PHYSICAL REVIEW B **68**, 094101 (2003)

High-pressure x-ray diffraction and Raman spectroscopic studies of the tetragonal spinel $CoFe_2O_4$

Zhongwu Wang,[1,2,*] R. T. Downs,[1,†] V. Pischedda,[1] R. Shetty,[1] S. K. Saxena,[1] C. S. Zha,[3] Y. S. Zhao,[2]
D. Schiferl,[2] and A. Waskowska[4]
[1]*Center for Study of Matter at Extreme Conditions (CeSMEC), Florida International University, VH-150, University Park, Miami, Florida 33199, USA*
[2]*LANSCE-12, MS-H805, Los Alamos National Laboratory, Los Alamos, New Mexico 87545, USA*
[3]*Cornell High Energy Synchrotron Source (CHESS), Wilson Laboratory, Cornell University, Ithaca, New York 14853, USA*
[4]*Institute of Low Temperature and Structure Research, Polish Academy of Sciences, P.O. Box 1410, 50-950 Wroclaw 2, Poland*

(Received 28 April 2003; published 2 September 2003)

In situ x-ray diffraction and Raman spectroscopy have been carried out to pressures of 93.6 and 63.2 GPa, respectively, to explore the pressure-induced phase transformation of $CoFe_2O_4$ spinel. $CoFe_2O_4$ adopts a distorted tetragonal spinel structure at one atmosphere. At a pressure of ~32.5 GPa, both x-ray diffraction and Raman spectroscopy indicate that $CoFe_2O_4$ transforms to the orthorhombic $CaFe_2O_4$ structure, which remains stable to at least 93.6 GPa. The bulk modulus (K_0) of the tetragonal and the high-pressure polymorphs were calculated to be 94(12) and 145(16) GPa, respectively, with $K' \equiv 4$. Upon release of pressure the orthorhombic phase persists and appears to be structurally metastable. At zero pressure, laser induced heating leads to a significant transformation back to the tetragonal phase. The high-pressure orthorhombic phase at one atmosphere is 14.7% denser than the tetragonal phase.

DOI: 10.1103/PhysRevB.68.094101 PACS number(s): 62.50.+p, 81.40.Vw

INTRODUCTION

Spinels with AB_2O_4 formula are ternary oxides that have important technological applications, including use as magnetic materials,[1] superhard materials,[2] high-temperature ceramics,[3] and high-pressure sensors through Cr^{3+} doping.[4] In particular, pressure-induced physical effects, including phase transformations and Jahn-Teller distortion in the tetragonal spinels, such as AMn_2O_4 (A = Zn, Mg, Cu, and Mn), have attracted considerable attention in recent studies[5–8] due to applications in geophysics and magnetic material sciences.[5–10] High-pressure polymorphs of Mg_2SiO_4 spinel represent the structural analogs of the most abundant minerals of the Earth's deep interior,[7,8] whereas Jahn-Teller distortion effects are weakened and further suppressed under pressure.[11,12]

The normal spinels, formula AB_2O_4, are characterized with $[A]$ and $[B]$ occupying the tetrahedral and octahedral sites, respectively, while the inverse spinels are characterized with $[B]$ occupying the tetrahedral site, and $[A]$ and $[B]$ both occupying the octahedral site.[10,13] Many spinels display cubic symmetry at ambient to high temperatures. However, inverse spinels are often distorted to tetragonal symmetry at lower temperatures.[6–8] So far, a number of studies have been conducted to examine the pressure-induced phase transformations of the cubic spinels,[13–18] but the results are still not fully understood, and there is still a basic lack of agreement on the structure of the post-spinel phases.[13–18] Furthermore, while numerous investigations of the tetragonal spinels have been carried out at ambient conditions,[19] only a few studies have been conducted under pressure.[6–8] In order to clarify the pressure-induced phase transformations of the tetragonal spinels and the relationship with the cubic spinels and corresponding high-pressure polymorphs, the distorted tetragonal spinel $CoFe_2O_4$ was examined to pressures of 93.6 and 62.3 GPa using x-ray diffraction and Raman spectroscopy, respectively. The two types of pressure data were combined to explore and to discuss the pressure-induced behavior of the tetragonal spinel $CoFe_2O_4$.

EXPERIMENT

A sample of $CoFe_2O_4$ was prepared by heating a stoichiometric mixture of $CoCO_3$ and Fe_2O_3 that had been ground together in a ball mill with ethanol. The mixture was heated to 800 °C in air for 8 h. After another milling, the product was pressed into an evacuated silica tube. Upon heating for 20 h at 1050 °C, the sample was quenched in water. The resulting crystals have an average size of 0.1 mm. X-ray diffraction indicates that this sample of $CoFe_2O_4$ adopts tetragonal symmetry at ambient conditions.

The sample was loaded into a high-pressure diamond-anvil cell (DAC) using a T301 steel gasket pre-indented to 60 μm, with a 150-μm hole, without a pressure medium. A few ruby chips were included as a pressure marker. The spectral measurements were conducted at room temperature and high pressure with a Raman spectrometer in the back scattering configuration.[12,15,18] A Ti^{3+}: sapphire laser pumped by an argon ion laser was tuned to 785 nm in order to effectively suppress the strong fluorescence of diamond. To avoid a heating effect, the laser power was operated at 3 mw (after filter) to excite the sample. Raman spectra were collected by using a high throughput holographic imaging spectrograph with a volume transmission grating, holographic notch filter, and thermoelectrically cooled charge-coupled device (CCD) detector (Spectra Physics) with a resolution of 4 cm^{-1}. A 15-min exposure was used for each spectral collection. Pressures were determined using the calibrated ruby pressure standard of Mao *et al.*[20]

High-pressure x-ray powder diffraction experiments were carried out at CHESS, Cornell University.[21] The sample loading was the same as for the Raman experiment, but with-

TABLE I. Raman modes of $CoFe_2O_4$ spinel observed at ambient conditions, their assignment, and pressure dependencies.

Tetragonal			Orthorhombic		
Raman modes at 1 atm (cm^{-1})	Raman shifts (cm^{-1}/GPa)	Mode Gruneison parameters (γ)	High-P phase extrapolated to 1 atm (cm^{-1})	Raman shifts (cm^{-1}/GPa)	Mode Gruneison parameters (γ)
188	0.15	0.08			
300	0.95	0.30			
471	1.70	0.34	447	1.45	0.47
563	2.01	0.37	579	1.52	0.38
617	2.18	0.33			
683	2.99	0.41			

out the ruby chips. Pressure was determined with the well-known equation of state (EOS) of platinum (Pt). Energy dispersive x-ray-diffraction spectra were collected with a fixed $2\theta = 11°$ on the bending magnet beam line. The energy calibration was made using well-known radiation sources (^{55}Fe and ^{133}Ba), whereas the angle calibration was made from the six peaks of the standard Au powder. X-ray-diffraction patterns at pressure were collected and integrated to compute cell parameters.

RESULTS AND DISCUSSIONS

The only single-crystal structure refinement on $CoFe_2O_4$ found in the literature reported that it is cubic with 80% of the tetrahedral site occupied by Fe.[22] A more recent Rietveld refinement of neutron powder data on nanoparticles of $CoFe_2O_4$ also indicates a cubic structure, with 66% of the tetrahedral sites occupied by Fe.[23] In addition, x-ray magnetic circular dichroism spectroscopic measurements provide an estimate that 84% of the tetrahedral site is occupied by Fe.[24] X-ray diffraction of our sample indicates that, at ambient conditions, $CoFe_2O_4$ displays tetragonal symmetry. We assume that the site occupancy is disordered, as found in the studies of the cubic material, and we assume that the sample belongs to $I4_1/amd$ space group ($Z = 8$), as do other similar tetragonal spinels such as $(Mn,Fe)_3O_4$.[25] Unit-cell parameters at ambient conditions were determined from the positions of the diffracted peaks with the sample in the diamond cell, but without applied pressure, and are $a_0 = 8.3794(3)$ Å, $c_0 = 9.7897(5)$ Å, and $V_0 = 687.44(12)$ Å^3. The distortion from cubic symmetry, defined in terms of $c/a = 1.17$, is significantly larger than observed in similar spinels, such as $ZnMn_2O_4$ ($c/a = 1.14$) and $CuMn_2O_4$ ($c/a = 0.93$).[6,8]

Factor group analysis yields 10 Raman modes, represented by $2A_{1g} + 3B_{1g} + B_{2g} + 4E_g$,[19] which can be compared with the five Raman active modes ($A_{1g} + E_g + 3T_{2g}$) of the cubic spinel.[15,18] In this study, only six Raman modes were observed from the tetragonal $CoFe_2O_4$ spinel (Table I and Fig. 1). Since the sample is powder, rather than a single crystal, we cannot give a precise mode assignment for the observed Raman peaks. However, the correlation between cubic and tetragonal spinels, as well as the site symmetry of tetragonal spinel, allows one to provide a reasonable explanation for the observed Raman modes. In the cubic spinel, including ferrites, the modes above 600 cm^{-1} usually corresponds to the motion of oxygen in the tetrahedral AO_4 group,[18] so the two peaks at 617 and 683 cm^{-1} are considered to represent A_{1g} symmetry. The other low-frequency

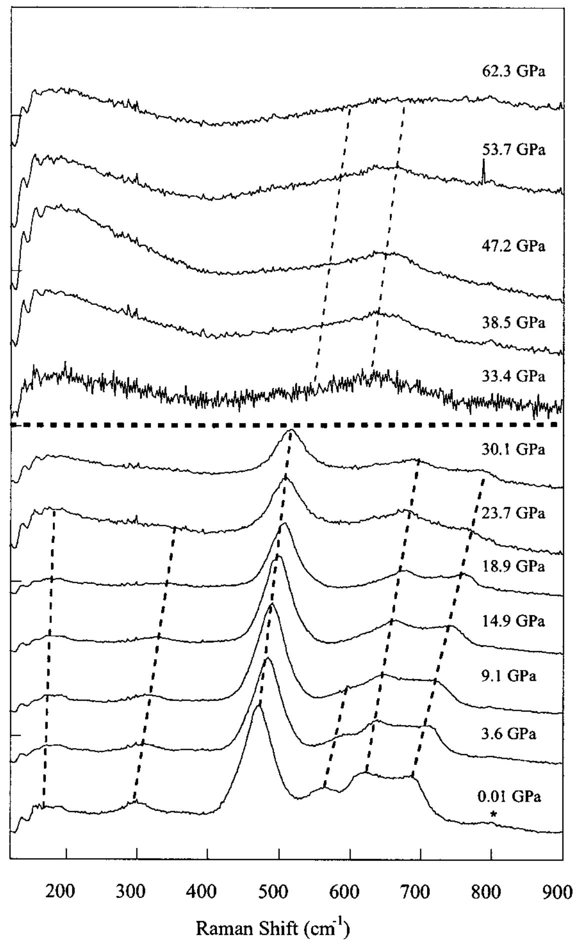

FIG. 1. Raman spectra of the $CoFe_2O_4$ spinel as a function of pressure. The dashed lines are meant to guide the eye towards characterizing the pressure shifts of the Raman modes. The horizontal dotted line represents the phase-transition boundary. The peak marked by $*$ is from laser.

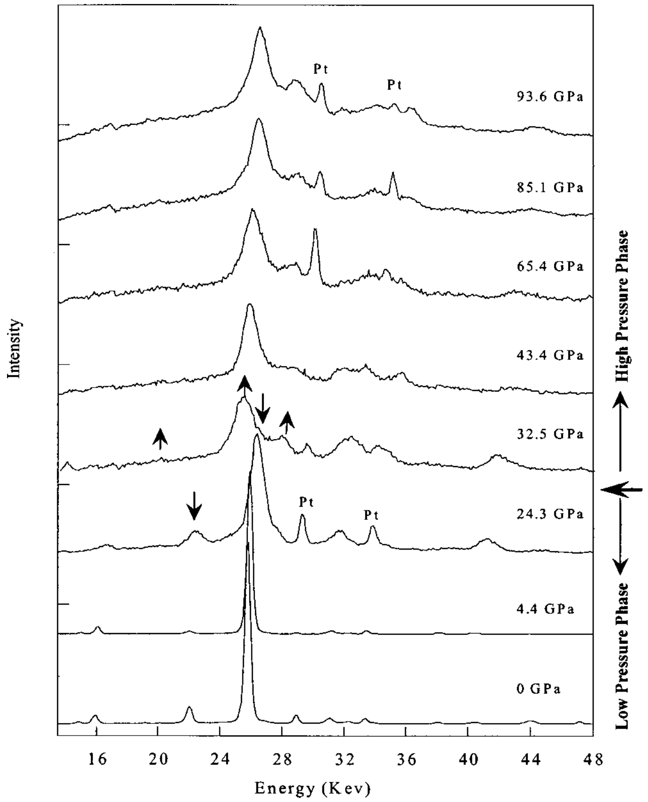

FIG. 2. X-ray diffractions of $CoFe_2O_4$ obtained during the compression run. The downward (↓) and upward arrows (↑) represent the disappearance of the tetragonal spinel and the appearance of the new phase, respectively. Pt signifies the peaks of platinum.

modes are characteristics of the octahedral site (BO_6).

Raman spectra of $CoFe_2O_4$ are plotted as a function of pressure in Fig. 1, which reveals that a phase transformation takes place at a pressure above 30.1 GPa and below 33.4 GPa. This phase transformation was confirmed by *in situ* x-ray powder diffraction (Fig. 2), in which the new phase was observed at 32.5 GPa. The diffraction profiles and Raman spectra do not indicate coexisting phases over a pressure interval, suggesting that a nondiffusion mechanism controls the pressure-induced phase transformation. This is different from that observed in $ZnTi_2O_4$ spinel, in which a sluggish transition mechanism was suggested to explain the coexistence of the two phases over a wide range of pressure.[15] The observed diffraction pattern of the high-pressure phase was successfully indexed according to the orthorhombic $CaFe_2O_4$ structure ($Pnma$, $Z=4$). Ambient condition unit-cell parameters were refined to $a_0=9.483(21)$ Å, $b_0=10.401(20)$ Å, $c_0=2.959(12)$ Å, and $V_0=293.8(12)$ Å^3 (Table II). The tetragonal spinel and high-pressure polymorph have the bulk modulus (K_0) of 94 (12) and 145 (16) GPa, respectively (Fig. 3). The high-pressure orthorhombic phase is 14.7% denser than the original tetragonal phase at zero pressure. However, since we did not employ any pressure medium in this study, a significant pressure gradient may exist. Basically, the existence of pressure gradient often results in a reduction of transition pressure. Thus the observed transition pressure in $CoFe_2O_4$ may be a little lower than that at hydrostatic conditions.

TABLE II. Observed and calculated x-ray-diffraction peaks of the high-pressure polymorph of $CoFe_2O_4$, which is recovered at room pressure. This phase was indexed according to the orthorhombic $CaFe_2O_4$ structure (D_{2h}^{16}-$Pnma$), with unit-cell parameters $a_0=9.483(21)$ Å, $b_0=10.401(20)$ Å, $c_0=2.959(12)$ Å, and $V_0=291.8(12)$ Å^3.

HKL	d_{obs} (Å)	d_{calc} (Å)	Res ($d_{obs}-d_{calc}$)
3 2 0	2.7038	2.7042	−0.0006
2 0 1	2.4892	2.4902	−0.001
1 3 1	2.1972	2.1945	0.0027
3 1 1	2.1129	2.1153	−0.0024
2 4 1	1.8115	1.8106	0.0009
6 0 0	1.5808	1.5799	0.0019
1 7 0	1.4666	1.4678	−0.0012

Numerous studies have been conducted on the pressure-induced phase transformations of the cubic spinels. Results indicate that most cubic spinels transform to an orthorhombic phase upon elevation of pressure.[13–18] The high-pressure phases that transform from the cubic spinels appear to have a similar diffraction pattern, and thus similar structure, as observed for the high-pressure polymorph of the tetragonal $CoFe_2O_4$ spinel. However, unlike our study of $CoFe_2O_4$ spinel, these pioneering studies did not reveal a significant difference between the densities and bulk moduli of the cubic spinels and their high-pressure orthorhombic phase. In some cases, the high-pressure orthorhombic phase is only slightly denser (within 2%) than the cubic phase. It has previously been shown that there is a strong correlation between bulk modulus and density in the spinels.[13–18] Thus it is expected that the cubic-orthorhombic transformations would result in only a small change in bulk modulus because there is only a small change in density. In our study, a significant difference between the two polymorphs of $CoFe_2O_4$ was observed in both the bulk modulus and the density. This may be reasonably interpreted as a consequence of the different structures of the starting materials. The $CoFe_2O_4$ used in this study has a tetragonal structure at ambient conditions, in which the distortion results in an increase of the unit-cell volume (687.44 Å^3) compared to a unit-cell volume of 592 Å^3 for its cubic polymorph.[22] Increasing the pressure on the tetragonal phase increases the distortion from cubic symmetry, so that the consequent transformation bypasses the cubic phase, and goes directly to the orthorhombic phase, resulting in a large volume change. Thus we observe that the tetragonal $CoFe_2O_4$ has a relatively small bulk modulus of 94(12) GPa and the orthorhombic phase has a larger bulk modulus of 145 GPa, close to the low limit of 150 GPa observed in other pressure-induced post-spinel polymorphs (observed to be 150–210 GPa).[13–17] The density difference between the cubic and the orthorhombic phases at ambient conditions is only ~1.4%.

While previous studies demonstrated that the cubic spinels transform to orthorhombic polymorphs under pressure,[13–17] a precise determination of the structures and

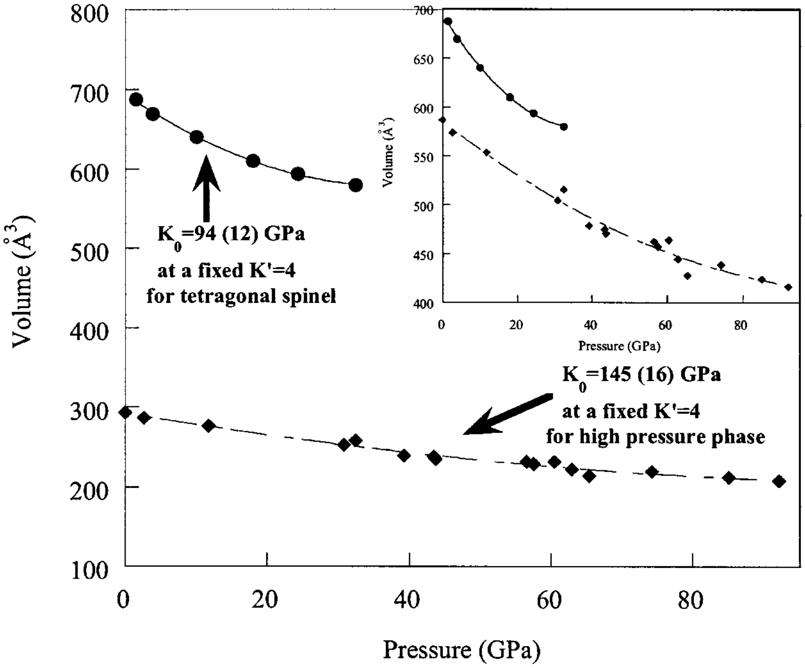

FIG. 3. The P-V data of both the tetragonal and high-pressure polymorphs of $CoFe_2O_4$ fitted to the Birch-Murnaghan equation with the constraint that $K' \equiv 4$. The plot shows the P-V curves of both phases. The inset shows the P-V curves of the tetragonal spinel ($Z=8$) and the high-pressure polymorph ($Z=4\times 2$) with the same choice of unit cell. This provides an alternate comparison between the bulk modulus and densities of the two structural polymorphs of $CoFe_2O_4$.

symmetries has still not been agreed upon. A significant factor may be the low resolution of the high-pressure x-ray powder-diffraction patterns, including data collected at the new generation synchrotron radiation sources. However, one conclusion can be made: the high-pressure post-spinel phase belongs to one of the three similar orthorhombic structures including the $CaFe_2O_4$ (*Pnma*, #62), $CaMn_2O_4$ (*Pmab* or *Pbcm*, #57), and $CaTi_2O_4$ (*Cmcm* or *Bbmm*, # 63) polymorphs. Here, we give new Raman spectroscopic data, which provides significant clarification of the structure of the high-pressure phase of $CoFe_2O_4$ (Fig. 2). According to factor group analysis, the three different structure types are associated with three different sets of Raman active modes:

$$CaFe_2O_4:\ 7A_{1g}+5B_{1g}+7B_{2g}+5B_{3g},$$

$$CaMn_2O_4:\ 6A_{1g}+7B_{1g}+6B_{2g}+5B_{3g},$$

$$CaTi_2O_4:\ 6A_{1g}+4B_{1g}+2B_{2g}+6B_{3g},$$

while the cubic and tetragonal spinels are associated with

$$\text{cubic:}\ 1A_{1g}+1E_g+3T_{2g},$$

$$\text{tetragonal:}\ 2A_{1g}+3B_{1g}+1B_{2g}+4E_g.$$

With the correlation between the Raman active modes of the two point groups (I and D_{2h}), the A_{1g} and E_g modes in the I representation transforms to the A_g modes of the D_{2h} representation, and the $B_{(1,2)g}$ modes resulting from F_{2g} mode of the cubic spinel transform to the $B_{1g}+B_{2g}+B_{3g}$ modes. As is plotted in Figs. 1 and 4, the parallel behavior of the new mode at 519 cm^{-1} at 32.5 GPa and the two A_{1g} modes of the tetragonal spinel upon elevation of pressure allows one to assume that the mode at 519 cm^{-1} is of A_g symmetry. As shown in Fig. 4(a), this new mode arising at 32.5 GPa is close to the mode at 563 cm-1 of the tetragonal spinel, but at 32.5 GPa, we can easily find that the A_{1g} mode is a little softening, and therefore switches to the position of the new observed mode. As distinguished from x-ray diffractions, the new phase has a significant decrease in volume compared to the tetragonal phase, so it is reasonable to assume that the new mode is exactly related to the A_g mode. Therefore the above explanation can allow us to assume that the other new mode at 579 cm^{-1} is of $B_{(1,2,3)g}$ symmetry. Moreover, the obtained Raman spectra of high-pressure polymorph of $CoFe_2O_4$ are quite different from those of the $CaMn_2O_4$ and $CaTi_2O_4$,[12] so we believe that the observed high-pressure $CoFe_2O_4$ phase exactly belongs to the $CaFe_2O_4$ structure. Such a result is easily understood as considering that both $CoFe_2O_4$ and $CaFe_2O_4$ have similar compositions and belongs to the two end members of the ferrite solution.

The pressure dependences of the observed Raman modes were calculated to be 0.15–2.99 cm^{-1}/GPa and

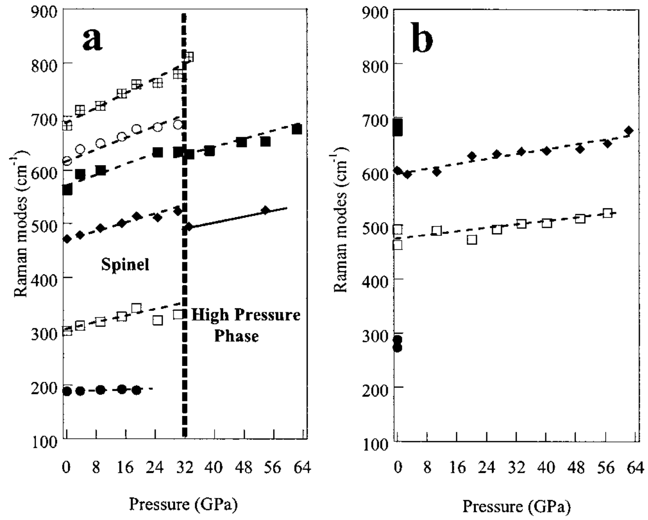

FIG. 4. The pressure dependence of the Raman modes of $CoFe_2O_4$. (a) compression run, and (b) decompression run.

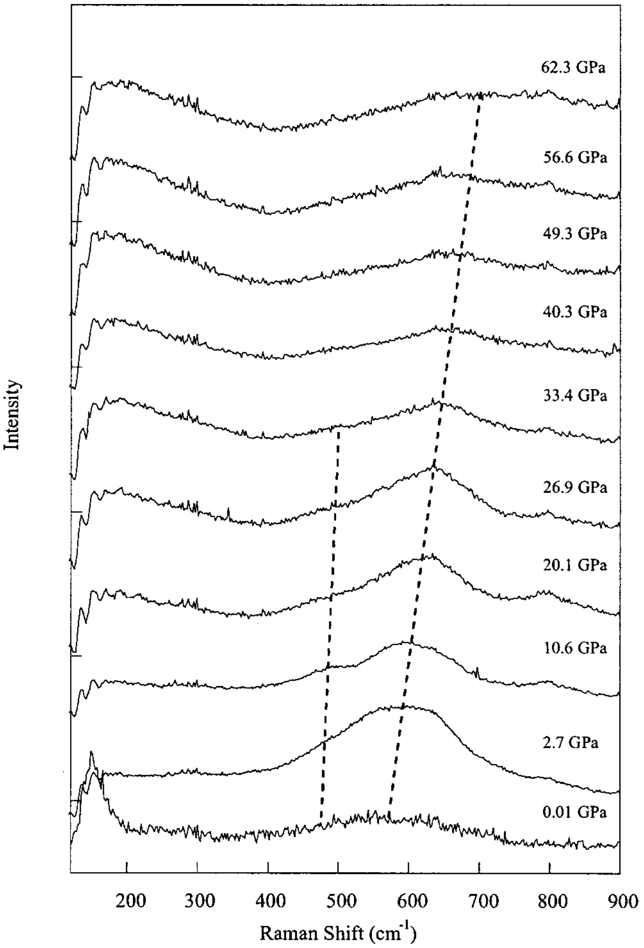

FIG. 5. The Raman spectra of the tetragonal spinel $CoFe_2O_4$ at reduced pressures.

1.45–1.52 cm^{-1}/GPa for the tetragonal and high-pressure orthorhombic polymorphs of $CoFe_2O_4$, respectively (Fig. 4 and Table I). With the bulk modulus calculated from our x-ray-diffraction data, the mode Gruneisen parameters (γ) can be obtained in terms of the following equation:

$$\gamma = -\frac{d\ln \nu}{d\ln P} = \frac{B_0}{\nu_0}\cdot\frac{d\nu}{dp},$$

where ν_0 and ν are the mode frequencies at one atmosphere and at high pressure, respectively; P and B_0 are pressure and bulk modulus in GPa. The obtained mode Gruneison parameters (γ) of the tetragonal and orthorhombic phase are 0.08–0.41 and 0.38–0.47, respectively (Table I).

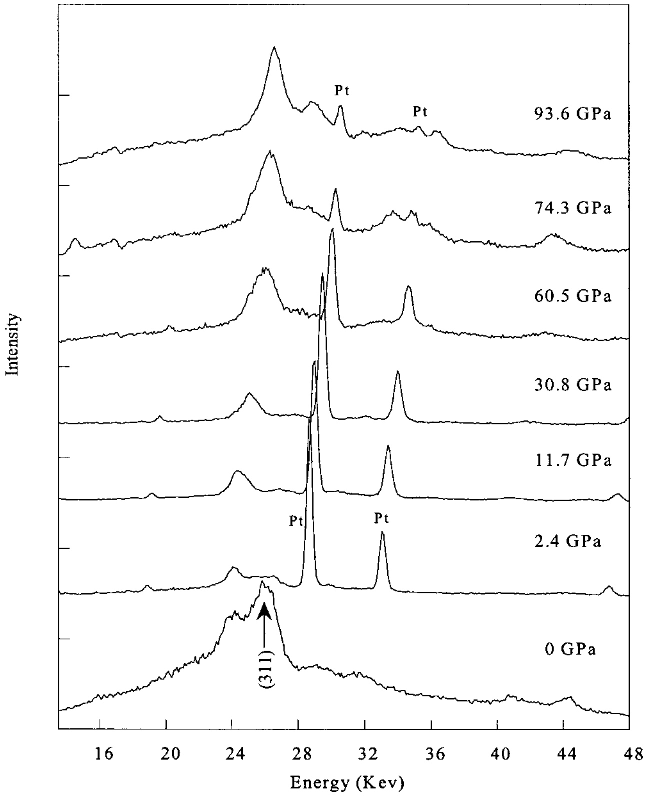

FIG. 6. X-ray diffraction of $CoFe_2O_4$ obtained during the decompression run. Pt signifies the diffraction peaks of platinum. The peak labeled (311) belongs to the tetragonal spinel phase.

Upon release of pressure, Raman spectra and x-ray-diffraction profiles were also collected, and are shown in Figs. 5 and 6. Those two data suggest that the high-pressure orthorhombic phase is metastable almost to ambient conditions. However, at zero pressure, we observed the existence of both the tetragonal and orthorhombic phases. This is clearly indicated in Fig. 6 at zero pressure by a significant increase of the intensity of a peak near (311) of the orthorhombic phase. During decompression, the pressure shifts of the Raman modes were measured and are plotted in Fig. 4(b). The spectra is very similar to that observed during compression. Again, at ambient conditions, we observe the other weak Raman modes characteristic of the tetragonal spinel. These further supports the conclusion derived from the x-ray-diffraction data. In order to check the stability of the high-pressure phase, laser power was elevated for the Raman collection of the recovered sample. We assume that elevation

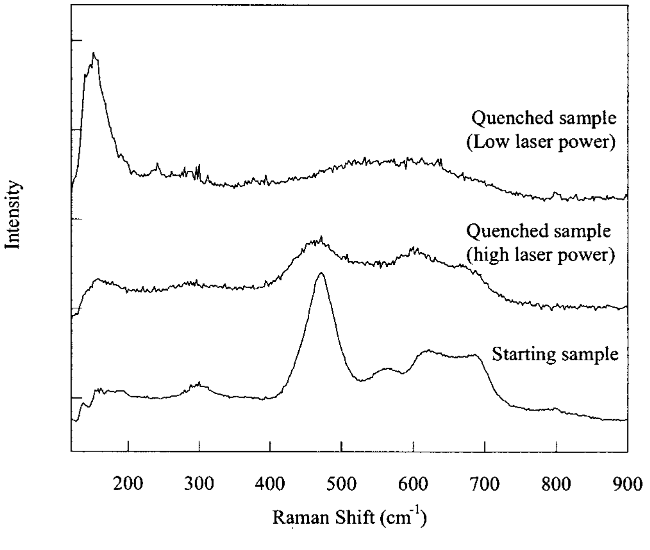

FIG. 7. Comparison of the Raman spectra of $CoFe_2O_4$ with different treatment conditions. All Raman spectra were collected at room pressure.

of the laser power heats the sample. The collected Raman spectrum is used in Fig. 7 to compare the tetragonal and high-pressure orthorhombic phases of $CoFe_2O_4$. It is clearly shown that the Raman spectrum at heated conditions is comparable to that of the tetragonal spinel phase. This implies the existence of a thermal induced instability of the high-pressure orthorhombic phase.

CONCLUSION

We have carried out *in situ* x-ray-diffraction and Raman spectroscopic studies to pressures of 93.6 and 63.2 GPa, respectively, to explore the pressure-induced phase transformation of $CoFe_2O_4$. The ferrite $CoFe_2O_4$ crystallizes with a tetragonal structure at room pressure. Upon elevation of pressure to ~32.5 GPa, x-ray diffraction and Raman spectroscopy indicate that $CoFe_2O_4$ transforms to an orthorhombic structure that is consistent with the $CaFe_2O_4$ polymorph, which remains stable to the peak pressure of 93.6 GPa. The bulk modulus (K_0) of the tetragonal and orthorhombic polymorphs, with $K' \equiv 4$, were calculated to be 94(12) and 145(16) GPa, respectively. The high-pressure orthorhombic phase is 14.7% denser than the tetragonal phase at ambient conditions. The orthorhombic phase shows considerable hysterisis and is quenchable upon release of pressure. However, the laser-induced thermal effect leads to a significant increase in the amount of the tetragonal phase at zero pressure.

ACKNOWLEDGMENTS

We acknowledge financial support from NSF and LANL, which made this research possible. We also appreciate the kind assistances of the staff at CHESS, Cornell University, leading to a successful collection of x-ray-diffraction patterns. Part of the work was conducted at the Cornell High Energy Synchrotron Source (CHESS), which is supported by NSF and NIH/NIGMS under Grant No. DMR 9713424.

---

[*] Fax: 505-665-2676. Email address: z_wang@lanl.gov

[†] On leave from The Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, USA.

[1] W. F. J. Fontijn, P. J. van der Zaag, L. F. Feiner, R. Metselaar, and M. A. C. Devillers, J. Appl. Phys. **85**, 5100 (1999).

[2] A. Zerr, G. Miehe, G. Serghiou, M. Schwarz, E. Kroke, R. Riedel, H. Fuess, P. Kroll, and R. Boehler, Nature (London) **400**, 340 (1999).

[3] B. N. Kim, K. Hiraga, K. Morita, and Y. Sakka, Nature (London) **413**, 288 (2001).

[4] A. H. Jahren, M. B. Kruger, and R. Jeanloz, J. Appl. Phys. **71**, 1579 (1992).

[5] X. Liu, S. Xu, K. Kato, and Y. Moritomo, J. Phys. Soc. Jpn. **71**, 2820 (2002).

[6] S. Asbrink, A. Waskowska, J. S. Olsen, and L. Gerward, Phys. Rev. B **57**, 4972 (1998).

[7] S. Asbrink, A. Waskowska, L. Gerward, J. S. Olsen, and E. Talik, Phys. Rev. B **60**, 12 651 (1999).

[8] A. Waskowska, L. Gerward, J. S. Olsen, S. Steenstrup, and E. Talik, J. Phys.: Condens. Matter **13**, 2549 (2001).

[9] S. H. Shim, T. S. Duffy, and G. Shen, Nature (London) **411**, 571 (2001).

[10] A. E. Ringwood and A. Reid, Earth Planet. Sci. Lett. **6**, 245 (1969).

[11] I. Loa, P. Adler, A. Grzechnik, K. Syassen, U. Schwarz, M. Hanfland, G. K. Rozenberg, P. Gorodetsky, and M. P. Pasternak, Phys. Rev. Lett. **87**, 125501 (2001).

[12] Z. W. Wang, S. K. Saxena, and J. J. Neumeier, J. Solid State Chem. **170**, 382 (2003).

[13] D. Levy, A. Pavese, and M. Hanfland, Phys. Chem. Miner. **27**, 638 (2000).

[14] Y. W. Fei, D. J. Frost, H. K. Mao, C. T. Prewitt, and D. Hausermann, Am. Mineral. **84**, 203 (1999).

[15] Z. W. Wang, S. K. Saxena, and C. S. Zha, Phys. Rev. B **66**, 024103 (2002).

[16] D. Andrault and N. Bolfan-Casanova, Phys. Chem. Miner. **28**, 211 (2001).

[17] C. Haavik, S. Stolen, H. Fjellvag, M. Hanfland, and D. Hausermann, Am. Mineral. **85**, 514 (2000).

[18] Z. W. Wang, P. Lazor, S. K. Saxena, and H. S. C. O'Neill, Mater. Res. Bull. **37**, 1589 (2002).

[19] L. Malavasi, P. Galinetto, M. C. Mozzati, C. B. Arroni, and F. Flor, Phys. Chem. Chem. Phys. **4**, 3876 (2002).

[20] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).

[21] Z. W. Wang, S. K. Saxena, V. Pischedda, H. P. Liermann, and C. S. Zha, Phys. Rev. B **64**, 012102 (2001).

[22] T. Inoue, J. Electrochem. Soc. **23**, 24 (1955).

[23] C. Liu, A. J. Rondinone, and Z. J. Zhang, Pure Appl. Chem. **72**, 37 (2000).

[24] R. A. D. Pattrick, G. Van der Laan, C. M. B. Henderson, P. Kuiper, E. Dudzik, and D. J. Vaughan, Eur. J. Mineral. **14**, 1095 (2002).

[25] V. Baron, J. Gutzmer, H. Rundlof, and R. Tellgren, Am. Mineral. **83**, 786 (1998).