THE ELECTRICAL AND THERMAL PROPERTIES OF TRANSITION METALS USING A PSEUDOPOTENTIAL APPROACH

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P R E F A C E

Lattice dynamical studies of solids are a pre-requisite for proper understanding of numerous properties of solids. During the past two decades or so, the lattice dynamics of metals has received considerable theoretical and experimental attention, especially because of the presence of conduction electrons. Recent developments in neutron in-elastic scattering technique to study the various properties have opened new avenues for theoretical research. Side by side, more accurate theories, based on much more sound footing and having least approximations, have been developed to interpret the experimental data. Particularly, the case of metals has been very interesting because of role of electron-ion interaction. Treatment of the electron-ion interaction which is a many body interaction characterized by long range screening of ions by electrons, has been problematic. Phenomenological theories[1] have been developed to incorporate it explicitly, but these all have met with limited success. In the recent past, the pseudopotential theory[2,3] has emerged as one of the most simple and most powerful technique to study the electron-ion interaction. The first principle non-local pseudopotentials were found to be very difficult to handle owing to the tremendous computational labour involved in it. Later it was found that the non-local part of the pseudopotential can be replaced by an effective term containing few parameters. Such as approach was originally adopted by

Heine and Abarenkov[4]. The pseudopotential has been applied quite successfully in interpreting atomic electronic and numerous other electrical and thermal properties of metals.

The application of pseudopotentials and model potentials in explaining the properties of metals can be divided into two aspects. On one hand, the empirical data relating to properties such as Fermi surfaces, optical absorption spectra or phonon spectra can be fitted to some effective potential containing adjustable parameters. On the other hand, one can calculate pseudopotentials and model potentials from first principles and apply the results to calculate the measured properties. The two points of view complement to one another allow the model potential to serve as a meeting ground between theory and experiment. Cohen and Heine[5] have reviewed this technique and have summarized the empirical model potentials which have been obtained for a large number of elements.

In view of the success of the pseudopotential approach in the simple and the noble metals, it is worthwhile to test the formulation to transition metals. The transition metals have large incomplete d-shells. The d-electrons are neither sufficiently bound to the atom for them to be unaltered in the metallic state nor sufficiently free for them to have a slowly varying pseudo-wave function permitting the application of perturbation treatment. Nevertheless, most properties of metals

depend upon integrals over the s-like and d-like states and in many cases meaningful values may be obtained in both simple and transition metals in terms of simple perturbation theory. In both the simple and the transition metals the pseudopotential equation is a valid starting point.

In the present investigation, the author has used a model pseudopotential[6] for transition metals which includes in a simple parametric way all the features dictated by the physics of the situation. The investigations have been carried out under the following two phases.

In the first phase of investigations. (i.e. using tight binding approach), the physical origin of the anomalies in the phonon dispersion curves of transition metals have been found to lie in the q-dependence of the electron-ion form factor. The form factor plays an important role in determining the phonon dispersion. In the evaluation of phonon dispersion curves of transition metals (i.e. Vanadium, Niobium, Tantalum, Chromium, Molybdenum and Tungsten), the dynamical matrix elements $D_{\alpha\beta}(q)$ are composed of three contributions i.e. coulombian contribution $D^{C}_{\alpha\beta}(q)$, the tight binding contribution $D^{T}_{\alpha\beta}(q)$ and electronic contribution $D^{E}_{\alpha\beta}(q)$. The energy wave number characteristic function $F(q)$, the Hartree dielectric function $\varepsilon(q)$, the local field correction $G(q)$ are used in the calculations as given by Singwi et al[7] and modified dielectric function $\varepsilon^{*}(q)$ as given

by Moriarty[8]. Overall the agreement is fair but more remarkable is reproduction of the anomalous features of the phonon dispersion. On comparison between author's and Animalu's[9] results, the trend in the phonon dispersion curves is in author's favour.

In the second phase of investigations (i.e. using effective mass correction approach), the hybridization plays a very important role in determining the electron-phonon interaction matrix elements. The effect of hybridization has been incorporated in terms of an effective mass, which depends upon d-state radius of the transition metals as defined by Harrison and Froyen[10]. In the calculation of phonon dispersion curves of the transition metals, the dynamical matrix elements $D_{\alpha\beta}(q)$ again are assumed to be composed of two contributions, i.e. the coulombian contribution $D^{c}_{\alpha\beta}(q)$ and electronic contribution $D^{E}_{\alpha\beta}(q)$.

The entire work is being presented in five chapters. A chapter-wise summary is given below.

The first chapter is introductory one and the physical concepts of pseudopotential, the excerpts from pseudopotential theory along with a review of different forms of pseudopotentials have been presented. Various theories developed so far have been briefly discussed. The simplicity and wide applicability of the pseudopotential approach have been discussed.

In the second chapter, the Fourier transform of unscreened transition metal model potential has been taken which is further

divided by a Hartree dielectric function, modified according to Singwi et al[7] to include the effect of exchange and correlation between conduction electrons, to obtain the screened form factor. The transition metal model potential contains two arbitrary parameters which have been evaluated by fitting to experimental phonon frequencies at zone boundaries. Thus the calculation of form factor, energy wave number characteristic and G(q) function is straight forward.

The third chapter mainly deals with the dynamical matrix, parameterisation of pseudopotential, the computation of the phonon dispersion relations in transition metals (i.e. Vanadium, Niobium, Tantalum, Chromium, Molybdenum and Tungsten) using the model potential and self consistent dielectric function of Singwi et al. The theoretical results of phonon dispersion curves have been found to be in good agreement with the experiment for all the transition metals, except for chromium, molybdenum and tungsten because the transverse branch T_1 in [110] direction (in the first phase of investigations) is not upto the same agreement in each case. It is worthwhile to report that the model potential also reproduces the observed crossing of transverse branch over the longitudinal one in [100] direction in the case of niobium and tantalum and crossing of the two transverse branches in the [110] direction in the case of niobium and tungsten.

Chapter fourth deals with the thermal properties, such as binding energy, elastic constants and compressibility. Appropriate theory is also given. The results of calculations are given in tabular form.

Chapter fifth deals with the electron transport properties, such as electrical resistivity and thermoelectric power of molten transition metals. The theory of scattering probability and Ziman's theory of electrical resistivity are discussed in detail. The structure factor S(q), appearing in the theory, is used from the experimental results of Waseda et al[11].

It is evident from the present investigation that the used model potential successfully interprets almost all the properties of transition metals and establishes in its own right its importance in the field of the lattice dynamics. From the present study one may gain confidence in choosing this form of model potential and applying it to study other various properties of transition metals.

The investigations have resulted in the following publications:-

1. Lattice dynamics of tantalum: a pseudopotential approach. IL Nuovo cimento 64B, 498 (1981).

2. Phonon anomalies in transition metals. Physica status Solidi (b) 108 , K-113 (1981).

3. Phonon anomalies in niobium using a model potential approach.
J. Phys. Soc. Japan 51, 111 (1982).

4. Phonon anomalies of Tantalum : a pseudopotential approach. Nuclear Physics and Solid State Physics Symposium (Organised by Department of Atomic Energy, Government of India), Banaras Hindu University, Varanasi (1982), SBA-4.

5. Lattice dynamics of b.c.c. transition metals. (Communicated to Philosophical Magazine).

6. The electrical resistivity of molten transition metals. (Communicated to Physica B).

C O N T E N T S