DYNAMICAL STUDY OF CRYSTALLINE AND NON-CRYSTALLINE MATERIALS

By

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CERTIFICATE

We are satisfied that the thesis entitled "Dynamical study of crystalline and Non-crystalline Materials" by G. SURYANARAYANA REDDY is worthy of consideration for the award of the degree of DOCTOR OF PHILOSOPHY and is a record of the original bonafide research work carried out by him under our supervision. The results in it have not been submitted in part or full to any other University or Institute for award of any Degree or Diploma.

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PREFACE

In the last decade, the study of lattice dynamics has attained much interest, because of important developments in experimental techniques like inelastic neutron scattering, Raman scattering, infrared spectroscopy and x-ray diffractometry. Through these studies one can obtain quite detailed and precise information on the lattice vibrations of solids, which were largely unobtainable earlier from the study of thermal properties of solids alone. In the past few years, the pseudopotential theory[1-8] has emerged as one of the most simple and most powerful technique to study the electron-ion interaction. The first part of the present work deals with a model potential approach, which is used to study the lattice dynamical properties of alkaline earth metals and transition metal alloys.

Amorphous materials are the subject of an increasing research effort, spurred by both science and technology. The study of amorphous materials helps our understanding of non-crystalline matter in general. The interpretation of the properties of amorphous materials imposes a particular challenge since the understanding of crystalline solid has, in the past, generally been based upon their crystal periodicity. The theoretical concepts based on translational invariance have been developed to deal with the lattice dynamics and electronic structure of crystalline matter[9]. No such general theory has yet been developed for disordered state. The second part of the present thesis deals with the theoretical study of different physical properties such as electrical, superconducting and vibrational properties for some disordered solid state materials e.g. zirconium based transition metal alloys and amorphous semiconductors and their alloys.

LATTICE DYNAMICAL PROPERTIES OF ALKALINE EARTH METALS AND TRANSITION-METAL ALLOYS.

The pseudopotential technique has emerged as a powerful tool in recent past to study the phonons, electrical transport properties, magnetic and superconducting properties of simple, noble and transition metals. The alkaline earth metals have been very recently investigated for their phonons[8(a)] and therefore, the pseudopotential approach has been tested for explaining the phonons establishing its validity. In the present work, we have used the model potential given by Nand et al.[6] to study the phonon frequencies of barium and strantian. The agreement obtained between theory and experiment is satisfactory.

In view of the success of the pseudopotential approach in studying the lattice dynamical properties of simple, alkaline earth, noble and transition metals[1-8], it is worthwhile now to test the formulation in the case of alloys also. The present investigations focus on transition metal alloys only. These materials have large incomplete d-shells. The d-electrons are neither sufficiently bound to the atom for them to be unaltered in their phases nor sufficiently free for them to have a slowly varying pseudowave function permitting the application of perturbation treatment. Nevertheless, most properties of these materials depend upon integrals over s-like and d-like states and in many cases meaningful values may be obtained for these materials in terms of simple perturbation theory. In the present work the author has used a model [illegible] pseudopotential for transition-metal alloys, which in a simple parametric way includes all the features dictated by the physics of the situation.

The effect of hybridization plays a very important role in determining the electron-phonon interaction matrix elements of transition metals and their alloys. The effect of hybridization has been incorporated in terms of an effective mass, which depends upon d-state radii of the transition-metal alloys as defined by Harrison and Froyen[5]. The computation of the phonon dispersion relations in transition metal alloys using the model potential and the dielectric function of Singwi et al.[10] have been presented. The theoretical results on phonon dispersion curves have been found to be in satisfactory agreement with experiment for transition-metal alloys. It is worthwhile to report that the model potential reproduces most of the observed strong anomalies in [111] and [100] symmetry directions in the case of Nb - Mo transition-metal alloys for different compositions.

VIBRATIONAL PROPERTIES OF AMORPHOUS SEMICONDUCTORS AND THEIR ALLOYS

Amorphous semiconductors, with the well established crystalline foundation as a departure point, offer new frontiers for research and hopefully, promise for technological developments. Amorphous semiconductors are non-crystalline and lack long range periodic ordering of their constituent atoms. That is not to say that amorphous semiconductors are completely disordered on atomic scale. Chemistry provides almost rigorous bond-length and to a lesser extent, bond-angle constraints on the nearest neighbour environment. Unlike amorphous metals, amorphous semiconductors do not consist of close-packed atoms, but rather they contain covalently bonded atoms arranged in an open net work with correlations in ordering up to the third, fourth nearest neighbours. The short range order is directly responsible for observable semiconductor properties such as optical obsorption edges and activated electrical conductivities. Hence in the present work the short range order upto only first nearest neighbour interactions have been taken into account as a prominent feature in the study of vibrational properties of amorphous semiconductors and their alloys.

For amorphous semiconductors and their alloys, the vibrational density of states $g(\omega)$ may be regarded as the primary quantity of interest. Infrared obsorption or Raman scattering will give a good indication of the main features of the density of states of amorphous semiconductors and their alloys, because neutron scattering technique, which largely supplanted infrared obsorption and Raman scattering in the case of crystalline materials, plays a lessor role for amorphous semiconductors and their alloys. Hence in view of all the above facts we have followed a theoretical approach based on very short range order which is appropriate to amorphous materials to investigate phonon density of states of C, Si, Ge and their alloys. The relevance of the obtained results to the interpretation of Raman and infrared spectra are discussed in the present thesis.

ELECTRICAL PROPERTIES OF AMORPHOUS TRANSITION-METAL ALLOYS.

The partial success of simple ziman model[11] Faber-Ziman theory[12] and s-d scattering model[13] in explaining the available experimental information on electrical resistivity and thermopower of amorphous transition-metal alloys makes us to investigate the compositional dependence of the electrical transport properties of amorphous Zr-based transition metal alloys (Cu_xZr_{1-x}, Ni_zZr_{1-x} and Co_xZr_{1-x}). The theory which we developed for transport properties of amorphous transition-metal alloys leads us to infer that there is no significant contribution from the different atom interactions in the case of amorphous transition-metal alloys. This different atom interaction or cross term $\left[M_x\text{-}Zr_{1-x},\ M = \text{Cu, Ni and Co}\right]$ contribution is an important deviation for amorphous system when the expressions from the liquid alloys are extended towards the amorphous metal alloys.

The quadratic nature of the composition dependence of the electrical resistivity and the thermopower in the case of amorphous transition metal alloys indicated that the electron scattering mechanism are entirely different from the liquid alloys. The effect of d-bands will also be crucial in determining the density of states of the fermi level to account for the compositional dependence of transition-metal amorphous alloys.

SUPERCONDUCTING PROPERTIES OF AMORPHOUS TRANSITION-METAL ALLOYS.

The author has studied the temperature coefficient of the electrical resistivity ($\partial\rho/\partial T$) with composition and further investigated the dependence of the temperature coefficient of the electrical resistivity on the electron-phonon interaction parameter (λ). The observation that in transition-metal-amorphous alloys, the dependence is non-linear in character, contradicts the earlier observed linear dependence by Grimvall[14] in the case of simple alloys. The non-linear dependence is given by $\partial\rho/\partial T = a + b\lambda^2 + c\lambda^4$, where a, b and c are constants. Using this relation the author calculates the values of electron-phonon parameter (λ) and then the superconducting transition temperature for Cu_xZr_{1-x}, Ni_xZr_{1-x} and Co_xZr_{1-x} by means of McMillan's formula[15]. A very good agreement between theory and experiment in the case of superconducting transition temperature for all values of composition in the case of Cu_xZr_{1-x}, Ni_xZr_{1-x} and Co_xZr_{1-x} has been observed.

The present investigations have resulted in the following research publications :

1. Model potential approach to the lattice dynamics of Barium.
   Phys. Rev. B33, 5839 (1986).
2. Lattice dynamics of niobium-molybdenum alloys : A pseudopotential approach Communicated.
3. Force constant variation from crystalline to amorphous Germanium.
   S.S. Commun. Vol.52, 359 (1984).
4. Phonon density of states of amorphous $Si_{0.5}Ge_{0.5}$.
   Phys. Stat. Sol. (b), 134, 17 (1986).
5. Phonon density of states of amorphous Si_xC_{1-x}
   J. Phys. Chem. Solids (1986).
6. Compositional dependence of the electrical transport properties of amorphous transition-metal alloys.
   Nuovo Cimento D-7, 212 (1986).
7. Non-linear dependence of the temperature coefficient of electrical resistivity on electron-phonon interaction constant in the case of transition-metal amorphous alloys.
   Phys. Stat. Sol(b) 128, K183 (1985).

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