PREFACE

The development of new materials is essential for technological advancement. There has been an increasing attention in research and development of ‘smart materials’. These materials originate from the synthesis of structural and functional materials and integration of a control mechanism. Shape memory alloys (SMA) form an important class of smart materials that can be used in high-tech industrial applications. The properties of these alloys can be changed and controlled by thermo-mechanical processing. The most relevant mechanical properties, such as shape memory and super-elastic effects, are related to first-order diffusionless martensitic transformation (MT) between the high-temperature, high-symmetric austenite phase and the low-temperature, low-symmetric martensite phase.

Shape Memory Effect (SME) was first observed in Au-Cd alloy in 1951. It has kindled much interest with its peculiar characteristics and its relationship to MT. However, detailed studies about the theory and application of the SME have begun with its observation in the equiatomic percent of Ti-Ni alloy in 1963. It is reported in 1964 that Cu-Al-Ni also shows SME. Recently studies on Cu-based alloys, focusing on Cu-Al-Ni and Cu-Al-Zn, have been carried out as a substitute for Ti-Ni alloys.

The binary alloys of copper and aluminium display shape memory characteristics but have a transformation temperature that is generally considered
too high for practical uses. The addition of elements Nickel, Zinc, Beryllium and Palladium produces a new ternary compound, which is of commercial application. These alloys have transformation temperatures which can be modified to lie near room temperature value. Cu-Zn-Al has the advantage that they are made from relatively cheap metals using conventional metallurgical processes.

To get a reliable characteristics of devices based on these alloys, detailed studies regarding the evolution of the order at high temperature, the limit of stability of the $\beta$ phases and their influence on the thermo-elastic martensitic transformation are to be conducted. The martensitic transformations are being studied by various authors, both experimental and theoretical.

The anharmonicity in solids due to the non-linearity of interatomic forces with respect to atomic displacements is the origin of thermodynamic properties such as thermal expansion or the deviation of the lattice specific heat at high temperatures. Moreover, the anharmonic nature of lattice vibrations in crystals plays an essential role in determining the lattice dynamics in the vicinity of structural phase transitions. Owing to the technologically important shape memory properties exhibited by the Cu-based alloys, MT has been widely studied on these materials and a good effort has been devoted to the study of anomalies preceding the transformation. The softening of the acoustic-phonon modes associated with the shear elastic constants observed in Cu-based shape-memory alloys on approaching the transition temperature is worth investigating. As the lattice distortion is an anharmonic phenomenon, an anharmonicity enhancement on approaching the MT is expected.
Higher order elastic properties are related to the anharmonicity of the crystal lattice. Elastic constants provide insight into the nature of binding forces between the atoms, since they are represented by the derivatives of the internal energy. A complete set of higher order elastic constants of materials is essential to estimate the physical parameters such as Debye temperature, compressibility and acoustic anisotropy.

There exists various theoretical and experimental techniques for the determination of higher order elastic constants of solids. The anharmonicity of the crystal lattices can be studied by making use of the higher order elastic constants of crystals. Elastic constants link specific heat, Grüneisen parameters and thermal expansion. Theoretical calculations from the thermodynamic and lattice dynamic points are useful in the study of the elastic and thermal properties of crystals. Elasticity in crystals throws light on the interatomic potentials, equations of state, phonon spectra and lattice specific heat of solids. Second-order elastic constants and their pressure variations provide insight into the nature of the binding forces since they are represented by the derivatives of the free energy of the crystal.

The present objective is to study the vibrational anharmonicity of long wavelength acoustic modes of selected Cu based shape memory alloys. We have calculated the complete set of second- and third-order elastic constants of Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd. A combination of Born and Huang’s deformation theory and Murnaghan’s finite strain elasticity theory has been used to get the expressions for the strain energy density of the lattice. The theory is based on the Keating’s approach by taking into account the two-body and three-body
interactions up to second nearest neighbors in the lattice. The calculated elastic constants are compared with the reported experimental values. The aggregate elastic properties like the adiabatic bulk modulus, shear modulus and anisotropy factor are also obtained. Pressure derivatives of the second-order elastic constants have been investigated. The mode Gruneisen parameters of the acoustic waves and hence the low temperature limit of the lattice thermal expansion and the Anderson–Gruneisen parameter are determined based on the quasi-harmonic approximation.

The present study consists of the following steps.

- Calculation of inter-lattice displacements of the atoms in the crystal.
- Determination of the second-order elastic constants.
- Determination of the third-order elastic constants.
- Calculation of the pressure derivatives of the second-order elastic constants.
- Determination of the low temperature lattice thermal expansion.

The thesis is divided into seven chapters. Chapter 1 gives a brief review of the work done in the field of smart materials in general and shape memory alloys in particular. An introduction to the theory of elasticity formulated by Born, Huang, Murnaghan and Bhagavantam is also presented. Chapter 2 gives the derivation of the expressions for the second- and third-order elastic constants of cubic crystals based on the method of homogeneous deformation and the Keating’s potential scheme. The results calculated for the second-order crystal potential parameters, second-order elastic constants and bulk elastic properties of Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd SMA are collected and compared with experimental values in Chapter 3.
Expressions for the pressure derivatives of the SOEC are derived using effective second-order elastic constants in Chapter 4. The results of third-order potential parameters, TOEC and the pressure derivatives of SOEC for the crystals Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd are obtained and are compared with the experimental values. Based on quasi-harmonic approximation, expressions for the elastic wave velocities along different crystallographic directions and the Gruneisen parameters for longitudinal and transverse modes are derived in Chapter 5. Equations of the low temperature limits of lattice thermal expansion in Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd are derived. Chapter 6 includes the variation of the elastic wave velocities and the mode Gruneisen parameters as a function of different propagation directions. The lattice thermal expansion and the Anderson-Gruneisen parameters of Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd are reported. Summary and future scope of the work presented in this thesis are given in Chapter 7.

Most of the work presented in this thesis have either been published in journals or presented in international and national conferences or are in the process of publication. A list of such papers is given below.


iv. Third-order elastic constants of Cu-Al-Ni, Santhosh Potharay Kuruvilla and C. S. Menon,


v. Third-order elastic constants of the shape memory alloy Cu-Al-Be, Santhosh Potharay Kuruvilla and C. S. Menon,


vi. Third-order elastic constants of the shape memory alloy Cu-Al-Zn, Santhosh Potharay Kuruvilla and C. S. Menon


vii. Elastic Anharmonicity in the shape memory alloy Cu-Al-Pd, Santhosh Potharay Kuruvilla and C. S. Menon

viii. Elastic constants and low temperature thermal expansion of the shape memory alloy Cu-Al-Ni, Santhosh Potharay Kuruvilla and C. S. Menon

*16th Swadeshi Science Congress*, November 7-9, D B Pampa College, Parumala, Kerala (2006).

ix. Elastic anisotropy and low temperature thermal expansion in the shape memory alloy Cu-Al-Zn, Santhosh Potharay Kuruvilla and C. S. Menon


x. Quasi-harmonic theory of elasticity and lattice thermal expansion of Cu based shape memory alloys, Santhosh Potharay Kuruvilla and C. S. Menon


xi. Phase transition studies in the shape memory alloy Cu-Al-Pd, Santhosh Potharay Kuruvilla and C. S. Menon


xii. Non-linear elasticity studies and lattice thermal expansion in the shape memory alloy Cu-Al-Pd, Santhosh Potharay Kuruvilla and C. S. Menon

xiii. Lattice thermal expansion of the shape memory alloy Cu-Al-Zn, Santhosh Potharay Kuruvilla and C. S. Menon


xiv. Non-linear elasticity and low temperature thermal expansion of the shape memory alloy Cu-Al-Be, Santhosh Potharay Kuruvilla and C. S. Menon


xv. Lattice thermal expansion of the shape memory alloys Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd, Santhosh Potharay Kuruvilla and C. S. Menon

*International Conference on Ferromagnetic Shape Memory Alloys*, November 14-17, SNBNCBS, Kolkata (2007).

xvi. Higher order elastic constants of the shape memory alloys Cu-Al-Ni, Cu-Al-Zn, Cu-Al-Be and Cu-Al-Pd, Santhosh Potharay Kuruvilla and C. S. Menon


xvii. Elastic characterization of actuator alloys – Cu-Al-Be and Cu-Al-Pd, Santhosh Potharay Kuruvilla and C. S. Menon