

RESONANCE SCATTERING IN THE STUDY
OF
SOLID AND LIQUID STATES

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Thesis submitted for the degree of

DOCTOR OF PHILOSOPHY

of the

UNIVERSITY OF MYSORE

Materials Science Division

NATIONAL AERONAUTICAL LABORATORY

Bangalore 560 017 (India)

1974

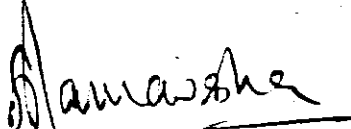
DECLARATION

I declare that this thesis has been composed by myself out of the investigations I carried out in the Material Science Division under the supervision of Professor S. Ramaseshan, Head, Materials Science Division, National Aeronautical Laboratory, Bangalore. The subject matter reported here has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title.

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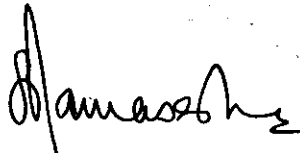
CERTIFIED



Supervisor

CERTIFICATE

I certify that this thesis has been composed by Mr. T. G. Ramesh out of the investigations he carried out in the Materials Science Division under my supervision. The subject matter of this thesis has not previously formed the basis of the award of any degree, diploma, associateship, fellowship or other similar title.



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ACKNOWLEDGEMENTS

I am deeply indebted to Professor S. Ramaseshan, Head of the Materials Science Division, National Aeronautical Laboratory, for his stimulating guidance throughout the course of the work reported in this thesis.

My grateful thanks are due to Dr. A.S. Reshamwala for the help and cooperation I received during the course of the experimental work and for the many discussions I had with him on high pressure techniques.

I would like to thank all my colleagues in the Materials Science Division for their cooperation during this work. Special thanks are due to Mr. Rajaram Nityananda and Mr. G.S. Ranganath for the many stimulating discussions I had with them on not only topics dealt with in this thesis but also on many allied problems.

It is a pleasure to thank Mr. M.T. Srivatsa and Mr. K.T. Pratapan of the Instrumentation Division, N.A.L., for their valuable suggestions and help during the development of the automatic recording system.

I thank Mr. K. Jagannatha Rao and Mr. Venu for the technical assistance in the experimental work, Mr. S.Raghavachar

for the typing of the manuscript and Mr. Krishnamoorthy for help in preparing the illustrations in the thesis.

I am thankful to Dr. S.R. Valluri, Director, National Aeronautical Laboratory, for his encouragement and permission to use all the facilities of the Laboratory.

Council of Scientific and Industrial Research, India, financed the work from 1968-70 in the form of a fellowship, which is also gratefully acknowledged.

T.G. Ramesh
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P R E F A C E

The thesis reports the theoretical and experimental studies carried out by the author on the application of resonance scattering of X-rays, neutrons and electrons to some problems on the physics of the solid and liquid states of matter.

The phenomenon of anomalous or resonance scattering of X-rays and neutrons arises whenever the frequency of the incident radiation is close to the absorption region. It is well known that the anomalous dispersion method provides a powerful tool in the solution of the 'phase problem' in crystallography. The first part of the thesis (with four chapters) is concerned with the novel applications of the resonance scattering of X-rays and neutrons in the fields of lattice dynamics of crystals, structure of binary alloys and amorphous systems. The second part of the thesis has three chapters and deals with the concept of the resonance scattering of conduction electrons manifesting itself in the remarkable high pressure behaviour of liquid caesium and cerium. Experimental studies of the thermo-electric power and resistivity of cerium at high pressures are also reported.

The first chapter presents the basic theory of resonance scattering of X-rays, neutrons and electrons. The results of this theory form the background material for the subsequent chapters of the thesis. Although no significantly new results are reported in this chapter, the method of presentation as far as the author is aware, is essentially new. It accomplishes the following:

(i) Instead of dealing with the phenomena of X-ray and neutron anomalous scattering separately, a unified approach has been worked out based on the celebrated 'optical theorem' of Bohr, Peierls and Placzek, and the partial wave method in the scattering theory. This approach emphasizes the interplay between the coherent and the incoherent channels during the scattering process. The phenomenon of anomalous scattering can be looked upon as a manifestation of either a resonant elastic or inelastic process or of both. X-ray anomalous scattering corresponds to a reaction in the elastic channel due to a resonant inelastic process, viz., the photoelectric absorption. Neutron anomalous scattering presents the case of both the elastic (n,n) and the inelastic (n, γ) processes going through resonance at the same energy.

(ii) The confusion that exists in the literature regarding the sign of the imaginary component of the scattering factor is clarified. It is pointed out that this discrepancy

really stems from the different space-time dependence assumed for the incident wave in the case of X-ray and neutron scattering. A unified convention for the scattering amplitudes and the structure factor is also presented.

(iii) The Breit-Wigner formalism for resonance scattering has been developed from first principles. These results are used not only in neutron anomalous scattering but also for treating the resonance scattering of conduction electrons in liquid caesium and cerium.

The second chapter deals with the problem of the determination of the polarization vectors of lattice waves using the method of anomalous neutron scattering. The displacement of atoms from their equilibrium positions under the influence of a lattice wave can be characterized by their respective eigenvectors. In a crystal containing n atoms per unit cell, the polarization vector for a lattice wave defined by wave vector \underline{q} and polarization index j represents a $3n$ dimensional vector constructed out of the n eigenvectors. The evaluation of the components of the polarization vector gives us information about the nature and relative amplitudes of vibration of the different atoms in the unit cell. The main objective in the study of the lattice dynamics of crystals is to arrive at the interatomic force constants which can be used in the understanding of

the various physical properties of the crystal. The normal practice is to choose the set of force constants which fits the experimentally determined lattice frequencies. However it has been demonstrated by Leigh, Szigetti and Tewary, and Cochran that the interatomic force constants cannot be uniquely determined from a knowledge of the lattice frequencies alone. This ambiguity in choosing the right set out of an infinite number of sets of force constants, all yielding the same frequencies, can be resolved if one has a knowledge of the polarization vectors also. However the determination of the polarization vectors of lattice waves propagating along a general direction in the crystal is rendered difficult because of the 'phase problem' associated with a complex eigenvector. We have proposed a method based on anomalous neutron scattering to solve this 'phase problem' which would enable one to obtain complete information on a complex eigenvector. The important result of this investigation is that in a non-centrosymmetric structure there will be a difference in the intensity of the coherent one-phonon peaks from opposite faces of the crystal under conditions of anomalous neutron scattering. In crystallography the violation of the Friedel's law in a non-centrosymmetric structure leads to $I(\underline{H}) \neq I(\bar{\underline{H}})$ (\underline{H} being a reciprocal lattice vector) and in lattice dynamics we get the analogous result, viz.,

$I(\underline{H}, \underline{q}) \neq I(\bar{\underline{H}}, \bar{\underline{q}})$ where \underline{q} represents the wave-vector of the lattice wave. This breakdown of the law similar to Friedel's law in crystallography leads to new relations with the help of which the 'phase problem' associated with the determination of the initial phase of the elliptic motion (complex eigenvector) can be solved. We also present the Argand diagram representation of the coherent inelastic scattering (one-phonon process) which helps in visualizing the intensity differences between a pair of reflexions under conditions of anomalous scattering. The procedures for extracting the components of the polarization vector in non-centrosymmetric and centrosymmetric two atom structures where they are in general complex and in Bravais lattices where they are always linearly polarized, have been worked out.

The third chapter is concerned with the problem of separating the individual static displacements in a binary alloy system using the anomalous dispersion method. It is well-known that in a binary alloy above the ordering temperature the atoms do not occupy the precise nodal positions of the lattice. This 'static displacement' is due to two factors, viz., the difference in the size of the atoms forming the alloy and the non-centrosymmetric arrangement of the neighbours in the cluster. The diffuse scattering associated with the static displacement of atoms modulates the short-

range order diffuse scattering in a way as to make it aperiodic in reciprocal space. The static displacement (S.D.) diffuse scattering can be separated from the short-range order diffuse scattering using the method of Boric and Sparks. However the static displacement coefficients that enter the expression for S.D. diffuse scattering involve both the atomic displacements of both the AA and BB pair of atoms in a AB alloy system. A search of the literature revealed the lack of a method of separating these individual contributions. We propose that a measurement of the diffuse intensity associated with short-range order and static displacement, at two wavelengths near the absorption region, leads to a separation of the atomic displacements due to AA and BB pairs of atoms for a given coordination shell. The relevant expressions for Fourier analysing the diffuse intensity data are also given. It is pointed out that if one uses the method of anomalous neutron scattering, the intensity of the diffuse scattering can be considerably enhanced at the expense of the Bragg reflexions.

The fourth chapter deals with the problem of separation of the partial structure factors in a liquid or amorphous binary system using the three wavelength method of anomalous scattering. The short range order in a binary system AB is characterized by the three partial structure

factors corresponding to AA, AB and BB pairs of atoms. A single scattering experiment cannot lead to a separation of these partial structure factors. Enderby, North and Egelstaff were the first to separate the partial structure factors of liquid Cu_6Sn_5 system using the neutron scattering technique with isotope enrichment. We have proposed another method for this separation using the intensity data collected in the resonance region. The proposed method is of general validity as regards to both X-ray and neutron anomalous scattering. For X-ray scattering from binary liquids, anomalous scattering method is perhaps the only tool to separate the different partial structure factors. The anomalous neutron scattering method, although it has many experimental advantages, is useful only for a few systems comprising of Cd^{113} , Gd^{157} , Sm^{149} , Eu^{151} etc., which are resonant scatterers. A model calculation on how the total coherently scattered intensity would vary in the presence of anomalous dispersion effects is also presented.

In the fifth chapter, we discuss the application of the 'virtual bound state' concept of Friedel to the high pressure behaviour of liquid caesium. The most interesting feature of the phase diagram of caesium is the anomalous density variation of the liquid with pressure, viz., the liquid becomes denser than the closest packed solid phase.

This is also reflected in the marked resistivity variation of liquid caesium with pressure. We have proposed a theoretical model to explain the resistivity behaviour with pressure which is also consistent with the density variation in the liquid phase. The important result of this study is that d-wave scattering resonance plays a vital role in the high pressure behaviour of liquid caesium. In our theoretical model the 6s-5d 'electron collapse' results in the formation of a 'virtual bound state' accompanied by d-wave scattering resonance. The 'two-species' model of liquid caesium has been examined on the basis of the above hypothesis and we suggest that the $6s \rightleftharpoons 5d$ dynamic conversion is due to the tunneling phenomenon. We have also drawn attention to the fact that the high compressibility of caesium in comparison with the other alkali metals is responsible for the strange behaviour of liquid caesium. Theoretical calculations of the resistivity based on the Ziman's formula are presented. The Breit-Wigner formulae for resonance scattering and Friedel sum rule have been used in evaluating the electron-ion form factor. The initial resistivity decrease leading to a shallow minimum in the low pressure region observed for the liquid alkali metals (with the exception of lithium) has been explained. The general features of the experimental resistivity versus pressure

graph can be accounted in our model although a substantial discrepancy between the theoretical and experimental values exists in the high pressure region. It is pointed out that this may be due to the breakdown of Ziman's resistivity formula under conditions of resonance scattering.

During the course of this investigation it occurred to us that a study of the thermo-electric power with pressure would throw more light on the electronic behaviour of these substances. The next two chapters are concerned with the development of new techniques and an experimental study on cerium where again the 'virtual bound state' picture plays a vital role.

The sixth chapter is devoted to the development of new techniques for measurement of the thermo-electric power and resistivity at high pressures. A detailed literature survey revealed that there have been relatively very few studies on thermo-electric behaviour of metals with pressure as compared with the resistivity studies. Further, most of these studies were confined to pressures up to only 5 kbar. Since most of the phenomena of interest take place at still higher pressures, we have developed new high pressure techniques for the measurement of the thermo-electric power.

A teflon thermo-power cell has been devised for the measurement of the thermo-power of solid and liquid metals up

to 40 kbar pressure and 250°C. The main advantage of this technique is that the pressure communicated to the sample is truly hydrostatic.

In order to raise the temperature range of measurement, we have developed a High temperature-High pressure thermo-power cell using a solid pressure communicating medium. This design of the cell permits measurements of the thermo-power up to 800°C and 30 kbar pressure. The same cell can also be utilised for the resistivity studies.

The collection of experimental data on thermo-power is laborious and time consuming, especially when one has to scan a wide temperature and pressure range. In order to circumvent this problem, we have constructed an automatic recording system for plotting directly the thermo-power as a function of either the mean temperature at a given pressure or the pressure at a specified mean temperature.

The last chapter of the thesis presents the experimental work on the thermo-electric and the resistivity behaviour of cerium at high pressures. Cerium, a rare-earth metal, has a unique phase diagram in that a solid-solid phase boundary ends in a critical point. The γ - α transition in cerium has been the subject matter of numerous investigations. Amongst the transport properties, however only the resistivity had been used as a probe. We have

measured the thermoelectric power of cerium in the temperature range 10-400°C and pressures up to 25 kbar, using the experimental techniques described in the earlier chapter. The important results of this experimental study are briefly summarized here.

(1) The absolute thermo-power of γ -cerium exhibits a large variation with pressure in the pre-transition region which is in sharp contrast with the resistivity behaviour.

(2) The γ - α iso-structural phase transition manifests itself as a sharp decrease in the magnitude of the thermoelectric power.

(3) The thermo-power of α -cerium decreases continuously with pressure leading to a change of sign at higher pressures.

(4) The temperature variation of the thermo-power of α -cerium exhibits a remarkable behaviour. In the pressure region close to the γ - α phase boundary, the thermopower of α -cerium varies markedly with temperature from negative values at lower temperatures to large positive values at higher temperatures. Further this rate of variation with temperature decreases considerably at higher pressures.

We have also obtained new data on the resistivity behaviour with pressure at a temperature above the critical point. The resistivity versus pressure isotherm exhibits

a broad maximum as the virtual bound state moves continuously across the Fermi surface. This verifies the earlier prediction of Blandin, Coqblin and Friedel concerning the resistivity behaviour above the critical point.

The experimental results on the thermo-electric power variation with pressure have been discussed on the basis of the Friedel-Anderson model and Hirst's modification of this model. The behaviour of the γ -phase can be accounted satisfactorily on the basis of the virtual bound state picture appropriate to cerium. The continuous decrease of thermo-power with pressure in the α -phase and the anomalous temperature dependence support the fractional valency model or the inter-configurational fluctuation model of α -cerium.

All the problems described in the thesis were worked out by the author under the guidance and supervision of Professor S. Ramaseshan, Head of the Materials Science Division.

Most of the results discussed in this thesis have been reported in the following publications:

- 1 Determination of the Polarization Vectors of Lattice Waves by Anomalous Neutron Scattering - Acta Cryst. (1971), A27, 332.
- 2 Determination of the Static Displacement of Atoms in a Binary Alloy System using Anomalous Scattering - Acta Cryst. (1971), A27, 569.

- 3 **Partial Structure Factors in a Liquid or Amorphous Binary System Using Anomalous Scattering** - J.Phys.C.(Solid State), (1971), 4, 3029.
- 4 **'Electron Collapse' and the Resistivity of Liquid Caesium** - Phys. Lett. (1972), 39A, 308.
- 5 **High Pressure Behaviour of Liquid Caesium** - Pramana (1973), 1, 21.
- 6 **A Teflon-Cell Technique for the Measurement of the Thermo-Power of Solid and Liquid Metals at High Pressures** - J.Phys.E.(Sci., Instr.), (1974). 7, 133.
- 7 **Thermo-Electric Power of Cerium at High Pressures** - Pramana (1974), 2, April issue.
- 8 **Unified Approach to the Theory of Anomalous Scattering** - Paper presented at the International Conference on Anomalous Scattering held in Madrid, 1974.

NOTATION

\underline{X} = Vector X .

f^* = Complex conjugate of f .

\bar{A} = Average of A .