

EXPERIMENTAL INVESTIGATION
ON LAYERED OXIDE AND
TERNARY INTERMETALLIC COMPOUND

THESIS SUBMITTED FOR THE DEGREE OF
DOCTOR OF PHILOSOPHY (SCIENCE)
OF THE
UNIVERSITY OF CALCUTTA

BY
RUMA RAY
SAHA INSTITUTE OF NUCLEAR PHYSICS
CALCUTTA 700064.

2001

Table of Contents

1 Transition Metal Oxide	1
1.1 Introduction	2
1.2 Transition Metal Oxides	2
1.2.1 Transition Element in the Ligand Field	4
1.2.2 Insulating Materials	7
A. A theoretical approach to explain conductivity	7
1.2.3 Conducting Oxides	9
1.3 Classification of the oxides	10
1.3.1 Classification according to the conduction band	11
1.4 Some Representative Conducting Oxides	12
1.5 Models for non-metal-metal transitions	13
1.5.1 Band Overlap	13
1.5.2 Crystalline Symmetry Change	14
1.5.3 Antiferromagnetism	14
1.5.4 Electronic Correlation	16
1.5.5 Other Mechanisms	17
1.6 Strongly Correlated Electron systems	18
1.7 Electron Correlations in Transition Metal Oxides	20
1.8 Effect of magnetic lattice dimensionality	22
1.8.1 Layered (2-d) magnetic system	24
1.8.2 Frustration in 2-d planner antiferromagnet	26
1.9 The layered alkali transition metal oxide system	28
1.9.1 Importance of the alkali cobalt oxide system	28
1.9.1.1 Dominant carrier information	29
1.9.1.2 Technological importance	30
1.9.1.3 Electron correlation in this system	31
1.10 NMR as an investigating tool	33
Bibliography	35

2 Experimental Approach	40
2.1 Nuclear Magnetic Resonance (NMR)	41
2.1.1 Basic theory of nuclear magnetic resonance	41
2.1.2 Some applications of NMR	42
2.1.3 Hyperfine interaction	43
2.1.3.1 Magnetic hyperfine interaction	43
2.1.3.1.1 Complete Knight shift tensor	49
2.1.3.1.2 Resonance frequency in metallic system	50
2.1.3.2 Electrostatic hyperfine interaction : Nuclear electric quadrupolar interaction	50
2.1.3.2.1 Elementary aspects	51
2.1.3.2.2 Electric quadrupole Hamiltonian	52
2.1.3.2.3 Quadrupolar Hamiltonian with axially symmetric EFG tensor	55
2.1.3.2.4 Quadrupolar interaction as a first order perturbation over Zeeman interaction	56
2.1.3.2.5 General expression of the spectral transition considering second order quadrupolar interaction	57
2.1.3.2.6 Effect of quadrupolar interaction on the transitional frequency of integral and half integral spin	60
2.1.3.3 Combined Magnetic and Nuclear Quadrupolar Interactions .	61
2.1.3.4 Powder pattern of the NMR line shape	62
2.1.3.5 Some examples of NMR line shape	64
2.2 NaCo ₂ O ₄ system for experimental investigation	65
2.2.1 Preparation of NaCo ₂ O ₄ sample	65
2.2.2 Sample Characterization	66
A. XRD studies in NaCo ₂ O ₄ system	66
B. ²³ Na NMR studies at 300 K in NaCo ₂ O ₄	67
2.3 Experimental tools	68
2.3.1 Nuclear magnetic resonance (NMR) - cw technique	68

A. Signal Averager	68
2.3.2 Temperature variation accessories	68
Varian V-4540 temperature controller	69
2.4 Appendix	70
Bibliography	73
3 Experimental Investigation on NaCo₂O₄	75
3.1 Physical properties of the alkali cobalt oxide system: NaCo ₂ O ₄	76
3.1.1 Crystal Structure	76
Structural similarity with other oxide systems	77
3.1.2 Transport properties	77
3.1.2.1 Resistivity Results	77
3.1.2.2 Thermoelectric power and Hall coefficient	79
3.1.2.3 Transport properties of NaCo ₂ O ₄ with decreasing carrier concentration	80
3.1.2.4 Specific heat in NaCo ₂ O ₄	81
3.1.3 Magnetic properties	82
3.2 Magnetic Susceptibility	82
3.3 ⁵⁹ Co NMR results	85
3.3.1 ⁵⁹ Co NMR at 300 K	85
3.3.2 ⁵⁹ Co NMR results in the temperature range 350-110 K	87
(a) Temperature variation of ⁵⁹ Co NMR spectra	87
(b) Analysis of NMR spectra	87
3.3.3 Temperature dependence of electric field gradient at ⁵⁹ Co site	89
3.3.4 ⁵⁹ Co NMR Knight shift in NaCo ₂ O ₄	89
3.3.4.1 Origin of the Knight shift at cobalt site	90
3.3.5 Construction of K_{iso} versus χ diagram	91
3.3.6 Temperature independent shift	95
3.3.7 Temperature dependent shift	96
Sign of the coupling constants	97

Magnitude of the hyperfine coupling constant	98
3.3.8 Possible positions of the cobalt ions in the unit cell	99
3.4 ^{23}Na NMR results	99
3.4.1 ^{23}Na NMR at 300 K	99
3.4.2 ^{23}Na NMR results in the temperature range 300-110 K	100
(a) Analysis of the ^{23}Na NMR line shape	100
3.4.3 Temperature dependence of electric field gradient at ^{23}Na site	101
3.4.4 Temperature dependence of Knight shift experienced by the ^{23}Na site	101
3.5 Estimation of EFG at both Co and Na sites	102
3.5.1 The Idealized Model	102
3.5.2 Point Charge Model Calculation of EFG at ^{59}Co and ^{23}Na sites	104
(a) Technique of the Calculations	105
3.6 Different contributions to the magnetic shift tensor at Co and Na sites	109
3.6.1 Nuclear-Electronic dipolar interaction contribution to the dipolar tensor at Co site	110
3.6.2 Nuclear-Electronic dipolar interaction contribution to the dipolar tensor at Na site	112
3.7 Different contributions to the line width of ^{59}Co and ^{23}Na NMR spectra	113
3.7.1 Demagnetizing field	113
3.7.2 Contribution to the line width due to nuclear - nuclear dipole interaction	113
3.7.3 Time dependent nuclear-electronic magnetic interaction contribution to the NMR line width	116
3.8 Understanding of metallic conductivity in NaCo_2O_4 system in the light of semi-emperical formula of critical cation-cation distance R_c	118
3.9 Extended works on this system by other groups	121
3.9.1 NMR results on NaCo_2O_4 system obtained by Itoh et. al.	121
3.9.2 Calculation of thermopower by Koshibae et. al.	122
3.10 Summary	123
3.11 Appendix	128
3.11.1 Each of the Na layer is 50% occupied	128

3.11.2 Overlap Integral	128
3.11.3 Calculation of EFG tensor with respect to a orthogonal and non-orthogonal frame of reference	128
3.11.4 Density of NaCo ₂ O ₄	131
Bibliography	132
4 Experimental Investigation on a Ternary Intermetallic Compound and its hydride	136
4.1 Introduction	137
4.1.1 Effect of hydrogen on electronic and magnetic properties	139
4.1.2 Experimental observation regarding the existence of paired protons in CeNiInH _x ($x \geq 1.0$) and H-H separation	140
4.1.3 Location of hydrogen	142
4.2 Experimental	143
4.2.1 Preparation and characterization of the parent systems and its hydrides for experimental investigation	143
4.2.2 Crystal structure and Magnetic properties of the Deuterated sample .	144
4.2.3 Nuclear magnetic resonance (NMR) - cw technique	145
4.2.4 Pulse NMR	145
Measurement of spin lattice relaxation time T_1	145
4.2.5 Temperature variation accessories	146
4.2.4.1 Oxford CF1200 cryostat	147
4.3 Developmental works	147
4.3.1 Construction of NMR probe	147
A. Tank circuits and impedance matching networks	148
B. Some important steps for coil construction	150
4.3.2 Development of resistivity setup by ac method	150
A. Current source	151
B. Requirement of Inverter and transformer	151
C. Kelvin Verley potentiometer	152

D. Unit gain buffer	153
F. Resistance measurement in CeNiIn	154
4.4 ^2D NMR in CeNiInD_x system	154
4.4.1 ^2D NMR line shape in CeNiInD_x ($x = 0.33, 1.01$)	154
4.4.2 Analysis of the experimental spectra	155
4.4.3 Intrinsic line width of the ^2D NMR line	157
4.4.4 Isotropic shift experienced by the NMR line	158
4.4.5 Lattice contribution to electric field gradient	158
4.5 Proton NMR in $\text{CeNiInH}_{0.53}$ down to liquid helium temperature	161
4.5.1 ^1H NMR line-shape in $\text{CeNiInH}_{0.53}$	162
4.5.2 Spin-Lattice relaxation time	163
4.6 Basic principles of PAS	165
4.6.1 Different measurable physical parameters in PAS	165
(a) Positron life time	165
(b) Doppler shift	166
4.6.2 Analysis of PAS results	167
(a) Analysis of the Doppler Broadened Line shape	167
(b) Analysis of Positron Lifetime spectrum	168
4.7 Experimental tools	168
4.7.1 Positron annihilation spectroscopy (PAS)	168
A. Positron source	168
B. Sample and Source configuration	169
C. Doppler broadening and Positron life time spectrometer	169
4.7.2 Leybold refrigerator cryostat	169
4.8 Positron annihilation studies on CeNiIn and LaNiIn	170
4.8.1 S parameter and positron life time τ in the temperature range 280–18 K	170
4.8.2 Contribution due to thermal expansion of lattice	173
4.8.3 Spin fluctuation in CeNiIn	175
4.9 Positron Annihilation studies on $\text{CeNiInH}_{1.60}$	176

4.9.1	Analysis of PAS results	177
4.10	Summary	179
4.11	Appendix	183
4.11.1	Anisotropic $c - f$ mixing	183
	Bibliography	185