Granular Materials

Granular materials constitute a wide class of artificially made or naturally occurring disordered media with a granular microstructure; included in the generic category are granular metals, discontinuous films, composites in general, porous media, aggregates, colloids, etc. Today, granular materials are an important area of research, not only for the basic scientific questions raised by many of their novel physical characteristics, but also for their numerous practical applications. However, what is generally recognized today was not recognized in the early 1960s, and it could be argued that granular materials research did not even exist as a cohesive area of study 25 years ago.

The history of granular metals dates back to the beginning of this century. In 1904 Maxwell-Garnett explained the ruby color of gold suspensions in silica through an effective medium theory (known today as the Maxwell-Garnett theory), and in 1914 Swann observed phenomena in the electrical conductivity of ultrathin metal films that in today's language would be referred to as percolation and hopping conductivity. In the 1930s Bruggman formulated a number of effective medium theories that were influential in the development of modern concepts of inhomogeneous media. However, it was not until the early 1970s that granular metals became a generic area of experimental and theoretical research. A group of solid-state physicists at RCA Laboratories made major contributions to this development.

The story of how granular metals were discovered at RCA Laboratories is a textbook case of serendipity and the unpredictable ways of research. In 1965 Ben Abeles and Yeduda Goldstein were studying phonon-assisted tunneling in Pb-Al superconducting tunnel junctions. An anomalous feature of their aluminum films was the high superconducting transition

temperatures, in the range of $T_c = 2.2\text{--}3.7$ K, compared to the 1.18 K literature value. This was good news from the point of view of expanding the temperature range for cryostats cooled by liquid helium, but it was bad news from the point of view of a paper on superconductivity in Al. It turned out that Abeles and Goldstein, relatively inexperienced at the time in thin film deposition of aluminum, had used alumina boats instead of the conventional tungsten filaments to evaporate their aluminum films. Oxygen outgassing from the alumina boats during the deposition led to films consisting of very fine aluminum grains surrounded by thin aluminum oxide. Abeles and co-workers discovered that this granular structure was responsible for the enhancement of T_c as well as other unique and interesting properties of this new class of granular superconductors.

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Soon after this discovery, the range of granular materials, and phenomena that could be studied, were greatly enlarged by a more versatile and controllable technique of co-sputtering metals and insulators introduced by Joe Hanak. What followed was a remarkably productive and creative period at RCA as well as at other laboratories in which many new granular materials were synthesized and their interesting and novel phenomena investigated. In fact, the case can be made that there is a connection between granular aluminum and the recent discovery of the high T_c oxide superconductors. Accounts of this interesting historical point are given by Alex Müller and Guy Deutscher in *Physical Phenomena in Granular Materials*, Volume 195, MRS Symposium Proceedings.

Following the discovery of granular superconductivity, G.D. Cody became curious about the optical properties of the granular metals. Colleagues with expertise in optics advised Cody that granular

metals would be dominated by dirt effects, so why bother with experiments. Cody's curiosity, coupled with lack of familiarity with the literature, prevailed and with the enthusiastic support of Ben Abeles he began a systematic study of the optics of granular Ag and Au. As the experimentalist of the team, he ran the Cary spectrometer at night while functioning during the day as a laboratory director. Roger Cohen, as the theorist on the team, reinvented, to his later surprise, a more generalized version of the Maxwell-Garnett theory! Despite this broadening of the granular metals research at RCA, the generic nature of the granular phenomena was still not grasped.

P. Sheng came to know granular metals in 1971 as a graduate summer intern at RCA laboratories. At that time, the transport characteristics of granular metals, such as the temperature and electric-field dependence of the conductivity, were not known. As a young graduate student joining the granular group, he vividly recalls the excitement in the air and the anxious anticipation of results from the laboratory. As in the optical work, there was a feeling that, with Ben Abeles leading the charge, the group was getting into a large unexplored territory.

Despite the intrinsic fascination of the material and the large amount of work done to clarify their properties, granular metals continued to be a "not-quite respectable" field of research in the early 1970s due to its "dirty" nature. However, the mid to late 1970s witnessed a transformation in the status of granular research as interest in disordered materials picked up. In particular, the use of granular metals for percolation, localization, superconductivity, and optical studies essentially integrated this once peripheral area of inquiry into the main stream of condensed matter and materials research. The first Electrical Transport and Optical Properties of Inhomogeneous Media (ETOPIM) conference of 1977, held at Ohio State University, signaled this transition. This fact was particularly brought out in the seminal review presented at that meeting by R. Landauer. At about the same time, the rise of oil industry research laboratories in the late 1970s and early 1980s added a geological and chemical perspective that broadened disordered material research into porous media, nanocrystals, aggregates, colloids, and other disordered systems, all of which may be classified as having a granular microstructure.

Editor's Note: This description of the development of granular materials is excerpted from the Preface to *Physical Phenomena in Granular Materials* (Volume 195, MRS Symposium Proceedings), edited by G.D. Cody, T.H. Geballe, and P. Sheng. The proceedings, from a symposium held during the 1990 MRS Spring Meeting in San Francisco, is dedicated to Ben Abeles in recognition of his 65th birthday.

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HISTORICAL NOTE

Concurrent with this broadening of the perspective were exciting theoretical developments in effective medium and percolation theories, as well as in classical wave and electronic localization phenomena in granular systems. In the former, improved bounds for physical characteristics of composite systems, e.g., electrical conductivity and elastic moduli, were found through new mathematical techniques, and the recognition and incorporation of microstructural effects in composites have improved the accuracy of effective medium theory predictions. In the latter, knowledge about the structure-scattering relationship has enabled the extraction and identification of new types of symmetry in random media, i.e., that of fractals. In short, what appeared initially as something dirty and peripheral to the mainstream of physics research has, in the span of 20 years, blossomed into one of the most exciting and fruitful areas of experimental and theoretical study. In this context, it is perhaps accurate to denote the RCA granular metals research of the late 1960s and early 1970s as one of the seeds whose germination and maturation contributed significantly to the robust character of disordered materials research today.

G.D. Cody
T.H. Geballe
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