ANL/IPNS/CP-93091
CONF-970814--

Version Date: 7/14/97

Inelastic Neutron Scattering From Zircon, J. C. Nipko and C.-K. Loong
Argonne National Laboratory, Argonne, IL 60439, U.S.A.

Abstract

A lattice dynamical investigation of zircon ($ZrSiO_4$) has been carried out to obtain a microscopic understanding of its thermodynamic properties, as well as to examine possible soft modes that may contribute to the phase transformation to scheelite type under high pressure. We have measured the neutron weighted phonon density of states of zircon from a polycrystalline sample. The neutron spectra reveal one-phonon excitations extending to 1130 cm^{-1}, with phonon bands centered at 226, 298, 363, 540, 661, 726, 945, and 1081 cm^{-1}. A quantitative analysis of the neutron results was carried out using a lattice dynamical rigid-ion model.

Keywords: Phonon density of states, Zircon, Lattice Dynamics

Corresponding Author: C. -K. Loong, IPNS/Bldg. 360, Argonne National Lab, Argonne, IL 60439; Fax: (630) 252 - 4163; e-mail: ckloong@anl.gov.

DISCLAIMER

Introduction

The silicate mineral zircon ($ZrSiO_4$) is of widespread geological occurrence and is a common accessory mineral of igneous rocks and sediments. It is a host mineral for the radioactive elements uranium and thorium in the earth's crust and is a natural candidate for usage as a nuclear waste storage material. Its low thermal conductivity and high melting point make it attractive for industrial applications. X-ray diffraction and spectroscopic studies [1] suggest that $ZrSiO_4$ undergoes a zircon to scheelite type phase transition at high pressure and temperature. Scheelite (space group $I\,4_1/a$) is closely related to the zircon structure (space group $I\,4_1/amd$) and is about 10% more dense than zircon.

The crystal structure of zircon (space group $I\,4_1/amd$) [2] is of tetragonal symmetry with a = 6.607 Å and c = 5.982 Å. In the lattice, Zr^{4+} and Si^{4+} occupy special positions and oxygen ions are located at (0,x,y) where y = 0.0661 and z = 0.1952. Fig. 1 shows the principle structural unit in zircon consisting of a chain of alternating edge-sharing SiO_4 tetrahedra and ZrO_8 triangular dodecahedra extending parallel to the *c* -axis. These chains are joined laterally (i.e. along the *a* -axis) by edge-sharing ZrO_8 dodecahedra.

We have studied the lattice dynamics of zircon to provide a microscopic understanding of the thermodynamic properties including the equation of state. In this paper, we report on the determination of the phonon density of states (DOS) of zircon obtained by inelastic neutron scattering using a polycrystalline sample. The measured neutron weighted phonon density of states was used as input in the refinement of a lattice dynamics model for the zircon system. The calculated phonon density of states was then used to calculate the temperature dependence of the lattice specific heat, which agrees well with the published experimental values.[3]

Experimental

The inelastic neutron scattering experiment was performed on a commercial sample of polycrystalline $ZrSiO_4$ obtained from Alfa Aesar Co. The sample was characterized by

neutron diffraction on the General Purpose Powder Diffractometer at IPNS and was found to be single phase zircon (weighted R factor of less than 5%).

The time-of-flight HRMECS spectrometer is equipped with wide-angle multidetector banks which, using an incident neutron energy (E_0) of 1600 cm^{-1} , allow measurements of inelastic scattering over a wide range of momentum and energy transfer. The energy resolution ΔE in full-width-at-half-maximum of the HRMECS spectrometer varies from approximately 4% of E_0 in the elastic region to ~2% near the end of the neutron-energy-loss spectrum. Approximately 60 g of polycrystalline zircon contained in an aluminum planar cell was mounted at a 45° angle to the incident neutron beam. Such a geometry decreases the neutron traverse length in the sample to < 5 mm for all detector angles thereby reducing multiple-scattering effects. Multiple scattering was estimated to be less than 5% of the total measured intensity and was corrected by removing a small flat background from the data. To reduce multiple-phonon excitations, the sample was cooled to 7 K for the experiments. Normal background scattering was subtracted from the data by using empty-container runs. Measurements of elastic incoherent scattering from a vanadium standard provided detector calibration.

Results and Discussion

Fig. 2 displays the measured neutron weighted phonon density of states for Zircon. The spectrum displays bands of phonon modes centered at 258, 371, 524, 653, 952, and 1081 cm^{-1}. The results of previous infrared and Raman spectroscopic measurements [4] on zircon are also displayed in Fig. 2 as vertical dashes. Many of the features in the neutron spectrum correspond to the optical data frequencies. In particular the band at 945 cm^{-1} is well matched to the highest four optical modes which have interpreted as internal stretch modes of the SiO_4 units. This correspondence suggests that the silicate groups can

be treated as molecular units in terms of the dynamics, since sharp neutron features may imply little phonon dispersion across the Brillouin zone.

The lattice dynamics model employed here is a rigid-ion model with axially symmetric atom-atom interactions. The model allows for nearest-neighbor Si-O interactions and nearest and next-nearest-neighbor for the Zr-O and O-O bonds. Third and fourth nearest neighbor O-O interactions were also included to improve overall structural stability. The model calculations were carried out using the GENAX program written by W. Reichardt and will be detailed elsewhere. The calculated neutron weighted phonon density of states is shown in Fig. 2 as the solid line. The calculated DOS reproduces all the observed salient features except the phonon bands are narrower.

Fig. 3 displays the specific heat measured at constant pressure for zircon compared to the constant volume specific heat calculated from the lattice dynamics model. The good agreement of model calculations with the observed neutron and specific heat data demonstrate that the lattice dynamic model gives a reasonable description of the phonon frequencies throughout the Brillouin zone. Therefore, further investigation of the possible soft modes and equation of state of zircon can proceed with the use of this phonon model.

Acknowledgments

Work performed at Argonne National Laboratory is supported by U.S. DOE-BES under contract No. W-31-109-ENG-38.

References

[1]. E. Knittle and Q. Williams, *Am. Mineral.* **78**, 245 (1993).

[2]. R. W. G. Wyckoff, Crystal Structure, Vol. III, 2nd ed., p. 15. Wiley, New York, 1963.

[3]. K. K. Kelly, *J. of Am. Chem. Soc.* **63**, 2750 (1941).

[4]. P. Dawson, M. M. Hargreave and G. R. Wilkinson, *J. Phys. C: Solid St. Phys.* **4**, 240 (1971).

Figure Captions:

Figure 1. The arrangement of SiO_4 tetrahedra and ZrO_8 triangular dodecahedra in $ZrSiO_4$.

Figure 2. Measured (open circles) and calculated (lines) generalized phonon density of states for zircon.

Figure 3. The calculated lattice specific heat at constant volume (solid line) and measured specific heat at constant pressure (open circles) for zircon. The horizontial line represents the Dulong-Petit limit.

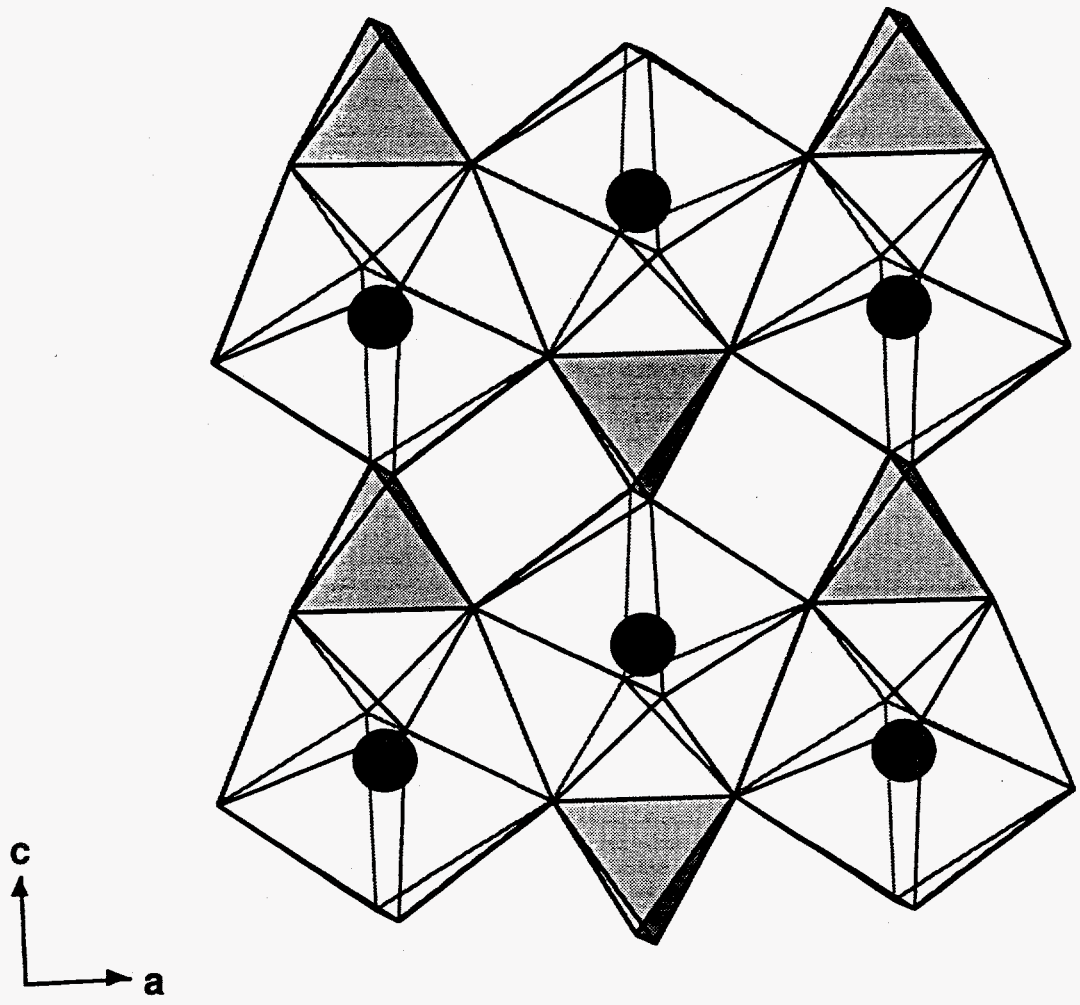

Figure 1: "Inelastic neutron scattering ..." J. C. Nipko, *et. al.*

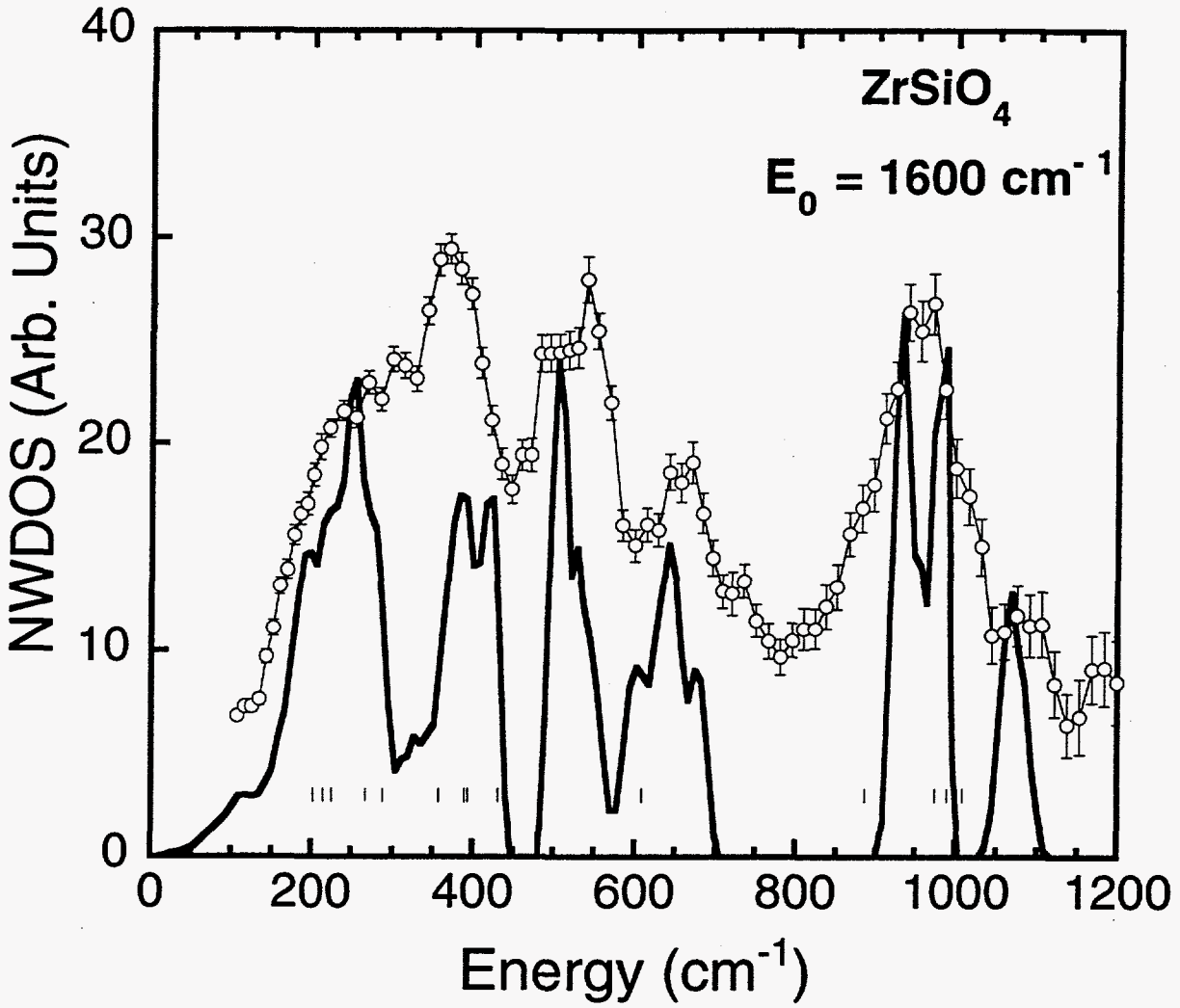

Figure 2: "Inelastic neutron ..." J. C. Nipko, et. al.

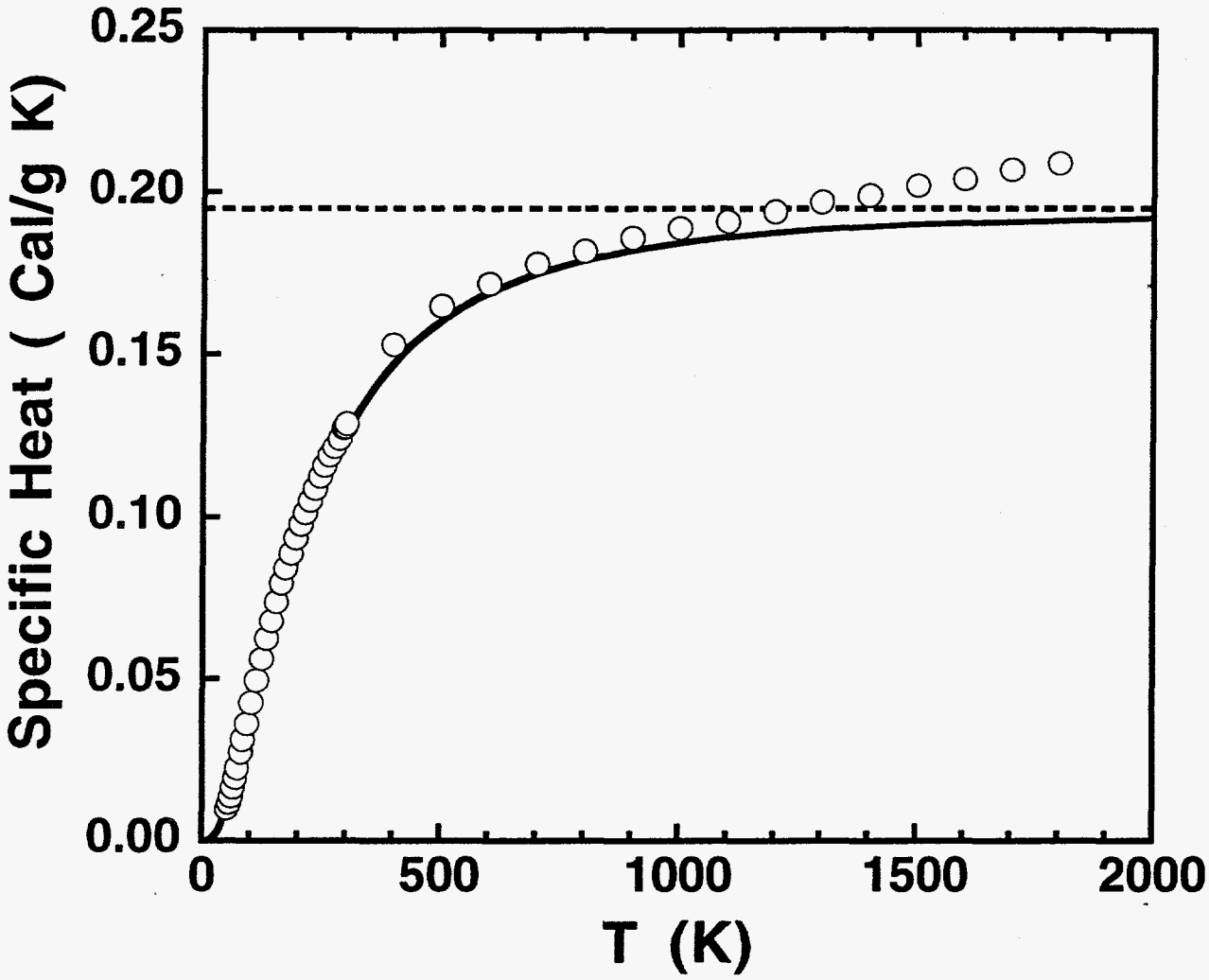

Figure 3: "Inelastic neutron ..." J. C. Nipko, et. al.