Solid State Communications Vol. 18, pp. 845–847, 1976. Pergamon Press. Printed in Great Britain

PHONON DISPERSION IN NiO*

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(*Received* 6 *October* 1975 *by A.A. Maradudin*)

The phonon dispersion relations in NiO have been measured using coherent inelastic neutron diffraction. Good fits to the data were obtained using various shell models. The room temperature phonon density of states was calculated and used to determine the temperature dependence of the lattice specific heat and the Debye temperature.

1. INTRODUCTION

NICKELOUS OXIDE is a type II antiferromagentic material below its magnetic ordering temperature (T_N = 523°K). The magnetically active metal ions lie in ferromagnetic sheets parallel to (111) planes with the spin direction reversed between adjacent sheets. Above T_N, the nuclear structure is f.c.c. As the temperature is lowered through the Néel point a contraction takes place along the normal between spin sheets producing a resultant rhombohedral nuclear structure and a magnetic domain structure. There are four principle magnetic domains corresponding to the four possible (111) planes in which the ferromagnetic ordering can occur. Due to the small size of the distortion one can treat the nuclear structure as pseudocubic with a cell angle of $\pi/2 + \delta$ where $\delta \simeq 3.5'$ at room temperature.[1]

Several papers have appeared in the literature dealing with inelastic neutron scattering studies of NiO and the other transition metal monoxides, MnO and CoO. Hutchings and Samuelsen[2] have determined the magnon dispersion relations in NiO. In MnO, the phonon dispersion relations have been examined by Haywood and Collins[3] and the spin waves by Collins[4] and Bonfante *et al.*[5] Sakurai *et al.*[6] have studied both the lattice dynamics and magnetic excitations in CoO.

2. EXPERIMENTAL DETAILS

The two specimens of NiO utilized in these measurements were single crystals of approximately 2 cm^3 volume cleaved from the same boule. The samples were in the multidomain state and their color was dark green to black. All measurements were performed with the triple axis spectrometer at the Missouri University Research Reactor. The majority of the acoustic phonons were examined with $\lambda = 1.02$ A and a lead analyzer. The low q acoustic modes were determined with an incident wavelength of 1.40 A employing either a lead or a beryllium analyzer. All optic modes were measured with $\lambda =$ 0.89 A and a beryllium analyzer. A zinc monochromating crystal was used throughout. Due to the low take off angle for the shortest wavelength, the spectrometer was operated in the opposite sense from the normal "W" configuration for the optic determinations to avoid high background levels. Constant Q scans were used for all but the very low q acoustic modes.

Instrumental resolution effects were examined following the formalism of Cooper and Nathans[7] as modified by Shaw.[8] The calculated frequency shifts were found to be less than the statistical uncertainties in the data and hence, the corrections have been omitted in the data presented here.

3. EXPERIMENTAL RESULTS AND DISCUSSION

The experimentally determined dispersion curves were fitted using both the normal shell model (NSM) and the three-body force shell model (TSM). These models have been described in detail elsewhere.[9,10] We show in Fig. 1 the best fit from each model along with the measured data. In Table 1 the parameters for each model obtained by a least square fitting procedure are presented.

Although the NSM gave the best fit, there are obvious deficiencies in that two widely different sets of parameters were found that gave essentially the same quality of fit. These two sets were obtained using slightly different fitting procedures. The set denoted by D11 was obtained from a 11 parameter NSM fit to the measured phonon data and the published value for the high frequency dielectric constant.[11,12] The other set, N11, resulted from a 11 parameter NSM fit strictly to the measured phonon data. We were able to go from one set to the other by either including or excluding the

* This paper is based on a dissertation submitted by R.A. Coy in partial fulfillment of the requirements for the Ph.D. degree in Physics at the University of Missouri, Columbia.

Table 1. Parameters obtained from the shell models. The significance of the NSM and TSM parameters are discussed in references 9 and 10 respectively

	NSM		TSM	
	N11	D11		
A	16.49	40.12	A	17.23
B	0.36	−6.09	B	−0.39
A'	5.79	3.15	Z	2.00
B'	−1.42	−0.60	$f(r_0)$	−0.11
A''	−2.16	−7.16	$r_0f'(r_0)$	0.05
B''	0.58	1.18	d_1	0.05
Z	1.00	2.09	d_2	0.42
α_1	0.009	0.067	Y_1	5.87
d_1	−0.162	−0.788	Y_2	−1.05
α_2	0.027	0.108	χ^2	0.373
d_2	−0.166	0.750		
χ^2	0.249	0.309		

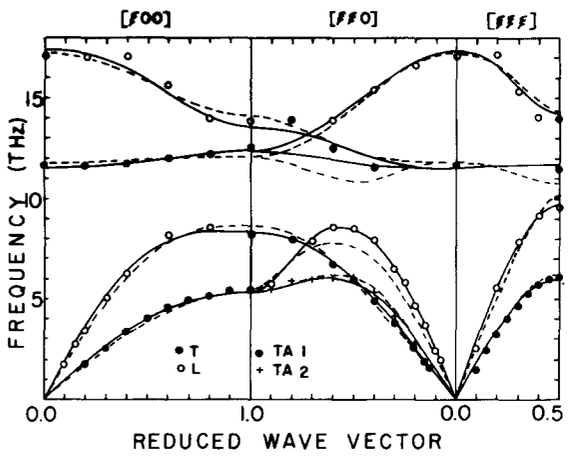

Fig. 1. Phonon dispersion of NiO at 297°K. The NSM fit, N11, is given by the solid lines. The dashed lines are the TSM fit.

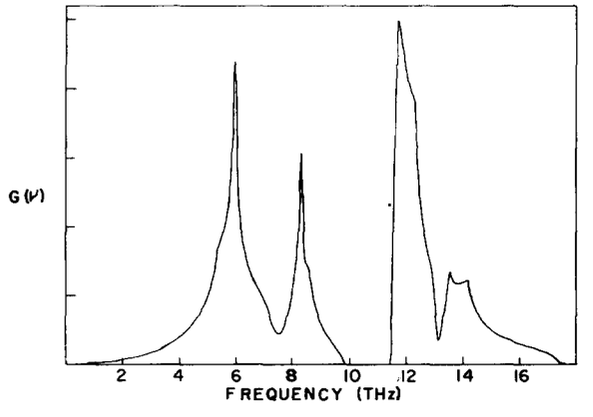

Fig. 2. NiO room temperature phonon density of states calculated from the NSM.

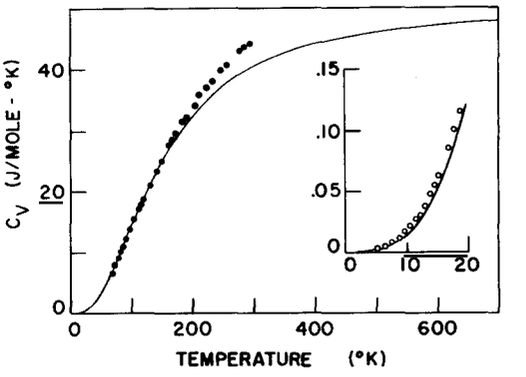

Fig. 3. The temperature dependence of the lattice specific heat of NiO. The solid data points are from the measurements of Seltz *et al.*[16] The open circles in the inset are from the measurements of White.[15]

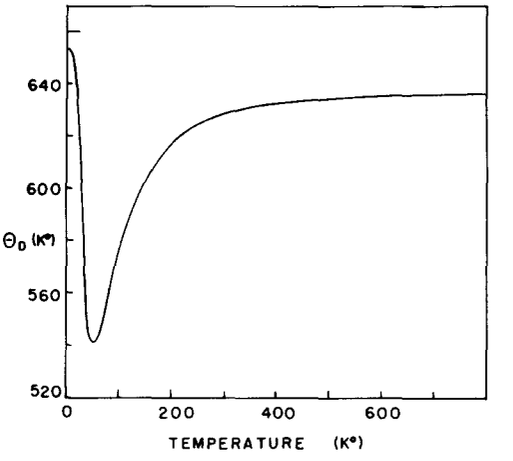

Fig. 4. Debye temperature of NiO.

dielectric constant fitting procedure in the least square fitting process. The D11 parameters are very similar, with the exception of the second neighbor short range parameters, to those obtained by Sakurai *et al.*[6] for CoO in its antiferromagnetic phase. Extension of the NSM to 15 parameters produced no significant change in the quality of fit.

A fundamental difference was noted between the initial slopes of the experimental room temperature dispersion curves and those derived from the ultrasonically determined elastic constant data of du Piessis *et al.*[13] This made it impossible to include elastic constant data in the shell model fitting procedure. Although ultrasonic sound velocities are measured in a energy-wave vector region that corresponds to $q = 0$ and $E = 0$ relative to phonon dispersion curves, the initial slopes of these curves can generally be related to the sound velocity. The ultrasonic elastic moduli for NiO were shown to

have marked temperature dependence in the vicinity of the Néel point.[13] We observe here that the initial slopes of the room temperature dispersion relations are more nearly represented by the sound velocities appropriate to the paramagnetic region rather than the room temperature values. Experiments are under way to improve instrumental resolution and to try to determine initial phonon slopes at much lower q values.

The room temperature phonon density of states, shown in Fig. 2, was calculated from the 11 parameter shell model using the extrapolation methods of Gilat and Raubenheimer.[14] The temperature dependence of the lattice specific heat, Fig. 3, and of the Debye temperature, Fig. 4, where determined from the room temperature frequency distribution.

Some preliminary measurements of the phonon dispersion relations at a temperature (600°K) well above the Néel point have been made. These measurements, although not complete, indicate that no large effects occur and that there is only a general softening with lattice frequencies reduced typically by about 3%.

Acknowledgements – The authors are grateful to Professor H.W. White for suggesting the problem and for kindly supplying the samples. We are indebted to Professor S.A. Werner, University of Missouri, Department of Physics, for very helpful discussions; to Mr W.J. Daughton for experimental assistance, and especially to MURR for beam port time. One of us (RAC) wishes to express his gratitude to MURR and to the O.M. Stewart Fellowship Committee for financial support during this project.

REFERENCES

1. BARTEL L.C. & MOROSIN B., *Phys. Rev.* **B3**, 1039 (1971).
2. HUTCHINGS M.T. & SAMUELSEN E.J., *Solid State Commun.* **9**, 1011 (1971); HUTCHINGS M.T. & SAMUELSEN E.J., *Phys. Rev.* **B6**, 3447 (1972).
3. HAYWOOD B.C.G. & COLLINS M.F., *J. Phys. Chem. Solids* **2**, 46 (1969); *J. Phys. Chem. Solids* **4**, 1299 (1971).
4. COLLINS M.F., *Proc. Int. Conf. Magnetism*, pp. 319–321 (1964).
5. BONFANTE M., HENNION B., MOUSSA F. & PEPY G., *Solid State Commun.* **10**, 553 (1972).
6. SAKURAI J., BUYERS W.J.L., COWLEY R.A. & DOLLING G., *Phys. Rev.* **167**, 510 (1968).
7. COOPER M.J. & NATHANS R., *Acta Cryst.* **23**, 357 (1967).
8. SHAW W., Ph.D. Thesis, University of Missouri (1971).
9. COCHRAN W., COWLEY R.A., DOLLING G. & ELCOMBE M.M., *Proc. R. Soc.* **293**, 433 (1966).
10. VERMA M.P. & SINGH R.K., *Phys. Status Solidi* **33**, 269 (1969).
11. GIELISSE P.J., PLENDL J.N., MANSUR L.C., MARSHALL R., MITRA S.S., MYKOLAJEWVCZ R. & SMAKULA A., *J. Appl. Phys.* **36**, 2446 (1965).
12. RAO K. & SMAKULA A., *J. Appl. Phys.* **36**, 2031 (1965).
13. DU PLESSIS P. de V., VAN TONDER S.J. & ALBERTS, *J. Phys. Chem. Solids* **4**, 1983 (1971).
14. GILAT G. & RAUBENHEIMER L.J., *Phys. Rev.* **144**, 390 (1966).
15. WHITE H.W., *J. Chem. Phys.* **61**, 4907 (1974).
16. SELTZ H., DEWITT B.J. & MCDONALD H.J., *J. Am. Chem. Soc.* **62**, 88 (1940).