RAPIDLY QUENCHED METALS

Vol. 2

RAPIDLY QUENCHED METALS

Proceedings of the Fifth International Conference on Rapidly Quenched Metals,
Würzburg, Germany, September 3-7, 1984

Edited by:

S. STEEB

Max-Planck-Institut für Metallforschung
Stuttgart, Germany

H. WARLIMONT

Vacuumschmelze GmbH
Hanau, Germany

VOLUME II

1985

NORTH-HOLLAND
AMSTERDAM • OXFORD • NEW YORK • TOKYO

ISBN: 0 444 86941 7

Published by:
North-Holland Physics Publishing
a division of
Elsevier Science Publishers B.V.
P.O. Box 103
1000 AC Amsterdam
The Netherlands

Sole distributors for the U.S.A. and Canada:
Elsevier Science Publishing Company, Inc.
52 Vanderbilt Avenue
New York, N.Y. 10017
U.S.A.

Library of Congress Cataloging in Publication Data

International Conference on Rapidly Quenched Metals
(5th : 1984 : Würzburg, Germany)
Rapidly quenched metals.

Sponsored by Deutsche Forschungsgemeinschaft and others.
Includes index.
1. Metals--Rapid solidification processing--Congresses. I. Steeb, S., 1931- . II. Warlimont, Hans, 1931- . III. Deutsche Forschungsgeminschaft. IV. Title.
TS247.I58 1984 671.3'6 85-5082
ISBN 0-444-86939-5 (v. 1)
ISBN 0-444-86941-7 (v. 2)

Printed in The Netherlands

PREFACE

The present proceedings contain the papers presented at RQ 5, the Fifth International Conference on Rapidly Quenched Metals, held at Wurzburg University, West Germany, from 3 to 7 September 1984. The conference marked another increase in interest in the field of amorphous and crystalline metals formed by rapid quenching from the melt. It was structured according to suggestions from the International Advisory Committee and put into a specific concept by the Organising Committee. The review talks, poster presentations and short invited papers combined with extensive poster discussions found wide interest among the participants.

It was a particular highlight of the conference that Professor Werner Buckel of Karlsruhe was honoured by the International Advisory Committee and by all the participants for his pioneering work in discovering amorphous states in vapour deposited metals and alloys and in investigating their low temperature properties. Professor Ulrich Gonser gave an enjoyable introduction and Professor Buckel himself a vivid description of this early work and of the personal experiences in exploring a hitherto unknown subject of solid state physics. The contributions of both are contained in these proceedings.

The persons and institutions who have contributed to the success of the conference by their personal engagement in committees or by financial support are listed on the following pages.

Most of the committee members acted as referees and Professor S. Steeb coped with the major part of the editorial work on these proceedings, which he carried out painstakingly and with great endurance.

My task of organising the conference was greatly facilitated and kept manageable by the energy, flexibility and competence of my conference secretary, Miss Rachel Patricia Wolverson, who was supported by the staff at the Vacuumschmelze and by Dipl Phys Martin Globl of the Institute of Physics at Wurzburg University who, under the direction of Professor Volker Dose and in cooperation with Dipl Phys Alfons Hartl along with about thirty members of staff and students, ran much of the organisation of the conference at Wurzburg itself.

According to a ballot taken among the participants and a final decision taken by the International Advisory Committee, the next conference of this series will be held in Montreal, Canada, in 1987.

It is my pleasure to acknowledge all the help and support the conference has received from so many sides and to express my hope that the conference itself and the present proceedings will be informative and encouraging for further work and success in this interesting interdisciplinary field of physics, chemistry, physical metallurgy and engineering.

November 1984

HANS WARLIMONT
Conference Chairman

FIFTH INTERNATIONAL CONFERENCE ON RAPIDLY QUENCHED METALS

INTERNATIONAL ADVISORY COMMITTEE

R. CAHN	Cambridge, UK
B. CANTOR	Oxford University, UK
S. CARGILL	IBM, USA
H. CHEN	Bell Laboratories, USA
J. DURAND	Université de Nancy, France
P. DUWEZ	California Institute of Technology, USA
T. EGAMI	University of Pennsylvania, USA
B. GIESSEN	Northeastern University, USA
C. GRAHAM	University of Pennsylvania, USA
N. GRANT	Massachusetts Institute of Technology, USA
H.-J. GÜNTHERODT	Universität Basel, Switzerland
W. JOHNSON	California Institute of Technology, USA
U. KÖSTER	Universität Dortmund, FRG
H. KRONMÜLLER	Max-Planck-Institut für Metallforschung, FRG
F. LUBORSKY	General Electric Company, USA
T. MASSALSKI	Carnegie Mellon University, USA
T. MASUMOTO	Research Institute for Iron, Steel and Other Metals, Tohoko University, Japan
T. MIZOGUCHI	Gakashuin University, Japan
P. RAMACHANDRA RAO	Banaras Hindu University, India
P. SHINGU	Kyoto University, Japan
F. SPAEPEN	Harvard University, USA
H. WARLIMONT	Vacuumschmelze GmbH, FRG

ORGANIZING COMMITTEE

H. WARLIMONT (Conference Chairman)	Vacuumschmelze GmbH, Hanau, FRG
V. DOSE	Universität Wurzburg, FRG
J. DURAND	Université de Nancy, France
U. GONSER	Universität Saarbrücken, FRG
H.-J. GÜNTHERODT	Universität Basel, Switzerland
P. HAASEN	Universität Göttingen, FRG
F. HAESSNER	Universität Braunschweig, FRG
J. HAFNER	Universität Wien, Austria
H. HILZINGER	Vacuumschmelze GmbH, Hanau, FRG
E. HORNBOGEN	Ruhr-Universität Bochum, FRG
U. KÖSTER	Universität Dortmund, FRG
H. KRONMÜLLER	Max-Planck-Institut für Metallforschung, Stuttgart, FRG
S. METHFESSER	Ruhr-Universität Bochum, FRG
B. MORDIKE	Universität Clausthal, FRG
B. PREDEL	Max-Planck-Institut für Metallforschung, Stuttgart, FRG
V. SCHUMACHER	Deutsche Gesellschaft für Metallkunde, Oberursel, FRG
S. STEEB (Proceedings Editor)	Max-Planck-Institut für Metallforschung, Stuttgart, FRG

SPONSORS

Deutsche Forschungsgemeinschaft, Bayerisches Staatsministerium für Unterricht und Kultus

Deutsche Gesellschaft für Metallkunde, Max-Planck-Institut für Metallforschung, European Office of Aerospace Research and Development (EOARD), US Army Research Office (USARDSG), Universität Würzburg, Deutsche Lufthansa AG

Allied Corporation Metglas Products, BASF AG, Robert Bosch GmbH, Concast Standard AG, Daimler-Benz AG, Degussa AG, Enka BV, Hitachi Metals Ltd, Leybold Heraeus GmbH, Metallgesellschaft AG, Nippon Steel Corporation, Siemens AG, Sony Corporation, Wielandwerke AG, Wilkinson Sword Ltd

IN MEMORIAM

POL E. DUWEZ

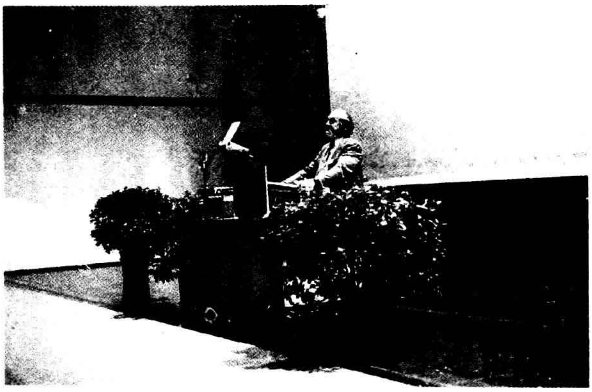
Pol Duwez was born and educated in Belgium. He first came to Caltech as a Research Fellow in 1933. After a five-year period back in Belgium he returned in 1941 as a Research Engineer on various defense projects at Caltech. In 1944 he became the Head of the Materials Section at the Jet Propulsion Laboratory. He joined the Caltech faculty as Associate Professor in 1947 and became Professor in 1952

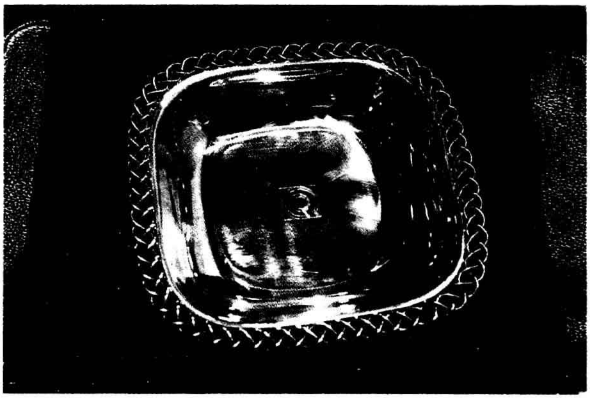
Immediately after his return to Caltech in 1941 he conducted the first experiments which demonstrated the existence and nature of waves of plastic deformation in solids which had been predicted theoretically by Theodore Von Karmán. He subsequently made many other original contributions to the field of materials science, and he became especially well-known for his discovery and study of amorphous metal alloys. The many students who studied with him now occupy prominent positions in academic institutions and industrial companies in the United States and other countries

Pol retired as Professor Emeritus in 1978. He continued to consult daily with his colleagues at Caltech until his final illness. He died on December 31, 1984, at the Huntington Memorial Hospital in Pasadena. He is survived by his wife Nera of Pasadena and his daughter Nadine, who lives in Paris.

For the RQ Community
Hans Warlimont
Chairman RQ5

INTRODUCTION





RAPIDLY QUENCHED METALS
S. Steeb, H. Warlimont (eds.)

INTRODUCTORY REMARKS

Hans WARLIMONT

Vacuumschmelze GmbH, 6450 Hanau, and University of Stuttgart, 7000 Stuttgart, Federal Republic of Germany

This conference series on rapidly quenched metals has been attended by an increasing number of participants and has attracted a greater number of contributions every time it was held. It is notable that this increase has continued here, even though less drastically than last time in Sendai, if it is realised that the subject of rapidly quenched metals with all their structural and property aspects such as the structure of amorphous metals, rapid solidification processing, amorphous magnetism, micro-crystalline materials etc have become topics of regular meetings of metallurgical societies, physical societies, magnetism conferences and special national and local conferences of all kinds. This shows the liveliness of the subject as a topic of scientific study, as a topic which still provides many open and controversial aspects and as a topic of great technological potential and interest.

What is the present state of the field? Based on taking a broad view and considering the research and progress presented at RQ 5, it may be appropriate to focus on some points of particular relevance for present discussions and future work.

STRUCTURE OF AMORPHOUS METALS

The model of dense random packing of hard spheres has been recognised to fail as a general basis to describe the structure of amorphous metals. It is rather a special case among several structural concepts and experimentally determined structural features. Structure determination by conventional and even by more advanced scattering methods proves to be extremely difficult and limited to simple, mostly binary systems. The present state of structure description is utterly dissatisfactory. Short-range order parameters which are defined in analogy to those adopted for scattering analyses on crystalline and liquid metals are insufficient for anything close to a complete structure description, and other forms of structure description have not yet been found. The question is: will amorphous structures ever be described by means similar to those applied to crystalline states in terms of well-defined ideal structures and well-defined defects?

The strong potential for more comprehensive and succinct structure analysis appears to lie in a combination of scattering experiments and nuclear measurements by techniques such as NMR, Mössbauer spectroscopy etc. They permit the recognition of the elements of the short-range ordered structure and a determination these structure elements supplemented by a description of their interconnection, perhaps by topological parameters, may be an answer.

PROPERTIES AND APPLICATIONS OF AMORPHOUS AND MICRO-CRYSTALLINE MATERIALS

Many properties of rapidly quenched amorphous and micro-crystalline materials have been measured in attempts to understand the physics as well as to just find the difference from properties of conventionally processed crystalline materials. Much of the work which is the major part of the studies has been interpreted qualitatively only. What is the reason?

The classical synthesis of results in solid state physics and in physical metallurgy, namely to relate structure to properties, is not yet possible because structures and microstructures are not sufficiently well-known in qualitative and quantative detail and thus the relation cannot be established.

The application of amorphous and of other rapidly quenched materials has begun and it is like at the beginning of all other metallic materials: they are being produced, processed and used successfully before the structure-property relations as such have been fully understood; but in the present days of high technology we need to understand and to master all materials as well as we can to manufacture products which satisfy high specifications and are fully reliable. Therefore, the complete understanding of structure-propertiy relations is indespensible.

CONCLUSIONS

It can be concluded that for both scientific and technical reasons much remains to be studied and understood in the field of amorphous and crystalline rapidly quenched metals. RQ 5 has shown that considerable steps have been achieved but that at the same time, new questions are opening up.

The time of easy experiments in rapid quenching is over, that of serious comprehensive studies has only just begun.

RAPIDLY QUENCHED METALS
S. Steeb, H. Warlimont (eds.)

HISTORICAL REMARKS AND HONOURS

U. Gonser

This is a special session for reminiscence about highlights of the past, and in particular we want to talk about amorphous metals. In this connection it seems necessary to make you acquainted with the German word *Stammbaum*. In the dictionary you will find the translation "family tree" which applies to humans, dogs and other animals. However the word *Stamm* has a wider meaning than "family" and in general, a *Stammbaum* represents the multiplicity of a development with all its branches and facets.

Here, of course, we are interested in the *Stammbaum* of the amorphous metals. In fig. 1 we have a picturesque exhibit of this wonderful *Stammbaum* and, indeed, it is a tall tree which is now in full bloom. This meeting exemplifies on the one side the vigorous roots producing these alloys and on the other the various strong branches representing magnetic, electrichal and mechanical properties and their applications; principles of glass forming, thermodynamics, phases and structures, short range order, surfaces, corrosion, catalysis, hydrogen and other additions - in short, the manifold branches which have developed.

If we were to chop the tree down - of course such a splendid *Stammbaum* should never really be hurt by cutting - but just imagine such a cut and what we would see are the annual rings, roughly a few over thirty. Thus it is remarkable that this young tree has grown to be so tall and magnificent in such a short time.

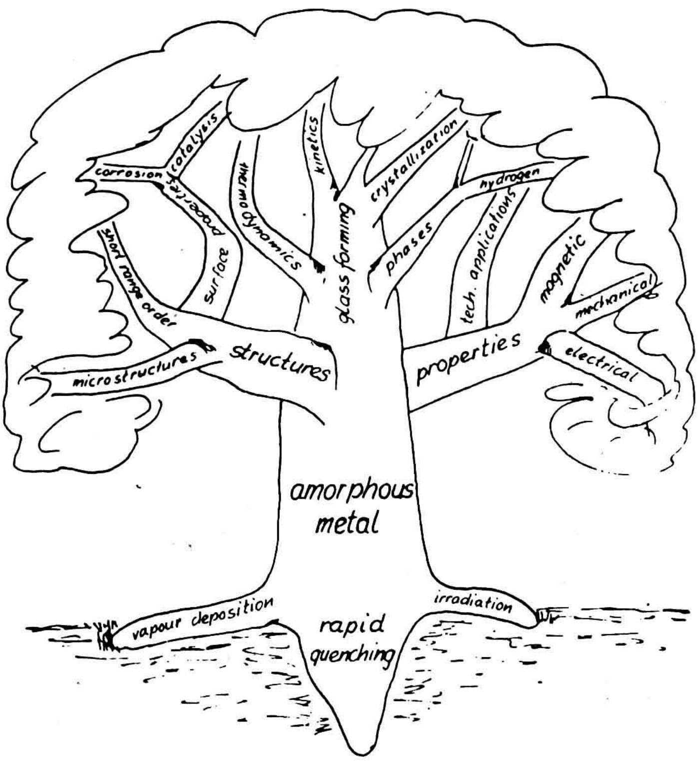


fig. 1

If we go back in time to the middle of this century, we discover a situation as shown in fig. 2: a very hard-working gardener taking good care of our very young *Stammbaum*.

The environment for studying amorphous or disordered systems was not at all favourable. To point this out one might quote the probably most published book in physics, *Introduction to Solid State Physics*, by Charles Kittel. His words and meanings are demonstrated in fig. 3. Thus, at that time the interest was directed solely toward the perfect crystal. Courage was needed to go in the other direction and swim against the current, producing disordered and amorphous material which some people regarded as garbage.

fig. 2

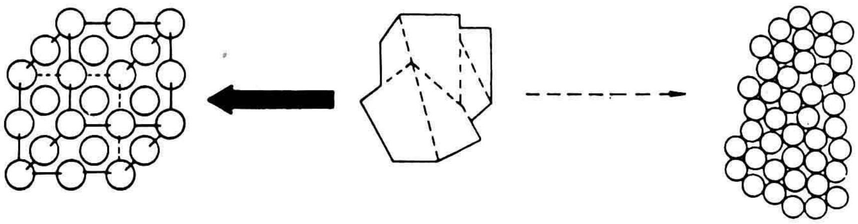


fig. 3

"MEASUREMENTS ON SINGLE CRYSTALS ARE ALWAYS MUCH MORE SIGNIFICANT AND INFORMATIVE THAN ARE MEASUREMENTS ON POLYCRYSTALLINE SPECIMENS."

Taking a closer look at our gardener, we recognize the familiar face of *Werner Buckel*. Actually, there were originally two gardeners, but unfortunately the other one, *R. Hilsch*, passed away twelve years ago. Effectively this team produced amorphous metal films by vapour deposition on cold substrates and made the first systematic investigations which were published in a series of articles in *Zeitschrift für Physik*.

These early investigations had a great influence on the development of the field of amorphous metals. The spirit of those days is reflected in a discussion which took place after a talk given by Werner Buckel in the late fifties:

Shockley got up and said: "I'd like to ask a question about the temperature rise in the reconstitution of the films. It seems to me that there must be a situation something like this: If you could lay down a film by putting atoms down one by one very gently with tweezers at random places, there should be a great deal of disorder in it. Now if the film is very thick, say a foot thick, if you should shoot a cosmic ray into it, and thereby nucleate a rearrangement, then the heat would not be able to get out. It seems to me that the temperature rise might be fairly substantial and the whole mass warms up because I should think you would have something like one atom in 10 to 20 with a bad bond, and this would mean some percentage of the melting temperature would be available."

Buckel replied: "Yes, maybe there is a lot of energy developed at one point. However, I wouldn't call it a temperature rise in the sense of thermodynamics. The heat is dissipated quite quickly."

After recalling a few highlights of the past it is now my great privilege and honour to announce the contribution of our gardener and pioneer, Werner Buckel. He is going to tell us about the early days of amorphous metals and demonstrate his ability to be both witty and philosophical at the same time.

RAPIDLY QUENCHED METALS
S. Steeb, H. Warlimont (eds.)

THE EARLY DAYS OF QUENCH CONDENSED AMORPHOUS FILMS

Werner BUCKEL

Physikalisches Institut, Universität Karlsruhe, D-7500 Karlsruhe, West Germany

It was a great honour for me to be invited to give this lecture. I very much enjoyed having the chance to give a short report on the beginning of our work on disordered metals which led us to the amorphous metals. It is also a great honour for me that our work found this international recognition. Many colleagues and co-workers made essential contributions to our work. They all have part of this honour. Many thanks to all who have been involved.

In 1939, Professor R Hilsch, my highly respected teacher, came from Göttingen to the University of Erlangen. Here he started his work on very low temperatures. I was a young physics student and had the great privilege of working with him. He built a small helium liquifier based on the principle proposed by E F Simon. A single expansion of helium gas from 150 bars pre-cooled to about 12 K by solid hydrogen produced approximately 50 ccm liquid He. This liquifier enabled us to study materials from 1.3 to 400 K. Hilsch's original idea - as far as I can remember - was to cool single crystals of alkali halides to very low temperatures in order to study the effects which may occur if the mean free path of opitically excited electrons becomes larger than the crystal. From his previous work with Professor Pohl at Göttingen, he could extrapolate that this should happen at He temperatures.

But when he had this nice He liquifier, Hilsch decided to study disordered metals, in particular superconducting metals. Here, the idea was to prepare metal films with various degrees of disorder by condensing the metal vapour onto a substrate at various temperatures. At that time we already knew that this preparation - we call it "quench condensation" - strongly influences the superconductivity of tin. Shalnikov published in 1938 the interesting observation that a thin film condensed onto a substrate at He temperatures becomes superconducting at 4.6 K, almost 1 K higher than normal bulk tin. This surprisingly large increase of T_c stimulated us to start a systematic study of quench condensed metal films[1].

In this paper I will discuss some of our earlier experiments. Towards the end I will try to give a little outlook on the future of research on amorphous and glassy metals.

First of all, we repeated Shalinkov's experiment. The first figure shows the resistance of a quench condensed tin film. The substrate was at 4 K during condensation[2]. The resistivity is rather high due to the high degree of disorder produced by quench condensation. The transition temperature is 4.6 K. The disorder decreased with increasing annealing temperature. Simultaneously, the transition temperature T_c shifted to the value of bulk tin; the residual resistivity diminishes monotonously.

At that time we were mainly interested in superconductivity and we asked ourselves whether it would be possible to increase the disorder even more and, simultaneously, to in-

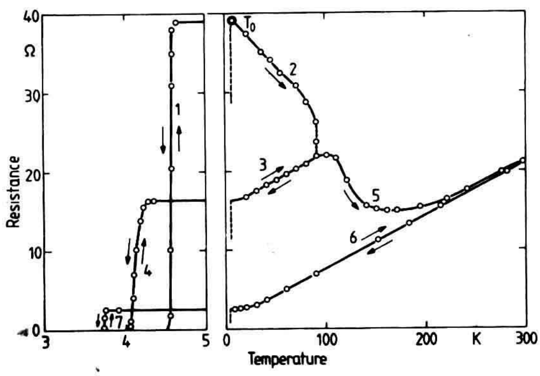


FIGURE 1
Resistance behaviour of a quench condensed Sn film. The substrate was at about 6 K during condensation.

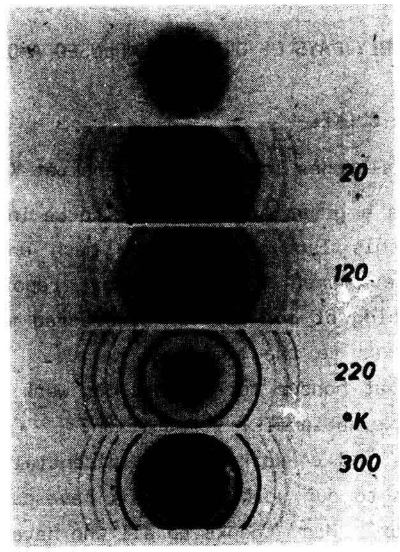


FIGURE 2
In situ electron diffraction diagrams of a quench condensed Sn film. The first pattern is taken from the substrate before condensation. The different patterns are taken after annealing to the temperatures given in the figure.

crease T_c as well. Almost at the same time, we started in situ electron diffraction studies on such quench condensed films. From now on I will present the results irrespective of the historical development.

From the electron diffraction one learns that the quench condensed Sn films grow in the normal white tin structure. Figure 2 shows the electron diffraction pattern taken from such a film. These are transmission pictures. Pattern (a) shows the intensity we had from the substrate; a little hole (20 μm in diameter) covered by a thin collodion film at 4 K. Pattern (b) was taken immediately after the quench condensation of pure tin. All lines of the white tin structure appear[3].

After this result, the question was: how can one increase the disorder in the crystalline state or even prevent crystallisation? The answer was rather obvious. One had to condense simultaneously with the tin atoms some foreign atoms which do not fit into the host lattice but which should have some affinity to tin so that they are not precipitated completely during the condensation process. We looked in Hansen's book on binary systems and found that Cu could be a good candidate. Tin has almost no solubility for Cu; however, some intermetallic compound exists in the system SnCu.

Therefore, we quenched condensed tin with 10 at% Cu onto a substrate at 4 K. The result of this experiment - which was done in the late forties - is shown in figure 3. pattern (b) shows the electron diffraction diagram of the as-quenched condensed film. This film grew amorphous. The amorphous state is rather unstable. The crystallisation temperature is near to 20 K. Crystallisation forms the white

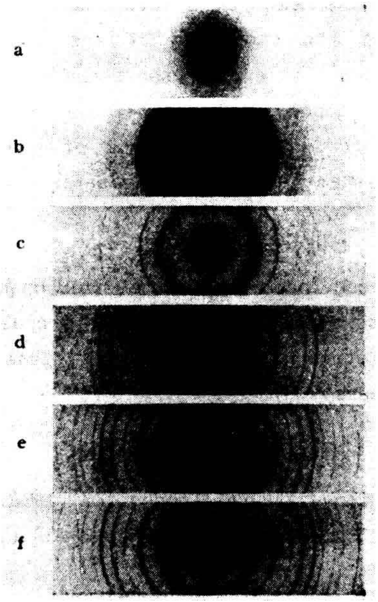


FIGURE 3
In situ electron diffraction diagrams of a quench condensed Sn film with 10 at% Cu. a) Substrate before condensation; b) SnCu film immediately after condensation; c) after annealing to 20 K; d-f) after annealing to 50 K, 200 K and 300 K respectively.

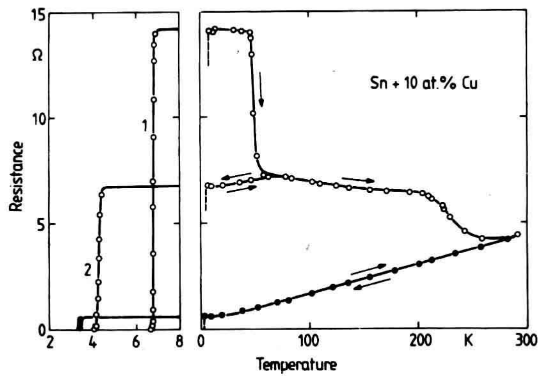


FIGURE 4
Resistance behaviour of a quench condensed $Sn_{90}Cu_{10}$ film. The substrate was at about 6 K during condensation.

tin structure. Let us now look at the resistance of such an alloy film. In figure 4 the resistance is plotted versus temperature as for the pure tin film. The resistance of the as-quenched film is a factor of two larger than that of a corresponding pure tin film. As expected, a sharp drop occurs with crystallisation. Also, the superconductivity has drastically changed. The amorphous film becomes superconducting at about 7 K [3].

Many interesting questions arose from this result. As that time we did not have a microscopic theory of superconductivity. Problems concerning the superconductivity could not be solved until the sixties. I cannot go into details here.

Summarising these results, one can say that we succeeded in preparing amorphous SnCu samples. We had to use a second component to stabilise the amorphous state. We also found that other materials, such as Au, Al Zn and even Ge, can act as stabilisers. We studied the crystallisation temperature as a function of the composition. These experiments have many common aspects with the problems discussed at this conference.

Let me close my paper with some personal remarks. Hilsch and his co-workers did not search for amorphous materials. However, we did systematic experiments on the influence of disorder in metals. These experiments led us to the amorphous state of metals and some surprising results concerning superconductivity, the superconductivity of amorphous bismuth, for instance. From this experience one should keep in mind that basic research has to be done and has to be supported outside any project with well-defined goals.