

Volume 52

**SOLID
STATE
PHYSICS**



ACADEMIC
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SOLID STATE PHYSICS

Advances in
Research and Applications

Editors

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VOLUME 52



ACADEMIC PRESS

San Diego

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ACADEMIC PRESS

A division of Harcourt, Brace & Company

525 B Street, Suite 1900, San Diego, CA 92101-4495, USA

<http://www.apnet.com>

Academic Press

24–28 Oval Road, London NW1 7DX, UK

<http://www.hbuk.co.uk/ap/>

International Standard Serial Number: 0081-1947/99

International Standard Book Number: 0-12-607753-3

Printed in the United States of America

99 00 01 02 03 MB 9 8 7 6 5 4 3 2 1

SOLID STATE PHYSICS

VOLUME 52

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Preface

This volume of the Series contains three articles on diverse topics. Okamoto, Lam, and Rehn consider the phenomenon of the crystal-to-glass transformation, which can result from ion or electron irradiation, ion beam mixing, thermal interdiffusion, application of high pressure, or severe mechanical deformation. The authors attempt to elucidate the mechanism for this transition by considering its relation to the phenomenon of melting. Specifically, they generalize Lindemann's hypothesis for melting, which invokes a critical mean square atomic displacement, to a generic measure of topological disorder that can be applied to static displacements as well. They show that the generalized hypothesis is equivalent to other concepts for amorphization, such as shear-modulus softening.

The article by Flatté and Byers examines how the use of localized real-space spectroscopies such as STM together with recent theoretical techniques appropriate for the study of the local electronic structure, can be used to understand how interacting electron systems respond to the presence of impurities. The specific application under consideration is to conventional low- T_C and anisotropic high- T_C superconductors.

After an incisive introduction to scanning tunneling microscopy and a brief guide to important bulk characteristics of impurities in superconductors having either isotropic or anisotropic order parameters, they turn to an extended survey of calculational techniques useful in elucidating the local electronic properties associated with defects in superconductors with emphasis on a generalized formalism based on the approach first introduced by Slater and Koster. They discuss calculations and theoretical and experimental results for both magnetic and non-magnetic impurities, as well as inhomogeneities of the pairing interaction in both kinds of superconductors. The didactic style of the article should make it generally useful to those interested in calculations of local electronic properties and their use in interpreting STM experiments.

In the final article, Edwards and collaborators present a comprehensive overview of the metal-insulator transition, one of the most venerable subjects of solid state theory. A physically based description of the principal ideas and models that have been used to describe such transitions is followed by a scholarly, extensively referenced review of four major systems that exhibit this behavior. These include the expanded fluid metals, most notably hydrogen and the other alkali metals, doped semiconductors, in particular, phosphorus-doped silicon, the transition metal oxides, including perovskite systems and the high- T_C superconducting cuprates, and finally, nanoparticles and connected arrays. While readers will need to consult the supplied key references for a detailed theoretical exposition of the ideas discussed here from a physical viewpoint, the absence of formalism, whose

presentation would have required a book-length monograph, is more than offset by the concise, authoritative and approachable perspective of the entire field that the authors present.

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Physics of Crystal-to-Glass Transformations

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I. Introduction

1. BACKGROUND

Amorphous metallic alloys have traditionally been produced either by condensation of metal vapor onto a cooled substrate¹ or by rapid quenching from the liquid phase.² The present paper, however, is concerned with solid-state amorphizing transformations that begin in the crystalline state. As a glass formation process per se, the crystalline-to-amorphous ($C \rightarrow A$) phase transformation is not a new phenomenon. The formation of amorphous phases over geological times in naturally occurring minerals such as zircon, thorite, and gadolinite, which contain one or more radioactive elements, is a well-documented phenomenon that dates back at least to 1893.³ It was not until 1962, however, that amorphization of a crystalline material (U_6Fe) by fission fragment damage was first demonstrated in the laboratory.⁴ Since then, radiation-induced $C \rightarrow A$ transformations have been observed in almost all types of crystalline materials, including metallic, ionic, and covalent systems.^{3,5,6,7,8} What is new, however, is the almost explosive growth in our understanding of the phenomenon during the past decade. Prior to the 1980s, radiation-induced amorphization of crystalline materials was widely regarded as another rapid solidification process, the liquid in this case being the "liquid-like" cores of displacement cascades. However, the discovery in the early 1980s that many types of intermetallic compounds can be amorphized by high-energy electrons (which do not produce cascades) demonstrated that crystalline solids can also be driven into the amorphous state by the more gradual process of defect accumulation.⁹

During the same period, it became evident that $C \rightarrow A$ transformations can be induced by other types of defect accumulation processes.¹⁰ For example, in 1983, Yeh *et al.* discovered that an intermetallic compound becomes amorphous during

¹ W. Buckel and R. Hilsch, *Z. Phys.* **138**, 109 (1954).

² W. Klement, Jr., R. H. Willens, and P. Duwez, *Nature* **187**, 869 (1960).

³ R. C. Ewing, *Nucl. Instrum. Methods* **B91**, 22 (1994).

⁴ J. Bloch, *J. Nucl. Mater.* **6**, 203 (1962).

⁵ K. C. Russell, *Prog. Mater. Sci.* **28**, 229 (1985).

⁶ P. R. Okamoto and M. Meshii, in *Science of Advanced Materials* (H. Wiedersich and M. Meshii, eds.), p. 33, ASM International, Metals Park, 1990.

⁷ P. M. Ossi, *Rivista del Nuovo Cimento* **15**, 1 (1992).

⁸ L. H. Howe, in "Intermetallic Compounds: Vol. 1, Principles" (J. H. Westbrook and R. L. Fleischer, eds.), John Wiley, New York (1994).

⁹ G. Thomas, H. Mori, H. Fujita, and R. Sinclair, *Scripta Metall.* **16**, 489 (1982); H. Mori, H. Fujita, and M. Fujita, *Jpn. J. Appl. Phys.* **22**, L94 (1983); D. E. Luzzi, H. Mori, H. Fujita and M. Meshii, *Acta Metall.* **34**, 629 (1986).

¹⁰ W. L. Johnson, *Prog. Mater. Sci.* **30**, 81 (1986).

absorption of hydrogen.¹¹ In another example, Schwarz and Johnson found that thermal interdiffusion reactions can lead to amorphous phase formation at the interface of two polycrystalline metals (La and Au).¹² Amorphous metallic alloys have also been produced by ball-milling of physical mixtures of elemental metallic powders¹³ and by mechanical deformation of initially homogeneous inter-metallic compounds.¹⁴ One of the most recent and striking discoveries is that of Mishima *et al.*, who found that crystalline ice-Ih becomes amorphous when subjected to a hydrostatic pressure.¹⁵ Since then, many other crystalline materials have been found to undergo pressure-induced amorphization.¹⁶

2. MOTIVATION

It is the purpose of this paper to review our current understanding of the $C \rightarrow A$ transformation. However, no attempt will be made to present a comprehensive review of all the various types of solid-state disordering processes that can induce the $C \rightarrow A$ transformation. Instead, our focus will be on understanding the relationship between the $C \rightarrow A$ transformation and melting. Melting of a crystalline solid is another phase transformation that results in a topologically disordered atomic structure. A well-equilibrated glass can be considered as a frozen liquid that has a static structure factor similar to that of a supercooled liquid at the glass transition temperature.¹⁷ This close resemblance of the atomic structures of liquids and metallic glasses has long been recognized in studies of glass formation. However, striking parallels in the way melting and amorphization occur have only recently been recognized.^{10,18} For example, we now know from high-voltage electron microscopy observations⁹ that amorphization can proceed in a heterogeneous manner analogous to the first-order nucleation and growth process characteristic of thermodynamic melting, or in a homogeneous manner characteristic of mechanical melting.^{9,19} We also know from Brillouin scattering

¹¹ X. L. Yeh, K. Samwer, and W. L. Johnson, *Appl. Phys. Lett.* **42**, 242 (1983); for a review, see K. Aoki and T. Masumoto, *J. Alloys Compounds* **231**, 20 (1995).

¹² R. B. Schwarz and W. L. Johnson *Phys. Rev. Lett.* **51**, 415 (1983).

¹³ C. C. Koch, O. B. Cavin, C. G. McKamey, and J. O. Scarbrough, *Appl. Phys. Lett.* **43**, 1017 (1983); for a review, see H. Bakker, G. G. Zhou, and H. Yang, *Prog. Mater. Sci.* **39**, 159 (1995).

¹⁴ R. B. Schwarz, R. R. Petrich, and C. K. Saw, *J. Non-Cryst. Solids* **76**, 281 (1985).

¹⁵ O. Mishima, L. D. Calvert, and E. Whalley, *Nature* **310**, 3935 (1984).

¹⁶ For a review, see S. M. Sharma and S. K. Sikka, *Prog. Mater. Sci.* **40**, 1 (1996).

¹⁷ R. W. Cahn, in *Physical Metallurgy* (R. W. Cahn and P. Hassen, eds.), Elsevier Science, Essex, England (1983).

¹⁸ R. W. Cahn and W. L. Johnson, *J. Mater. Res.* **1**, 724 (1986).

¹⁹ D. Wolf, P. R. Okamoto, S. Yip, J. F. Lutsko, and M. Kluge, *J. Mater. Res.* **5**, 286 (1990).

studies²⁰ that the onset of amorphization during irradiation of metallic compounds is preceded by a shear softening very similar to that which precedes the onset of melting during heating of most metals.²¹ Such parallels between these two disordering processes suggest that the $C \rightarrow A$ transformation can be considered as a melting transformation, albeit a nonequilibrium one, occurring at temperatures below the glass transition temperature.

Although the analogy between melting and amorphization disregards important differences in the dynamical aspects of liquids and glasses, melting concepts have provided much of our current insight into the nature of the $C \rightarrow A$ transformation. In this paper, we will examine various theories and models of melting that have been used to explain the $C \rightarrow A$ transformation as a kinetically constrained melting process. In principle, melting concepts should provide a basis for a unified conceptual approach to both ordinary melting and the $C \rightarrow A$ transformation. A major obstacle, however, has been the lack of a suitable disorder parameter of sufficient generality that can be used to characterize both heat-induced melting and the ever-growing number and variety of isothermal disordering processes capable of inducing the $C \rightarrow A$ transformation. We will show that a unified thermodynamic approach to melting and amorphization can be developed by focusing on the roles of the static and dynamic mean-square atomic displacements as generic measures of topological and thermal disorder, respectively. By treating static atomic displacements as "frozen" thermal disorder, we turn quite naturally to a generalized version²² of the original Lindemann melting hypothesis²³ for a broader view of melting that includes the $C \rightarrow A$ transformation as a disorder-induced melting process. As will be seen, a thermodynamic criterion for melting based on the generalized Lindemann melting hypothesis can explain, and even predict, a wide variety of experimental observations.²⁴

We begin in Part II with a brief description of key features of the liquid-to-glass transition that are relevant to an understanding of the $C \rightarrow A$ transformation. Here, we discuss the concept of the ideal glass and the possibility of achieving the ideal glassy state via the $C \rightarrow A$ transformation. This is followed by a discussion in Part III of the Born, Egami-Waseda, and Lindemann lattice instability criteria

²⁰ P. R. Okamoto, L. E. Rehn, J. Pearson, R. Bhadra, and M. Grimsditch, *J. Less-Common Met.* **140**, 231 (1988); L. E. Rehn, P. R. Okamoto, J. Pearson, R. Bhadra, and M. Grimsditch, *Phys. Rev. Lett.* **59**, 2987 (1987).

²¹ J. L. Tallon, *Phil. Mag.* **A39**, 151 (1979); J. L. Tallon and W. H. Robinson, *Phil. Mag.* **A36**, 741 (1977).

²² A. Voronel, S. Rabinovitch, A. Kisliuk, V. Steinberg, and T. Sverbilova, *Phys. Rev. Lett.* **60**, 3402 (1988).

²³ F. A. Lindemann, *Z. Phys.* **11**, 609 (1910).

²⁴ N. Q. Lam and P. R. Okamoto, *MRS Bulletin*, Vol. XIX, No. 7, 41 (1994); *Surf. Coatings Technol.* **65**, 7 (1994).

for melting. In Part IV, the generalized Lindemann melting hypothesis for a defective crystal is discussed, and this hypothesis is shown to be equivalent to a generalized T_o -concept that results directly from a disorder-induced softening of the shear modulus.²⁴ We also examine the connection between the generalized Lindemann criterion and microscopic and thermodynamic theories of melting. The glass formation ranges predicted by the generalized Lindemann melting criterion are compared both with experimental data and with those predicted by other lattice instability criteria and CALPHAD calculations. This is followed in Part V by a review of the general features of radiation-induced amorphization of intermetallic compounds. Here, we compare experimental observations with the predictions of the generalized Lindemann melting criterion and with the results of molecular dynamics simulations of defect-induced amorphization. Various aspects of the generalized Lindemann melting criterion relevant to other types of disordering processes are also discussed. These include ion implantation, ion beam mixing, mechanical deformation, and grain-size effects that can induce amorphization of nanocrystalline materials. We also address the long-standing controversy concerning the interpretation of the temperature dependence of ion beam mixing and examine the possible role of the ideal glass transition as a resolution to the controversy. We close with a brief summary and outlook for other applications of the generalized Lindemann melting concept to materials problems, including fracture, in Part VI.

II. The Liquid-to-Glass Transition

3. GENERAL CHARACTERISTICS

When a liquid is cooled sufficiently below the melting point of its crystalline phase, the relaxation time for structural rearrangement increases dramatically. If crystallization can be avoided by sufficiently rapid cooling, most supercooled liquids will enter a metastable glassy state.²⁵ The liquid-to-glass transition can be characterized experimentally by a temperature called the glass transition temperature, T_g , at which the viscosity of the supercooled liquid is typically 10^{13} poise. This viscosity corresponds to relaxation times of the order of minutes to hours. Upon cooling a liquid toward T_g , various physical and thermodynamic properties change with temperature, as shown schematically in Fig. 1. Following Cahn,¹⁷ we can identify three temperature ranges defined by the thermodynamic melting temperature, T_m , and the glass transition temperature, T_g . Above T_m , the liquid has a lower Gibbs free energy than the perfect crystal and therefore represents the equi-

²⁵ M. H. Cohen and D. Turnbull, *J. Chem. Phys.* **34**, 1164 (1959).

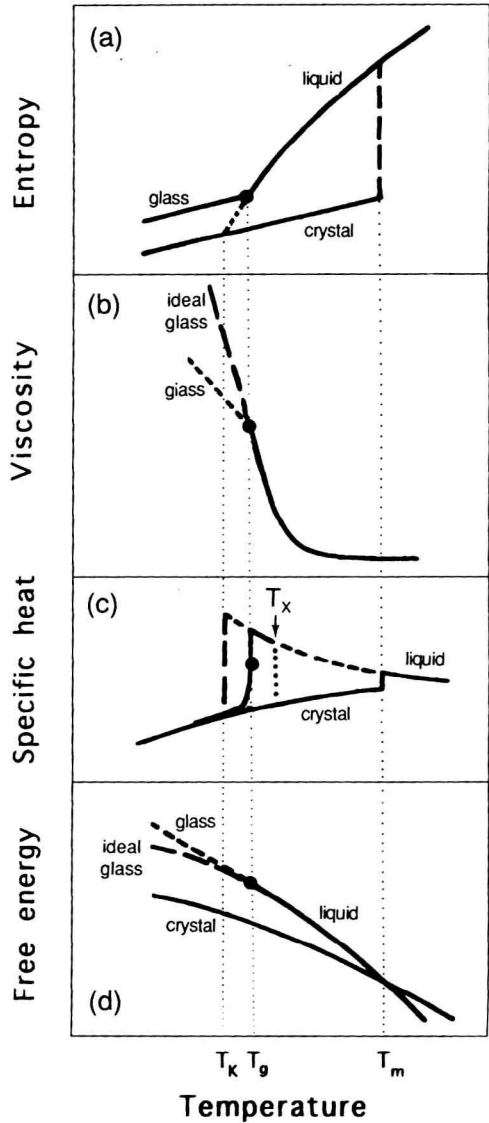


FIG. 1. Schematic of the glass transition showing the effects of temperature on the entropy, viscosity, specific heat, and free energy. T_x is the crystallization temperature. [From Ref. 17.]

librium state. Between T_m and T_g , the liquid is thermodynamically supercooled. Although the viscosity can increase by more than 10 orders of magnitude over this temperature range, the atomic transport through the melt remains sufficiently fast to allow the supercooled liquid to maintain configurational equilibrium even for

the rapid cooling rates typical of rapid solidification processes.¹⁷ As the temperature falls toward T_g , the entropy difference between supercooled liquid and crystal decreases while the difference in their specific heats increases.²⁶ At T_g , the specific heat capacity of the supercooled liquid drops to a value equal to that of the crystal due to the freezing out of all translational degrees of freedom. The inflection or midpoint of the drop in specific heat is often taken as the glass transition temperature. Below T_g , the relaxation time for atomic rearrangement becomes so long relative to experimental time scales that the supercooled liquid drops out of configurational equilibrium and congeals into a rigid isoconfigurational glass having the entropy, enthalpy, and density of the supercooled liquid at T_g . Hence, when plotted as a function of temperature, as shown by the short dashed line in Fig. 1(d), the free energy curve for such an "unrelaxed" or nonideal glass is a straight line having the same slope (e.g., entropy) as that of the supercooled liquid at T_g .

4. THE IDEAL GLASS TRANSITION

It is important to recognize that the glass transition is not a thermodynamic phase transition but is simply a deceleration of the relaxation processes in the supercooled liquid to a point where configurational equilibrium cannot be achieved during experimentally accessible time scales. Thus, the glass transition temperature is a kinetically determined parameter that depends on the time scale used to measure thermodynamic or physical property changes. In general, the slower the cooling rate (e.g., the longer the time scale), the lower the glass transition temperature. Kauzmann, however, pointed out that there must be a lower limit to the glass transition temperature below which a liquid cannot be supercooled no matter how slow the cooling rate.²⁷ Returning to Fig. 1, we see that, during cooling, the equilibrium entropy of the supercooled liquid decreases more rapidly than that of the perfect crystal. Extrapolation of the entropy curve thus leads to a paradox first pointed out by Kauzmann, namely that below some temperature T_K the entropy of the glass should become less than that of the perfect crystal. Although this possibility does not violate any known thermodynamic law, it constitutes a paradox because it is difficult to see how a disordered, nonperiodic structure might have a lower entropy than a perfectly periodic one of the same density. To resolve this paradox, some theorists have postulated that the supercooled liquid would become absolutely unstable at T_K and undergo a second-order transition to the crystalline state.²⁸ Kauzmann also believed that a continuous transition must occur at T_K , but not to the crystalline state. He argued that the thermally activated atomic mobility at T_K would

²⁶ This presumes that the cooling rate is fast enough to avoid crystallization at temperature T_X (see Fig. 1).

²⁷ W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).

²⁸ F. Simon, *Ann. Physik* **68**, 278 (1931).

be too low to permit crystallization by any known mechanism, and therefore proposed that, at T_K , the supercooled liquid would simply congeal continuously to a glass having the same entropy as the perfect crystal. This unique glassy state can be considered as the ideal glass, and T_K the ideal glass transition temperature.

The ideal glass is generally considered to be an unattainable state much like that of the perfect crystal. This is true if one tries to reach the ideal glassy state by cooling a liquid at a sufficiently slow rate or by lowering the Gibbs free energy of an unrelaxed glass via isothermal annealing for long times at temperatures below T_K . At such low temperatures, the atomic mobility is so low that, under normal circumstances, both approaches would require infinitely long times to achieve the ideal glassy state. However, Fig. 1(d) suggests that, below T_K , it may be possible to produce the ideal glass via the $C \rightarrow A$ transformation by introducing enough disorder that the Gibbs free energy of the defective crystal becomes equal to that of the ideal glass. This is illustrated schematically in Fig. 2, which shows the Gibbs free energy of the perfect crystal, of the liquid, and of two defective crystalline states indicated by the dotted curves.²⁹ Also shown are two unrelaxed glasses, 1 and 2, associated with different cooling rates such that $T_{g1} > T_{g2}$. As the glassy state with the lowest Gibbs free energy, the ideal glass would be the glassy state most easily reached from below, but the most difficult one to reach from above, for example, by annealing glass 1. However, even if it were possible to produce the ideal glass via the $C \rightarrow A$ transformation, how would one confirm it? One way would be to demonstrate that the glass transition temperature of the resulting glass is in fact the ideal glass transition temperature, T_K . We discuss how this might be done in the following section.

5. DETERMINATION OF THE IDEAL GLASS TRANSITION TEMPERATURE

If the specific heat capacities of the supercooled liquid (c_p^L) and the perfect crystal (c_p^c) are known as a function of temperature, then their entropies can be calculated using the equations

$$S^L(T) = S_o^c + \Delta S_m + \int_{T_m}^T \left(\frac{c_p^L}{T} \right) dT \quad (5.1)$$

$$S^c(T) = S_o^c + \int_{T_m}^T \left(\frac{c_p^c}{T} \right) dT \quad (5.2)$$

²⁹ The Gibbs free energy curves of the defective crystals assume that the defects do not anneal out even at high temperatures.