Revealing Pressure-Induced Anomaly in Sound Velocities, and New Thermoelasticity of α-Fe2O3 Hematite at High Pressure: Implications for the Earth's Interior

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Abstract

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Revealing Pressure-Induced Anomaly in Sound Velocities, and New Thermoelasticity of α-Fe_2O_3 Hematite at High Pressure: Implications for the Earth's Interior

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Key Points:

- Revealing Morin transition-induced anomaly in the shear wave velocity at high pressure
- First results on sound velocities and elasticity of hematite at simultaneously high pressures and temperatures
- Understanding the mechanism for anomalous behavior in V_S at high pressure, and providing consequences for modelling of the Earth's interior

Abstract

Elastic wave velocities of polycrystalline hematite have been measured at simultaneously high pressures and temperatures up to 6.5 GPa and 1100 K using ultrasonic interferometry in conjunction with synchrotron X-ray techniques. Here, a pronounced pressure-induced anomaly in the shear wave velocity of hematite is observed at ~3.5 GPa and 300 K, which is attributed to the occurrence of (weak)ferromagnetic-to-antiferromagnetic Morin transition of hematite upon compression. By contrast, this anomalous behavior in V_S at high pressure is unexpected absence in V_P. With further increase of pressures and temperatures up to 6.5 GPa and 1100 K, no apparent discontinuity is observed in sound velocities, probably resulting from the Néel transition in hematite. Using two-dimensional linear fitting approaches, the

bulk and shear moduli and their pressure and temperature dependences for hematite are derived. These findings and new high-*P* thermoelasticity data will be of significant importance for its geophysical and materials science implications.

1. Introduction

Iron-bearing oxides have attracted considerable interest, and play an important role in the mineralogy of Earth's mantle and outer core, due to their complex crystal structure, sound velocities, magnetic and elastic properties under high pressure-temperature (*P-T*) conditions. Hematite (α-Fe_2O_3), as an important end-member of FeO-Fe_2O_3 series (*i.e.,* FeO wüstite, Fe_2O_3 hematite, Fe_3O_4 magnetite, a new Fe_4O_5 compound, and so on) in geophysics, is of particular interest for the understanding of high *P-T* behaviors and properties of ferric oxides in the composition, the unclear role of Fe^{3+} in the nature and dynamics of the Earth's mantle, as well as the technological applications (Bykova et al., 2016; Tuček et al., 2015; Shim et al., 2009; Dobson et al., 2005; Ovsyannikov, et al., 2012; Badro et al., 2002; Pasternak et al., 1999; Rozenberg et al., 2002; Olsen et al., 1991; Ito et al., 2009; Bykova, et al., 2013; Ono et al., 2005; Liu et al., 2003; Schouwink, et al., 2011).

Under ambient conditions, hematite is a thermodynamically stable iron oxide with a corundum hexagonal-close-packed (*hcp*) crystal structure, where the Fe^{3+} cations are located in distorted oxygen octahedra (Pauling and Hendricks, 1925). Below the Morin temperature (T_M) of ~263 K, Fe_2O_3 is preferred to adopt an antiferromagnetic (AFM) structure, and it transforms into a weakly ferromagnetic (FM) phase above its Morin temperature, owing to a slight canting in the alignment of the antiferromagnetic planes in the corundum structure until the Néel temperature of ~948 K (Morrish, 1994; Shull, et al., 1951; Amin and Arajs, 1987). It was ever proposed that the pressure-temperature boundary from the Morin transition was quite sensitive to both the pressure condition and sample microstructure (Liebermann et al., 1968, 1970, 1986; Sato and Akimoto, 1979; Praise et al., 2006; Syono et al., 1984). At high pressure, the T_M exhibited a dramatic rise and reached room temperature upon compression up to around 2-5 GPa, as determined by the variations in magnetic and elastic properties with pressures (Liebermann et al., 1968, 1970, 1986; Sato and Akimoto, 1979; Praise et al., 2006; Syono et al., 1984; Bezaeva et al., 2015).

To date, numerous studies on the structural evolution in compressed Fe_2O_3 have been carried out using various experimental high-pressure techniques *(e.g.,* dynamic shock-wave and static compression experiments), however, the crystal structure, phase stability and magnetic properties of Fe_2O_3 at high pressure still remain open questions (Shim et al., 2009; Badro et al., 2002; Pasternak et al., 1999; Rozenberg et al., 2002; Olsen et al., 1991; Ito et al., 2009; Ono et al., 2005; Syono et al., 1984; Bezaeva et al., 2015; Greenberg et al., 2018; Sanson et al., 2016). For example, at pressures above ~50 GPa, α-Fe_2O_3 undergoes a first-order phase transition from the corundum-type hematite structure to a metallic high-pressure phase (also called Mott insulator-metal transition), which is accompanied by a remarkable volume collapse of ~10% (Shim et al., 2009; Badro et al., 2002; Pasternak et al., 1999; Rozenberg et al., 2002; Olsen et al., 1991; Ito et al., 2009; Ono et al., 2005; Syono et al., 1984; Bezaeva et al., 2015; Greenberg et al., 2018; Sanson et al., 2016). Previous high-pressure x-ray diffraction and Mössbauer spectroscopy studies reported a high-pressure new phase having an orthorhombic perovskite structure (space group: *Pbnm*) (Olsen et al., 1991; Syono et al., 1984), which was controversial to the recent result by Pasternak et al. (1999) using the combined experimental techniques of X-ray diffraction, Mössbauer spectroscopy and electrical resistance measurements. As identified only from the X-ray diffraction observations, it is difficult to determine what the exact structure of the new high-pressure phase is? However, the recent Mössbauer spectroscopy measurements showed that only one Fe^{3+} site was observed in the new high-pressure phase, indicating that the new phase may be ascribed to the Rh_2O_3(II)-type structure, but not the orthorhombic perovskite-type one (Pasternak et al.,1999).

Bulk and shear moduli, as well as their pressure and temperature dependences of minerals/materials are important parameters in understanding their high *P-T* behavior and physical properties. The equation of state and compressibility/bulk modulus (K_0) of hematite have been studied by synchrotron-based static compression experiments and theoretical calculations, however, these reported values are still quite scattered and not well constrained, ranging from 199 GPa to 241.7 GPa with the associated pressure derivative ($\partial K/\partial P$) changing from 3.1 to 4.53 (Olsen et al., 1991; Liebermann et al., 1968, 1970, 1986; Sato and Akimoto, 1979; Wilson and Russo, 2009; Finger and Hazen, 1980; Catti et al., 1995). Sound velocities and elasticity of single-crystal and polycrystalline hematite first have been measured at pressures up to 3 kbar and temperatures of 200~300 K by Liebermann *et al.* (1968, 1970, 1986), where the changes in the elastic moduli (*i.e.*, bulk and shear moduli) across the magnetic Morin transition of T_M =261 K for hematite at ambient pressure were observed (Liebermann et al.,1970, 1986), and the new elasticity data were reported as K_0 = 206.6 GPa and G_0 = 91.0 GPa with the associated pressure derivatives of K' = 4.53 and G' = 0.73 (Liebermann et al.,1970, 1986).

Despite the importance of iron-bearing oxides (*i.e.*, FeO-Fe_2O_3 system), to date, most previous studies are focused on the phase transition and/or compressibility/bulk modulus at high pressure and ambient temperature, only elucidating the nature of pressure-induced phase transformation and/or bulk modulus/density changes *vs*. pressures (Shim et al., 2009; Badro et al., 2002; Pasternak et al., 1999; Rozenberg et al., 2002; Olsen et al., 1991; Ono et al., 2005; Liu et al., 2003). Very few attention has been devoted to studying the sound velocities and elasticity of α-Fe_2O_3 hematite at high pressure (Liebermann et al., 1968, 1970, 1986), let alone at the simultaneous high-pressure and high-temperature conditions, especially in terms of the shear-related properties. In this study, simultaneous high-pressure and high-temperature sound-velocity measurements on polycrystalline α-Fe_2O_3 hematite are performed in a large volume press using the state-of-the-art technique of ultrasonic interferometry in conjunction with x-ray diffraction and radiographic imaging (Zou et al., 2012, 2013, 2018a, 2018b; Liu et al., 2007; Irifune et al., 2008). Here, we reveal pressure-induced anomalies in the shear properties of hematite, and explore the mechanisms underlying this abnormal behavior. An internally consistent set of new thermoelasticity data for hematite is also reported based on our currently measured sound velocities and densities data.

2. Experimental Methods

The polycrystalline α-Fe_2O_3 hematite specimen used in the current study was commercially obtained from *Trans-Tech. Inc*., USA. Acoustic compressional (*P*) and shear (*S*) wave velocities of polycrystalline α-Fe_2O_3 hematite were simultaneously measured at high pressure and high temperature using ultrasonic interferometry in conjunction with synchrotron x-ray diffraction and x-radiographic imaging techniques in a multi-anvil apparatus at the National Synchrotron Light Source (NSLS), Brookhaven National Laboratory, USA. The experimental setup and the pressure-temperature (*P-T*) path for the present experiments are shown in Fig. 1(a) and 1(b), where each point represents a pressure-temperature (*P-T*) condition that x-ray diffraction and acoustic data for α-Fe_2O_3 hematite are collected. Details of the high *P-T* cell assembly can be found elsewhere (Zou et al., 2012, 2013, 2018a, 2018b; Liu et al., 2007; Irifune et al., 2008). Briefly, a mixture of amorphous boron and epoxy resin was used as the pressure-transmitting medium, and a graphite furnace was used as a heating element. The temperature was directly measured by a W/Re25%-W/Re3% thermocouple located immediately next to the specimen. The α-Fe_2O_3 hematite specimen was embedded in a NaCl and *h*-BN powder mixture (10:1 wt %), which can provide a hydrostatic environment for the sample.

A dual-mode $LiNbO_3$ transducer (10° Y cut) was mounted outside the pressure chamber, which can generate and receive *P* and *S* waves simultaneously. Travel times were measured using the transfer function method with a standard deviation of ~0.4 ns for the *S* wave and ~0.2 ns for the *P* wave (Zou et al., 2012, 2013, 2018a, 2018b; Liu et al., 2007; Irifune et al., 2008). The sample length at high pressure and/or high temperature was directly derived by the x-radiographic imaging method. During our experiments, x-ray diffraction patterns for both the specimen and NaCl pressure marker were collected using a solid-state detector with a diffraction angle of $2\theta \approx 6.45°$. The x-ray diffraction patterns of the sample were refined to determine the unit-cell volumes and hence the densities.

3. Results and Discussion

At ambient conditions, the polycrystalline Fe_2O_3 hematite possesses a hexagonal-close-packed (*hcp*) crystal structure, where the Fe^{3+} cations are located in distorted oxygen octahedra, as shown in Fig. 1(c). In this experiment, we performed five heating/cooling cycles at pressures and temperatures up to 6.5 GPa and 1100 K, as shown in Fig. 1(b). The sample was annealed at the peak *P-T* of each cycle for several minutes to release nonhydrostatic stress accumulated in the chamber during cold compression. After annealing, we collected the data of ultrasonic travel times, x-ray diffraction and x-radiographic imaging data at each *P-T* condition. Representative echo trains for the compressional wave (50 MHz) from the interfaces (between the anvil and the buffer rod, the buffer rod and the sample, and the sample and the pressure marker) at 6.5 GPa and 1100 K are shown in Fig. 1(d). It is found that echoes from these interfaces can be clearly identified, ensuring a precise determination of the compressional and/or shear travel times even at the highest *P-T* conditions.

Prior to our ultrasonic measurement experiments, the purchased polycrystalline hematite specimen is characterized by x-ray diffraction and SEM observations in Figs. 2(a)-(c), showing that the as-measured hematite mineral has a pure hexagonal-close-packed (*hcp*) structure [in Fig. 2(c)] and free of visible microcracks. The bulk density of the bulk hematite specimen used in this study is ~5.24(2) g/cm^3 as determined by the Archimedes immersion method, reaching ~99.5% of the theoretical x-ray density of 5.267 g/cm^3. This means that the porosity of the specimen is about 0.5%, indicating a negligible effect on the elasticity of polycrystalline hematite within uncertainties. After annealing and resintering of the bulk hematite mineral at the peak *P*-*T* conditions of 6.5 GPa and 1100 K, a typical x-ray diffraction pattern of hematite at 6.5 GPa and 1100 K is shown in Fig. 2(b), indicating that the specimen is still a corundum-structured material, and no other phases such as wüstite or magnetite are observed throughout the current high *P*-*T* experiments. Further SEM analyses of the recovered hematite from the current ultrasonic measurements show that the specimen exhibits an equilibrated and homogeneous microstructure with an average grain size of ~500 nm [in Fig. 2(c)]. Further energy-dispersive x-ray composition measurements (SEM-EDX) on the recovered specimen yield a stoichiometric Fe_2O_3 composition within uncertainties.

As shown in Fig. 2(d), the compressional (V_P) and shear (V_S) wave velocities of hematite at 300 K after annealing are plotted as a function of pressure. Clearly, the shear wave velocities (V_S) exhibit a pronounced pressure-induced discontinuity at ~3.5 GPa after annealing along cooling, which is absence of the compressional wave velocities (V_P) with pressures up to ~4.6 GPa. This pressure-induced anomaly in V_S is proposed to be attributed to the occurrence of Morin transition of α-Fe_2O_3 hematite upon compression, also called the (weak)ferromagnetic-to-antiferromagnetic phase transition (see in Fig. S1), which agrees well with the previously reported results by *in situ* acoustic velocity measurements at high pressure where a pronounced discontinuity occurred at ~3 GPa by Liebermann et al., (1970, 1986), and is also consistent with the observations from the previous high-pressure magnetic and electrical measurements near 2~5 GPa at room temperature (Ovsyannikov et al., 2012).

To further explore the pressure-induced anomaly in the shear behavior, elasticity of bulk (K_S) and shear (G) moduli as a function of pressure are shown in Fig. S2. Clearly, the above-mentioned pressure-induced anomaly in shear velocity is also observed in the shear modulus upon compression by direct high-pressure sound velocity measurements. By contrast, this anomalous behavior is absent in the pressure-volume (P-V) data from our static compression experiments combined with synchrotron x-ray diffraction study, further indicating that this anomaly is not a volume-related structural transition at high pressure.

To know about the high P-T behavior of hematite, the density changes of hematite with pressures and temperatures derived from the current synchrotron x-ray diffraction data are shown in Fig. 3(a). Clearly, the density increases with pressures and decreases with temperatures without dramatic density collapses or jumps observed during the current P-T range. When fitting the current densities data to a two-dimensional equation of $\rho = \rho_0 + \frac{\partial \rho}{\partial P} P + \frac{\partial \rho}{\partial T}(T - 300)$, we obtained the ambient-condition density of ρ_0 = 5.251(5) g/cm^3 for hematite, and its pressure and temperature derivatives of $\frac{\partial \rho}{\partial P}$ = 0.027(2) g·cm^{-3}·GPa^{-1} and $\frac{\partial \rho}{\partial T}$ = -0.00016(1) g·cm^{-3}·K^{-1}.

Fig. 3(b) and 3(c) show the compressional and shear wave velocities of Fe_2O_3 hematite along different isotherms under high pressure. It is found that the compressional wave velocity exhibits a monotonical increase with pressures and a decrease with temperatures up to 6.5 GPa and 1100 K. At temperatures above 300 K, however, the shear wave velocity (V_S) shows a normal behavior without an apparent Morin-transition-induced discontinuity as mentioned in Fig. 2(d) and Fig. S1-S2 where a pressure-induced anomalous shear wave velocity occurs at ~3.5 GPa and 300 K. This result indicates that the hematite is absence of the occurrence of the Morin transition or the (weak)ferromageitic-to-antiferromagnetic phase transition at the current pressure range and temperatures above 300 K.

Based on the acoustic velocities and densities,the bulk and shear moduli are calculated using $\rho V_P^2 = B_S + 4G/3$ and $\rho V_S^2 = G$, and the results are shown in Figs. 3(d) and 3(e). Clearly, the pressure-induced anomaly in V_S at ~3.5 GPa and room temperature is also observed in the derived shear moduli at 300 K (see in Fig. 3e), but is absent in the shear moduli at temperatures higher than 300 K. When fitting all the experimental data at the entire *P-T* conditions of this study to the two-dimensional linear equation of $M = M_0 + \frac{\partial M}{\partial P} P + \frac{\partial M}{\partial T}(T-300)$, we obtained the adiabatic ambient-condition bulk and shear moduli as well as their pressure and temperature derivatives, yielding K_{S0} = 235.7(8)GPa, G_0 = 87.9(3) GPa, $\partial K_S/\partial P$ = 3.08(23), $\partial G/\partial P$ = 1.45(9), $\partial K_S/\partial T$ = −0.026(2) GPa/K, and $\partial G/\partial T$ = -0.020(1) GPa/K (see Fig. 3 & Table 1).

However, it is worth noting that the above-mentioned pressure-induced anomaly in the shear behavior of hematite occurred at pressures above ~3.5 GPa and 300 K after annealing (see Fig. 1d and Fig. S1-S2), which is attributed to the pressure-induced Morin transition or the (weak)ferromagnetic-to-antiferromagnetic phase transition upon compression. Therefore, it is reasonable to include only the weak-ferromagnetic Fe_2O_3 data, but exclude the antiferromagnetic Fe_2O_3 data during fitting. Fitting of all the weak-ferromagnetic phase data (antiferromagnetic phase data are excluded) of hematite to the two-dimensional linear equation yields K_{S0} = 235.4(8)GPa, G_0 = 88.0(3) GPa, $\partial K_S/\partial P$ = 3.29(25), $\partial G/\partial P$ = 1.36(10), $\partial K_S/\partial T$ = −0.027(2) GPa/K, and $\partial G/\partial T$ = -0.019(1) GPa/K (see Fig. 4 & Table 1).

Clearly, the derived bulk and shear moduli as well as their temperature dependences by using the above two fits at different *P-T* ranges are almost the same values within their mutual uncertainties (see Table 1). However, the weak-ferromagnetic α-Fe_2O_3 exhibits a stronger

$\partial K_S/\partial P$ = 3.29 and a weaker $\partial G/\partial P$ = 1.36, as compared to those ($\partial K_S/\partial P$ = 3.08, $\partial G/\partial P$ = 1.45) for the nominal two phases (weak-ferromagnetic + antiferromagnetic mixture phases) compounds at the entire *P-T* range.

Our experimentally obtained elasticity of bulk and shear moduli of α-Fe_2O_3 hematite and their pressure and temperature dependences are summarized in Table 1 for comparison with previous studies (Olsen et al., 1991; Liebermann et al., 1968, 1970, 1986; Sato and Akimoto, 1979; Wilson and Russo., 2009; Finger and Hazen., 1980; Catti et al., 1995). It is found that our obtained bulk modulus of K_{S0} = 235.4(8) GPa for weak-ferromagnetic α-Fe_2O_3 hematite is in good agreement with the directly acoustic result of K_{S0} = 241.7 GPa by Liebermann et al, (1970, 1986), and is also consistent with the previously synchrotron-based static compression experiments of K_0 = 230~231 GPa within mutual uncertainties (Olsen et al., 1991; Sato and Akimoto, 1979; Catti et al., 1995), but ~12% higher than the sound velocity result of K_{S0} = 206.6 GPa for the antiferromagnitic α-Fe_2O_3 (Liebermann et al., 1968), and the theoretical result of ~215 GPa (Wilson and Russo, 2009). This difference may be due to the use of different experimental techniques and the well-known debinding of GGA for theoretical calculations. For shear modulus, our experimentally derived G_0 = 88.0 GPa is consistent well with the previous acoustic studies by Liebermann et al. (G_0 = 91.0 GPa) for antiferromagnetic phase (Liebermann et al., 1968).

As shown in Table 1, our obtained pressure dependence of the bulk modulus $\partial K_S/\partial P$ = 3.29(25) for weakferromagnetic α-Fe_2O_3 hematite from the current synchrotron-based acoustic study is in good agreement with the previous static compression experiments of $\partial K_S/\partial P$=~3.5 by Olsen et al. (1991) and Catti et al. (1995), as well as the theoretically predicted $\partial K_S/\partial P$=3.1 (Wilson and Russo, 2009). However, our obtained pressure-dependence in bulk modulus ($\partial K_S/\partial P$=3.1) is significantly lower than the acoustic results of $\partial K_S/\partial P$=4.53 by Liebermann et al. (1968) for antiferromagnetic phase of α-Fe_2O_3. This large discrepancy may be due to the narrow pressure range (the maximum pressure is only up to 3 kbar) of the previous acoustic measurement in the high-pressure chamber (Liebermann et al., 1968). In contrast, the experimental value of $\partial G/\partial P$=1.36(10) in weak-ferromagnetic hematite is significantly higher than that (G'=0.73) for the antiferromagnetic α-Fe_2O_3 (Parise et al., 2006).

Table 1. Summary of the elasticity of α-Fe_2O_3 hematite, compared with the previously experimental and theoretical results

Minerals	K_{S0} (GPa)	G_0 (GPa)	$\partial K_S/\partial P$	$\partial G/\partial P$	$\partial K_S/\partial T$ (GPa/K)	$\partial G/\partial T$ (GPa/K)	Refs.
Fe_2O_3 hematite	235.4(8)	88.0(3)	3.29(25)	1.36(10)	-0.027(2)	-0.019(1)	This study (*weak-ferromagnetic phase*)
	235.7(8)	87.9(3)	3.08(23)	1.45(9)	-0.026(2)	-0.020(1)	This study (*nominal two phases -entire P-T range fitting*)
	215	--	3.1	--	--	--	Wilson et al. (2009): Theor.
	241.7	--	4.5*	--	--	--	Liebermann et al. (1970, 1986) (*weak-ferromagnetic α-Fe_2O_3*)
	206.6	91.0	4.53(13)	0.73(3)	--	--	Liebermann et al. (1968) (*antiferromagnitic phase*)
	231(10)	--	4.0*	--	--	--	Sato and Akimoto (1979) (*weak-ferromagnetic α-Fe_2O_3*)
	230(5)	--	3.5(6)	--	--	--	Olsen et al. (1991)
	230	--	3.5	--	--	--	Catti et al. (1995)

*fixed values

As major candidates of the Earth's mantle and core, it is of great importance to understand the sound velocities, elastic moduli and its pressure derivatives of typical Fe-O minerals with various Fe-O ratios, such as hematite, magnetite and wüstite. As shown in Fig. 4(a), both compressional (V_P) and shear (V_S) wave velocities decrease with the increasing Fe/O ratios in Fe-O minerals. It is found that the values of V_P and V_S in α-Fe_2O_3 hematite are about ~25% and ~30% higher than those for $Fe_{0.95}O$ wüstite (Jacobsen et al., 2004), respectively. This composition-dependent trends in the acoustic velocities are also observed in the K_S and G, as shown in Fig. 4(b).

To further explore high-pressure elasticity of iron-bearing oxides, the pressure dependences of the bulk and shear moduli for hematite are shown in Fig. 4(c), as compared with those for magnetite and wüstite by Jacobsen et al (2004). Clearly, the Fe_3O_4 magnetite possesses a smaller value of $\partial K_S/\partial P \approx 3.0$ as compared with those for hematite ($\partial K_S/\partial P \approx 3.3$) and wüstite ($\partial K_S/\partial P = 3.7$). By contrast, the $\partial G/\partial P$ decreases with increasing Fe/O ratios, and it exhibits a negative value of -0.22 and -0.23 for magnetite and wüstite by Jacobsen et al (2004), respectively. This shear modulus softening is likely due to the strong magnetoelastic coupling in magnetite and wüstite, which indicates their structural instability at high pressure.

It is accepted that the bulk modulus value is inversely proportional to the unit-cell volume, and hence for similar-structured materials/minerals, the product of $K_0 \times V_0$ should be approximately constant (Anderson, 1970). As shown in Fig. 4(d), the ambient-condition bulk modulus (K_0) is plotted as a function of the reciprocal volume of the formula unit [$1/(V_0/Z)$] (where Z is the number of formula units in the cell) for typical corundum-structured oxides ($Z = 6$), yielding an apparent linear relation in Fig. 4(d). It is found that our experimentally obtained data of K_0-[$1/(V_0/Z)$] relations for α-Fe_2O_3 hematite apparently agree well with the linear behavior in other corundum-structured materials such as Al_2O_3 (Syassen, 2008), Cr_2O_3 (Kantor et al., 2012), Ti_2O_3 (Nishio-Hamane et al., 2009), Ga_2O_3 (Lipinska-Kalita et al., 2008) and V_2O_3 (McWhan and Remeika, 1970) (see in Fig. 4d).

4. Implications

With high abundance of iron and oxygen in the Earth's crust and mantle, iron oxides are considered to be important minerals which makes significant contributions to properties of the Earth. Understanding sound velocities and elasticity of iron oxides at extreme high P-T conditions plays an important role in interpreting the structural stability, composition and mineralogy of the Earth's interiors. Our results demonstrate that the structural stability and sound velocities/elasticity for typical Fe-O minerals [*e.g.*, Fe_3O_4 magnetite (Zou et al., 2018), Fe_2O_3 hematite (Liebermann et al., 1968, 1970, 1986) and FeO wüstite (Jacobsen et al., 2004)] are quite different, which is very sensitive to the Fe/O ratio at various pressures and temperatures, probably providing significant consequences for modelling of the Earth's interior.

Among iron oxides, hematite (α-Fe_2O_3) is one of the major components of banded-iron-formations which is deposited in the oceans and recycled into the Earth's interior by subducting into the Earth's depths to the core-mantle boundary region (Bezaeva et al., 2015). As major components of subducted *BIFs*, the exposed phases of iron oxides are strongly dependent on pressures and temperatures of the Earth's interior. From the amount of *BIFs* subducted into the Earth's mantle, the *BIFs* is estimated to ~50% Fe_2O_3 by volume calculated from the obtained velocities/elastic data. As clearly seen from our experimental observations in Fig. 2(d) and Fig. S1-S2, a pronounced pressure-induced anomaly in the shear wave velocity of hematite occurred at ~3.5 GPa and room temperature after annealing. These pressure-induced velocity anomalies in hematite would be a good evidence that provides further confirmation of the previously reported (weak)ferromagnetic-to-antiferromagnetic Morin transition of hematite upon compression by magnetization measurements (Liebermann et al., 1968, 1970, 1986; Bezaeva et al., 2015). However, it is worth mentioning that such pressure-induced anomaly/discontinuity is quite difficult to observe in the bulk moduli with pressures upon static compression as determined from x-ray *P-V* data. The reason is due to the associated second-order magnetic phase transitions of hematite at high pressure as ever proposed by Liebermann *et al.* (1968, 1970, 1986).

On the other hand, we know that the temperature of the Earth's crust interiors is far above the Morin transition of T_M ~250 K at ambient pressure but doesn't exceed the Curie temperature of ~948 K for hematite (Morrish, 1994; Shull et al., 1951; Amin and Arajs, 1987), we thus reasonably assume that hematite present in Earth's crust is in its (weak)ferromagnetic state. For the Earth, only the first kilometers of crust may be affected by the process with ~2 GPa pressure wave. This effect eventually resulted in a pressure-induced anomaly or demagnetization at pressures above 1.5 GPa and room temperature, which is probably the reason for our observed anomaly in the shear behavior at ~3.5 GPa and 300 K in hematite mineral, or for the pressure demagnetization in hematite-bearing rocks by Bezaeva et al (2015). The different transition-pressures may be attributed to the use of different experimental techniques, or the effects of nonhydrostatic stress accumulated in the chamber which may significantly affect the pressure sensitivity of the Morin transition as proposed by Coe et al (2012). This magnetoelastic interaction is not unique to hematite among minerals of geophysical interest, but includes all magnetically ordered materials such as FeO, CoO, MnO, NiO and Cr_2O_3 (McWhan and Remeika, 1970), which opens the question of interactions when elastic properties are measured using ultrasonic interferometry techniques. Generally, order-disorder transition temperatures for the magnetic oxides are formulated as a function of pressure. When studying minerals' and rock's magnetism, it is often necessary to understand the detailed spin orientation. Using ultrasonic interferometry techniques, it is possible to diagnose the orientations of the spins and the detailed nature of the domain structure, sound velocities and elasticity, yielding important information on the spin alignment through studies of spin wave-phonon interactions. The special importance to geophysics may be due to elasticity discontinuities of crystals across magnetic phase transitions. To date, considerable attention has been devoted to studying elastic behavior in the region of order-disorder transition temperatures, but much work remains to be done. Especially, the pressure effects of order-order transitions such as the Morin transition, and high *P-T* velocities/elasticity in hematite cannot be overlooked.

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