results.* We believe that the following experimental results require explanation: a) the fundamental difference between the nature of the dendrite growth in the undoped and doped samples; b) the crystallographic orientation of the interior dendrites.

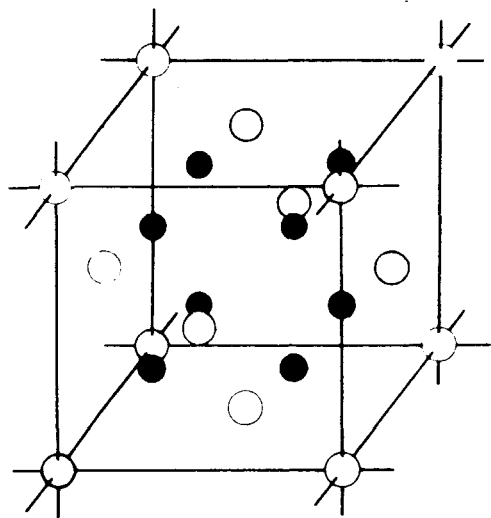


FIG. 3. The  $\text{PbF}_2$  lattice. Lead (open circles) occupies the sites of an fcc lattice. If the cube drawn here is cut into eight parts by three planes parallel to the faces of the cube and passing through the centers of its edges, then it is a simple matter to find the positions of the fluorine ions (the filled circles): There are eight ions at the centers of the eight resulting cubes.

Figure 3 shows the  $\text{PbF}_2$  lattice. If we were to take all the fluorine ions out of it, we would end up with the lattice of metallic lead, with the one distinction that the size of the unit cell of lead is  $4.95 \text{ \AA}$ , while that of  $\text{PbF}_2$  is  $5.92 \text{ \AA}$ . The formation of Pb crystals thus does not require a diffusion of lead atoms; it is sufficient that fluorine vacancies undergo a diffusion and become neutralized at the surface of a growing dendrite as the result of a transport of electrons from the cathode along the growing metal dendrite. We believe that the growth of Pb dendrites can be described as follows: The passage of a direct current causes a simultaneous motion of fluorine vacancies ( $V^+$ ) and interstitial atoms ( $I^-$ ) (because of the requirement of local electrical neutrality). Metallic lead forms through a "condensation" of neutral fluorine vacancies. Since the electron conductivity of  $\text{PbF}_2$  is negligible, a precipitation of Pb can occur only at the surface of a growing dendrite, where electrons are captured by  $V^+$ 's. The rate of precipitation must reach a maximum at the end of a dendrite, where the electric field is at a maximum.

It is reasonable to suggest that the energy of a  $V^+$  at the surface of an undoped sample is lower than that in the interior. It then follows that a production of  $V^+ + I^-$  pairs at the surface is predominant in such a sample at a sufficiently low temperature. This circumstance would explain the surface growth of the dendrites in the undoped samples. The  $I^-$ 's move toward the anode through the interior, while the  $V^+$ 's move toward the cathode along the surface, causing a surface growth of dendrites. As the temperature is raised,  $V^+ + I^-$  pairs also appear in the interior of the sample, leading to the observed "sprouting" of dendrites in the interior of the sample at a high temperature.

In doped Tb the situation is different. Near a Tb ion the energy of formation of charge carriers is evidently lowered greatly. The conductivity due to  $V^+ + I^-$  pairs generated in the interior is predominant in the sample, and the flux of  $V^+$ 's toward the cathode occurs primarily from the interior. This process causes a sprouting of den-

drites in the interior of the sample, with almost no surface growth.

Explaining the crystallographic orientation of the growth of the bulk dendrites in the doped samples is more complicated. We say this because the electrical properties of a cubic crystal are isotropic, and we would naturally expect a growth of dendrites along the shortest distance between the cathode and the anode. In principle, the reason for a selection of directions might be the large difference between the specific volumes of Pb and  $\text{PbF}_2$ , which leads to the appearance of a huge elastic stress. A minimization of this elastic energy might be one factor determining the growth direction. (One could cite the analogy with the formation of rod-like defects in silicon,<sup>5</sup> in which interstitial Si atoms generated during the annealing of CZ-Si also form long linear defects directed along  $\langle 110 \rangle$  directions. These defects correspond to thin acicular inclusions of a denser hexagonal modification of silicon.<sup>5</sup>) The suggestion that the elastic energy has a strong effect on the dendrite growth correlates with the fact that the growth of the dendrites at the surface (Fig. 2) and also at the boundaries of blocks (Fig. 1) is isotropic. The surface of the sample and the boundaries of blocks are of course the locations at which a relaxation of elastic energy occurs most easily.

Unfortunately, the “anisotropy factor” of the elastic constants of  $\text{PbF}_2$ ,  $d = C_{11} - C_{12} - 2C_{44}$ , is small. Therefore, in order to determine whether the elastic energy is indeed the factor which primarily determines the shape and growth direction of the interior dendrites or whether we need to invoke other mechanisms, we need to carry out an accurate calculation of the elastic energy. At this point, we have not succeeded in this direction. (The fact that the energy of the “elastic” attraction between two point defects in a cubic lattice is at a maximum specifically along the  $\langle 100 \rangle$  direction<sup>6</sup> may be evidence “in favor” of the elastic energy.)

An interesting practical application of the effect observed here might be the fabrication of long metal “wires” of submicron diameter (“quantum wires”). These conductors might be used as a new class of quasi-1D systems and might compete with some similar entities which are presently being fabricated by electron nanolithography. This development will of course require further research in order to determine the optimum conditions for fabricating wires of tiny diameter.

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