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Revision 1

Thermal conductivity anomaly in spin-crossover ferropericlase under lower mantle conditions

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Iron in ferropericlase experiences a spin crossover from a high spin to a low spin under lower mantle conditions, which generates anomalies in many properties such as the heat capacity and sound velocity. In this study, the effect of the spin crossover on thermal conductivity was evaluated by considering the effects of the spin crossover on P wave velocity and heat capacity at constant volume but ignoring the effect on mean free path. The spin crossover completely changes the conventional pressure and temperature dependences of the thermal conductivity. The spin crossover can significantly reduce the thermal conductivity of ferropericlase. The pressure dependence of the thermal conductivity of ferropericlase will show a double-valley feature across the spin-crossover region at the appropriate temperature (e.g., 1000 K). In contrast to the conventional decrease in the thermal conductivity with temperature, the thermal conductivity of ferropericlase in the Earth's D" layer may increase with temperature in some temperature regions. The unusual effect of spin crossover on the thermal conductivity can be expected in other minerals with spin crossover. The spin crossover effect needs serious consideration when estimating the thermal conductivity at the core-mantle boundary.

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Introduction

Thermal conductivity of the mantle minerals is one of the key parameters that control mantle convection. The heat flux from the core, which is determined by the heat conductivity of the thin layer overlying the core-mantle boundary (CMB), is critical to the understanding of many processes such as the Earth's evolution, mantle convection, and geodynamo, while the thermal conductivity of the lower-mantle minerals at the CMB is fundamental in estimating the heat flux from the core. Thus, the lattice thermal conductivity of ferropericlase ($Mg_{1-x}Fe_xO$), bridgmanite and post perovskite have been investigated intensively both by experiments [*Beck et al.*, 2007; *Dalton et al.*, 2013; *Goncharov et al.*, 2010; *Hofmeister*, 2014; *Hsieh et al., 2017, 2018; Imada et al.*, 2014; *Katsura*, 1997; *Manga and Jeanloz*, 1997; *Manthilake et al.*, 2011; *Ohta et al.*, 2014; *Ohta et al.*, 2017; *Osako and Ito*, 1991; *Okuda et al., 2017; Rainey and Kavner*, 2014; *Hofmeister and Branlund 2015*] and theoretical calculations *[de Koker, 2009; 2010; Dekura et al., 2013; Haigis et al., 2012; Stackhouse et al., 2010; 2015; Tang and Dong, 2010; Tang et al., 2014; Ghaderi et al. 2017; Zhang et al., 2017].* The spin-state crossover of iron in the lower mantle minerals has been found to affect significantly their elasticity, thermodynamic properties and transport properties [*Lin et al.*, 2013]. The spin crossover may profoundly affect the lattice thermal conductivity of the lower mantle. However, knowledge of the spin-crossover effect on the lattice thermal conductivity is very limited. To our knowledge, first-principle calculations were conducted on the Mg endmembers of ferropericlase, bridgmanite and post perovskite. Only a few experiments measured the lattice thermal conductivity of ferropericlase with pressures surpassing the spin-transition pressure [*Hsieh et al.,* 2018; *Ohta et al.,* 2017]. Ohta *et al.* [*Ohta et al.*, 2017] observed an anomalous reduction in thermal conductivity of ferropericlase in the spin crossover region. *Hsieh et al.* [2018] shows that the reduction only occurs in ferropericalse with very high iron concentration. The mechanism for the reduction has not been fully explored. The controversial experimental results call for theoretical investigations on the effect of spin crossover on the thermal conductivity.

The lattice thermal conductivity can be expressed as (Hofmeister and Branlund 2015),

$$k_{lat} = \frac{\rho}{3ZM} C_V V_P^2 \langle \tau \rangle \quad (1)$$

where V_P is the compressional velocity, C_V is heat capacity at constant volume, M is the molar formula weight, Z is the number of formula units in the primitive unit cell, and $\langle \tau \rangle$ is the mean free lifetime. The Eq. 1 has been used to satisfactorily describe the lattice thermal conductivity of several perovskites [*Hofmeister*, 2010]. As shown in Eq. 1, k_{lat} is sensitive to the sound velocity and heat capacity. Both are extremely affected by the spin crossover of iron in ferropericlase. The spin crossover causes an anomalous softening in the bulk modulus and significantly reduces the V_P of ferropericlase [*Crowhurst et al.*, 2008; *Fei et al.*, 2007; *Komabayashi et al.*, 2010; *Lin and Tsuchiya*, 2008; *Mao et al.*, 2011; *Marquardt et al.*, 2009; *Tsuchiya et al.*, 2006; *Wentzcovitch et al.*, 2009; *Z Q Wu et al.*, 2013; *Yang et al.*, 2015], which results in an unusual positive temperature dependence of the V_P of ferropericlase within part of the spin-crossover region [*Wu and Wentzcovitch*, 2014]. The temperature insensitivity of V_P in the mid-lower mantle caused by the opposite temperature dependence of V_P of bridgmanite and ferropericlase is consistent with the P-wave disruption in the plume image below the Hawaii and Iceland hot spots at a depth of 1500–2000 km and the global disruption of the faster-than-average V_P structure at the depth of ~ 1700 km [*van der Hilst and Karason*, 1999; *Wu and Wentzcovitch*, 2014; *Z Q Wu*, 2016; *Z Q Wu and Wentzcovitch*, 2017; *Zhao*, 2007]. The spin crossover of iron in ferropericlase also generates an anomaly in the thermodynamic properties of ferropericlase such as a several-fold increase in the thermal expansion and a peak in the heat capacity [*Z Wu et al.*, 2009], which controls the structural feature of the large low shear velocity provinces above the CMB [*Huang et al.*, 2015] and significantly modifies the mantle flow[*Bower et al.*, 2009; *Shahnas and Peltier*, 2015; *Shahnas et al.*, 2016; *Shahnas et al.*, 2017; *Shahnas et al.*, 2011]. Thus, we can expect that the spin crossover can dramatically impact the thermal conductivity of ferropericlase. However, its effect on thermal conductivity has not yet been studied in detail.

Theoretical model

The Gibbs free energy of ferropericlase in a mixed spin (MS) state, $G(n,P,T)$, is given by[*Z Q Wu et al.*, 2013]

$$G(n,P,T) = nG_{LS}(P,T) + (1-n)G_{HS}(P,T) + G_{mix} \qquad (2)$$

where n is the fraction of the low spin state (LS), G_{LS} and G_{HS} are the Gibbs free energies of the pure LS and HS states, respectively, and G_{mix} is the free energy of mixing of an HS/LS mixture

$$G_{mix}(n) = -TS_{mix}(n) = k_B T X_{Fe}[n \ln n + (1-n)\ln(1-n)] \quad (3)$$

Here, X_{Fe} is the iron concentration in ferropericalse ($\mathrm{Mg}_{1-X_{\mathrm{Fe}}}Fe_{X_{\mathrm{Fe}}}\mathrm{O}$) and the entropy of mixing is assumed to be that of an ideal solution, which is justified by the negligible iron-iron interactions implied by the independence of the spin transition pressure on iron concentrations up to the concentration ~ 0.2 [*Tsuchiya et al.*, 2006; *Persson et al.*, 2006]. The minimization of the free energy with respect to the LS fraction, n, gives

$$n(P,T) = \frac{1}{1 + m(2S+1)\exp\left[\frac{\Delta G_{LS-HS}^{stat+vib}}{X_{Fe} K_B T}\right]} \quad (4)$$

where $\Delta G_{LS-HS}^{stat+vib}$ is the difference in the Gibbs free energy from the static and vibration contribution between the HS and LS states, and $S=2$ and $m=3$ are the spin and electronic configuration (orbital) degeneracy values of the HS state, respectively.

Since $V(n) = nV_{LS}(P,T) + (1-n)V_{HS}(P,T)$, we have the following expression for the bulk modulus, $K(n)$,

$$\frac{V(n)}{K(n)} = n\frac{V_{LS}}{K_{LS}} + (1-n)\frac{V_{HS}}{K_{HS}} - (V_{LS} - V_{HS})\frac{\partial n}{\partial P} \quad (5)$$

where V_{HS} and V_{LS} are the volume of HS and LS, respectively, and $K_{HS/LS}$ is the bulk modulus of the pure HS/LS states. The first two terms in the right side of Eq. 5 are the weight average of those of the HS and LS states. The last terms in Eq. 5 appears only at the spin-crossover region and is always positive since $\frac{\partial n}{\partial P} > 0$ and $V_{HS} > V_{LS}$. Therefore, spin crossover causes an anomalous softening in the bulk modulus and reduces the compressional velocity. We defined

$$R_{V_P^2} = (\frac{V_P}{V_P^{mix}})^2 \quad (6)$$

where $V_P^{mix} = nV_P^{LS} + (1-n)V_P^{HS}$ is the weight average of the V_P of LS and HS.

The entropy is given by

$$S = -\left(\frac{\partial G}{\partial T}\right)_P = nS_{LS} + (1-n)S_{HS} + (G_{HS} - G_{LS})\left(\frac{\partial n}{\partial T}\right)_P + S_{mix}, \quad (7)$$

The lattice heat capacity at constant volume (C_V) and at constant pressure (C_P) is calculated from the entropy

$$C_V = T\left(\frac{\partial S}{\partial T}\right)_V \quad (8)$$

$$\begin{aligned} C_P = T\left(\frac{\partial S}{\partial T}\right)_P &= nC_P^{LS} + (1-n)C_P^{HS} \\ &+ 2T(S_{LS} - S_{HS})\left(\frac{\partial n}{\partial T}\right)_P + T(G_{HS} - G_{LS})\left(\frac{\partial^2 n}{\partial T^2}\right)_P + T\frac{\partial S_{mix}}{\partial T} \end{aligned} \quad (9)$$

The contribution of the spin crossover on the heat capacity, which is described by the last three terms in Eq. 9, can be positive or negative at the spin-crossover region. We defined

$$R_{C_V} = \frac{C_V}{C_V^{mix}}, \quad (10)$$

where $C_V^{mix} = nC_V^{LS} + (1-n)C_V^{HS}$ is the weight average of C_V of LS and HS.

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We introduce $k_{latt}^{mix} = \frac{\rho}{3ZM} C_V^{mix} (V_P^{mix})^2 \langle \tau \rangle$ to approximately describe the thermal conductivity of the mechanic mixture of LS and HS. The unusual effect of the spin crossover on the thermal conductivity of ferropericlase can be described by

$$R_k = \frac{k_{latt}}{k_{latt}^{mix}} = R_{V_P^2} R_{C_V} \tag{11}$$

Here, we ignore the effect of the spin crossover on the mean free lifetime $\langle \tau \rangle$. $\langle \tau \rangle$ of MS may be smaller than the weight average of that of LS and of HS because of increased scattering in MS with two types of iron. Thus, R_k probably is reduced further after including the spin-crossover effect on $\langle \tau \rangle$.

Wu et al., have studied the effect of the spin crossover on thermodynamic properties and sound velocities of ferropericlase with X_{Fe}=0.1875 [*Z Q Wu et al.*, 2009; 2013]. These data were used here to investigate the effect of spin crossover on thermal conductivity of ferropericlase with X_{Fe}=0.1875. At low iron concentration (X_{Fe} < 0.2), where n(P,T) is insensitive to the X_{Fe}, the anomalous softening in bulk modulus caused by spin crossover increases almost linearly with X_{Fe} (*Z Q Wu et al.*, 2013; Wu and Wentzcovitch 2017) and the last three terms in Eq. 9 also linearly depend on X_{Fe}. Thus we can use the relation $1-R_{V_P^2}$ 9$\propto X_{Fe}$ and $1-R_{C_V} \propto X_{Fe}$ to estimate approximately the effect of the spin crossover on thermal conductivity of ferropericlase with low iron concentration.

Result

As shown in Fig. 1a, the minimum of $R_{V_P^2}$ is ~ 0.6 at room temperature at the spin-crossover region. Although the effect of the spin crossover on V_P decreases

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with increasing temperature because of the broadening of the spin-crossover region, the spin crossover can still reduce $R_{V_P^2}$ to 0.84, even at a high temperature of 4000 K. With increasing temperature, the spin crossover first slightly reduces both C_V and C_P and then increases significantly C_V and C_P and generates a peak value of C_V and C_P around the temperature where V_P shows the minimum value (Fig. 1). Thus, in contrast to $R_{V_P^2}$, which is always smaller than 1 at the spin-crossover region, R_{C_V} can be larger or smaller than 1. The *PT* region with $R_{C_V} > 1$ overlaps well with the region where $R_{V_P^2}$ is significantly smaller than 1. The regions with $R_{C_V} < 1$ surround the region with $R_{C_V} > 1$. The temperature of peak value of R_{C_V} is close to that of the minimum of $R_{V_P^2}$. With increasing temperature, the peak value of R_{C_V} remains almost constant at ~ 1.15, while the effect of the spin crossover on V_P decreases notably (Fig. 1).

The spin crossover causes a significant anomaly in the thermal conductivity (Fig. 2). At room temperature, the reduction of the thermal conductivity dominantly results from the effect of the spin crossover on V_P . The effect of the spin crossover on V_P can reduce the thermal conductivity of ferropericlase with X_{Fe}=0.1875 by ~ 40%, which can roughly explain the experimental results (Fig. 3). This finding suggests that the unusual reduction in the thermal conductivity of ferropericlase at spin-crossover pressures at room temperature reported by Ohta *et al*[*Ohta et al.*, 2017] might mainly result from the unusual effect of the spin crossover on V_P. Since $1-R_{V_P^2}$ 10$\propto$ X_{Fe}, the spin crossover can reduce the thermal conductivity of ferropericlase with X_{Fe} =0.1 by

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roughly 20%. This value is close to the experimental uncertainty for thermal conductivity [*Hsieh et al.,* 2018]. This factor coupled with the broad pressure range of spin crossover makes the experimental observation of the reduction of thermal conductivity challenge for ferropericlase with low iron concentration. This may explain why *Hsieh et al.,* (2018) only found the clear reduction of thermal conductivity in spin-crossover region for ferropericlase with X_{Fe}= 0.56 among three concentrations X_{Fe}=0.56, 0.1 and 0.08.

One unusual feature is that the spin crossover not only reduces the thermal conductivity but also generates a negligible effect on the thermal conductivity in the middle of the spin-crossover region above 2000 K. The effect of the spin crossover on V_P decreases noticeably with increasing temperature (Fig. 1a), while the peak value of R_{C_V} is approximately 1.15 at any temperature (Fig. 1b). Therefore, above a certain temperature (~2000 K), the effect of increasing C_V almost cancels out that of the decreasing V_P, and the spin crossover has a negligible effect on the thermal conductivity in the middle of the spin-crossover region. The pressure region with the negligible effect broadens with increasing temperature. Outside of the region, the spin crossover reduces significantly the thermal conductivity. Thus, R_k fluctuates significantly with pressure and temperature within the spin-crossover region. The pressure regions with the thermal conductivity fluctuations broaden dramatically with temperature (Fig. 3).

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Therefore, the spin crossover can completely change the conventional temperature and pressure relation of the thermal conductivity, even under CMB conditions. In general, the lattice thermal conductivity increases with pressure and decreases with temperature. The normal pressure dependence of the thermal conductivity can be expressed as [*Hofmeister*, 1999]:

$$\frac{\partial \ln k_{latt}}{\partial P} = \frac{1}{K_T}\left(4\gamma + \frac{1}{3}\right) \qquad (12)$$

where K_T is the isothermal bulk modulus and γ is the Grüneisen parameter. As shown in Table 2, the unusual fluctuation in the thermal conductivity of ferropericlase caused by the spin crossover can be compared to the normal pressure dependence of the thermal conductivity. In fact, the normal pressure dependence of the thermal conductivity at a relatively low temperature, as described by Eq. 12, is not sufficient to balance the rapid decrease in the thermal conductivity caused by spin crossover (Table 2). The thermal conductivity of ferropericlase will exhibit a double-valley feature with increasing pressure at relative low temperature. A temperature of 1000 K may be appropriate for the experimental observation of the double-valley feature. As shown in Fig. 3, at room temperature, the two valleys are very close each other with a 3.5 GPa interval, which challenges the experimental observation. The distance between valleys increase quickly with temperature (Table 1), while the double-valley feature weakens with temperature (Table 2). Overall, 1000 K should be a good choice.

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The theoretical calculations [*Stackhouse et al.*, 2010; *Tang and Dong*, 2010] predicted that the lattice thermal conductivity of pure simple cubic MgO at high temperature follows the T^{-1} relation. The T dependence of the thermal conductivity for $Mg_{1-x}Fe_xO$ becomes more gradual than T^{-1} because of the mass disorder introduced by replacing Mg with Fe. Manthilake *et al.* [*Manthilake et al.*, 2011] found the $T^{-0.24}$ dependence of the thermal conductivity of $Mg_{1-x}Fe_xO$ with x=0.05 and 0.2 at 8 and 14 GPa. As shown in Table 3 and Fig. 3c, the unusual fluctuation in the thermal conductivity of ferropericlase caused by spin crossover can also be compared to the normal T dependence of the thermal conductivity, and the spin crossover will dramatically change the T dependence of the thermal conductivity of ferropericlase. In some of the PT range, the positive T dependence of the thermal conductivity produced by the spin crossover may cancel out the normal T dependence, and the thermal conductivity of ferropericlase even increases with temperature, while in the other part of the PT range, the thermal conductivity of ferropericlase decreases with T much faster than the normal T dependence because of the spin-crossover effect (Fig. 2 and 3c). Thus, spin crossover generates a complicated T dependence of the thermal conductivity of ferropericlase.

Implications

The spin crossover occurs not only in ferropericlase but also in bridgmanite and post perovskite [*Badro et al.*, 2004; *Lin et al.*, 2013]. Iron can be Fe^{2+} and Fe^{3+} and can occupy the Mg and Si sites in bridgmanite and post perovskite. The theoretical

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and experimental studies indicate that only Fe^{3+} in the Si site experiences a high spin to a low spin transition with a transition pressure at 15-50 GPa at 300 K [*Catalli et al.*, 2010; *Hsu et al.*, 2011; *Jackson et al.*, 2005; *Lin et al.*, 2012; *Stackhouse et al.*, 2007]. The spin transition in bridgmanite is also a smooth transition. The pressure range of the spin crossover broadens with increasing temperature. The spin crossover causes a significant softening in the bulk modulus of bridgmanite [*Shukla et al.*, 2016]. These features are common in minerals with a spin crossover (e.g., [*Hsu*, 2017; *Y Wu et al.*, 2016]). Thus, the unusual effect of the spin crossover on the thermal conductivity of ferropericlase should also apply to other minerals with a spin crossover such as bridgmanite and post perovskite. In this study, the spin crossover significantly affects the thermal conductivity of ferropericlase, even at the CMB conditions. The bridgmanite and post perovskite have a similar transition pressure to ferropericlase at room temperature. The recent experiments did not observe the spin transition effect on thermal conductivity of bridgmanite at the lower-mantle pressure [*Hsieh et al., 2017; Okuda et al., 2017*], which is consistent with that the measured samples do not contain iron in Si site. However, if there is a significant amount of Fe^{3+} in the Si sites of bridgmanite and post perovskite, the spin crossover potentially dramatically changes the thermal conductivity of the lower mantle at the CMB and affects our estimation of the heat flow from the core to mantle.

Because of the unusual effect of the spin crossover on the thermal conductivity of ferropericlase, the thermal conductivity of ferropericlase with a spin crossover no

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longer complies with the conventional pressure and temperature dependence. Considering the broad temperature and pressure range where the spin crossover significantly affects the thermal conductivity (Fig. 2), we should be careful in extrapolating the thermal conductivity of minerals with spin crossover to Earth's interior conditions.

Spin crossover not only change the sound velocity and heat capacity but also affect the mean free lifetime $\langle\tau\rangle$. $\langle\tau\rangle$ of MS may be smaller than the weight average of that of LS and of HS because of increased scattering in MS with two types of iron. Thus, R_k probably is reduced further after including the spin-crossover effect on $\langle\tau\rangle$. This study combining with the effect of the spin crossover on the mean free lifetime $\langle\tau\rangle$, which remains to be investigated in the future, will allow us to fully understand the spin crossover effect on the thermal conductivity of ferropericlase.

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Table 1. The valley/peak values of R_k and the corresponding pressure that they occur for ferropericalse with X_{Fe}=0.1875. The number in parentheses is the pressure variation required to change R_k 5%

T (K)	Valley 1		Peak		Valley 2	
	value	P (GPa)	value	P (GPa)	value	P (GPa)
300	0.59	38 (0.8)	0.66	40.5 (1.0)	0.65	41.5 (1.1)
1000	0.74	47.5 (2.0)	0.83	54.5 (3.5)	0.80	60 (4.5)
2000	0.81	60 (6.0)	0.92	74 (7.5)	0.85	89 (11)
3000	0.84	72 (9.0)	0.95	93.5 (12)	0.87	118.5 (17)
4000	0.86	84.5 (13.5)	0.97	114.5 (16)	0.88	148.5 (19)

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Table 2. The maximum and minimum of the pressure dependence of R_k at various temperatures and the corresponding pressure for ferropericalse with X_{Fe}=0.1875 . $\frac{\partial \ln k_{latt}}{\partial P}$ for high spin state in the last row is calculated with Eq. 12 at pressure and temperature of $\left(\partial R_k \partial P\right)_{\min}$. The number in parentheses is the pressure variation required to change $\partial R_k \partial P$ 10%

T (K)		300	1000	2000	3000	4000
$\left(\partial R_k / \partial P\right)_{\min}$	value (10^{-2}/GPa)	-12	-2.9	-1.1	-0.7	-0.5
	P (GPa)	36 (0.2)	42 (0.6)	51.5 (0.9)	61 (1.1)	70.5 (1.4)
$\left(\partial R_k / \partial P\right)_{\max}$	value (10^{-2}/GPa)	7.7	2.1	1.2	0.9	0.6
	P (GPa)	44 (0.4)	50 (0.5)	66 (0.8)	82 (1.1)	99 (1.5)
$\left(\partial \ln k_{latt} / \partial P\right)$ (10^{-2}/GPa)		1.88	1.89	1.83	1.75	1.7

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Table 3. The maximum and minimum of the temperature dependence of R_k at various pressures for ferropericalse with X_{Fe}=0.1875. The last row shows $\frac{\partial \ln k_{latt}}{\partial T}$ for $T^{-0.24}$ dependence of thermal conductivity at pressure and temperature of $\left(\partial R_k/\partial T\right)_{\max}$. The number in parentheses is the temperature variation required to change $\partial R_k/\partial T$ 10%.

P (GPa)		<32	40	80	100	136
$\left(\partial R_k/\partial T\right)_{\min}$	Value (10^{-4}/K)	0	-6.5	-3	-1.8	-1.1
	T (K)		360 (10)	1300 (40)	1800 (50)	2800 (80)
$\left(\partial R_k/\partial T\right)_{\max}$	Value (10^{-4}/K)	0	7	2.0	1.5	1.2
	T (K)		600 (20)	1980 (30)	2800 (50)	4050 (70)
$\frac{\partial \ln k_{latt}}{\partial T}(=-0.24/T)$			-4	-1.21	-0.86	-0.59

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Figure caption

Figure 1. (a) $V_P\ /V_P^{mix}$ and (b) $C_V\ /C_V^{mix}$ for ferropericalse with X_{Fe}=0.1875 as function of temperature and pressure.

Figure 2. $k\ \ /k^{mix}$ as function of temperature and pressure for ferropericalse with X_{Fe}=0.1875.

Figure 3. (a) pressure dependence of $k\ \ /k^{mix}$ at various temperatures for ferropericalse with X_{Fe}=0.1875. (b) the pressure dependence of k at room temperature measured by Ohta et al (2017). The dashed line in (a) describes the ratio of the solid green line over the dashed green line in (b). and (c) the temperature dependence of $k\ \ /k^{mix}$ at various pressures

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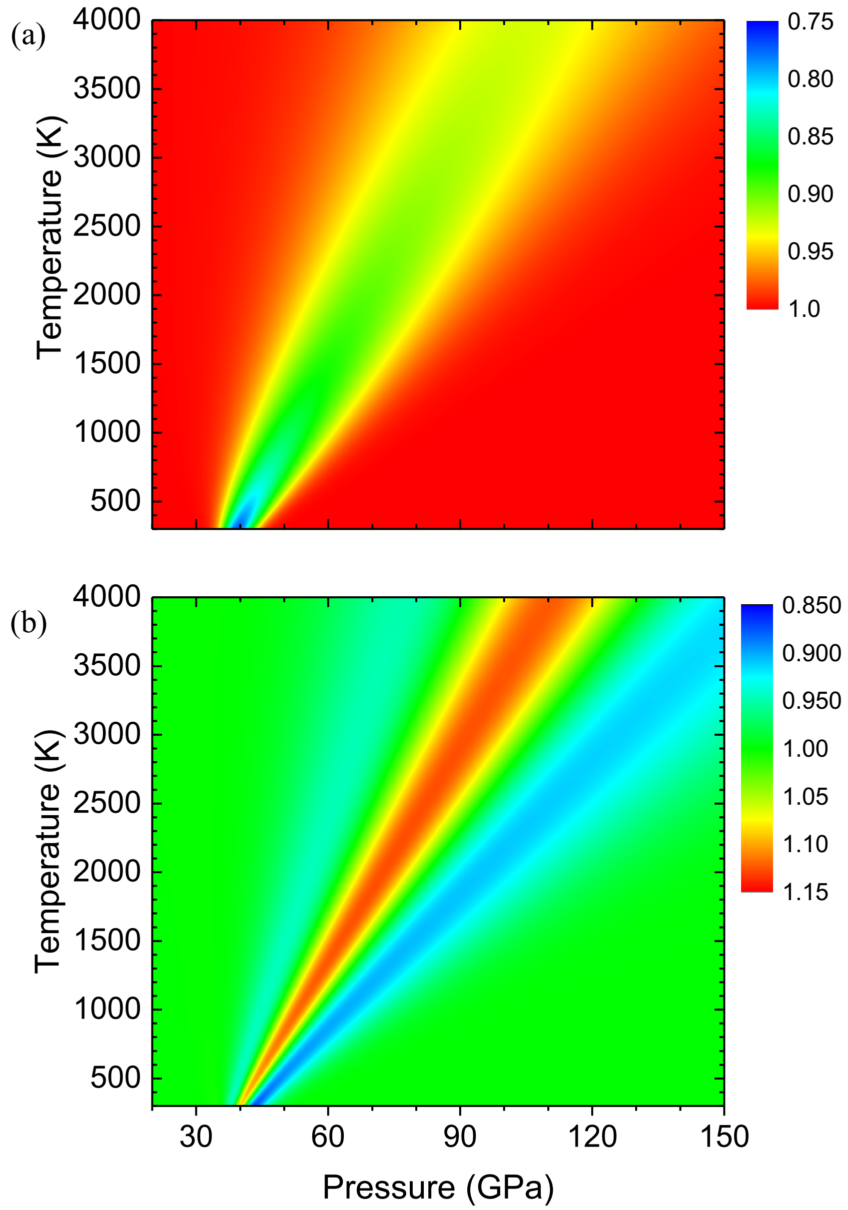
(a)
Temperature (K)
4000
3500
3000
2500
2000
1500
1000
500
0.75
0.80
0.85
0.90
0.95
1.0
(b)
Temperature (K)
4000
3500
3000
2500
2000
1500
1000
500
0.850
0.900
0.950
1.00
1.05
1.10
1.15
30
60
90
120
150
Pressure (GPa)

Figure 1

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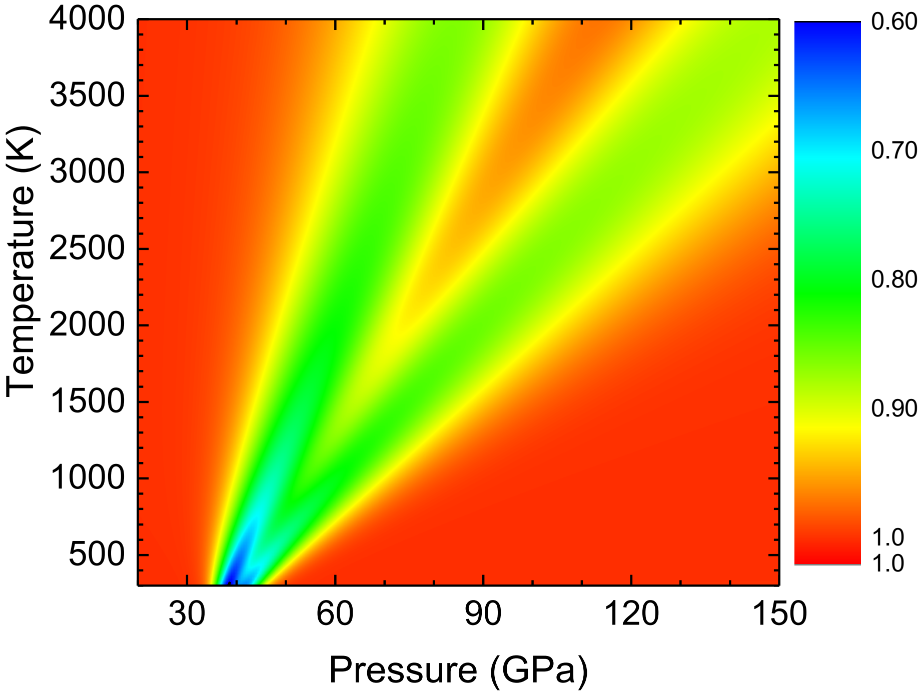

Figure 2

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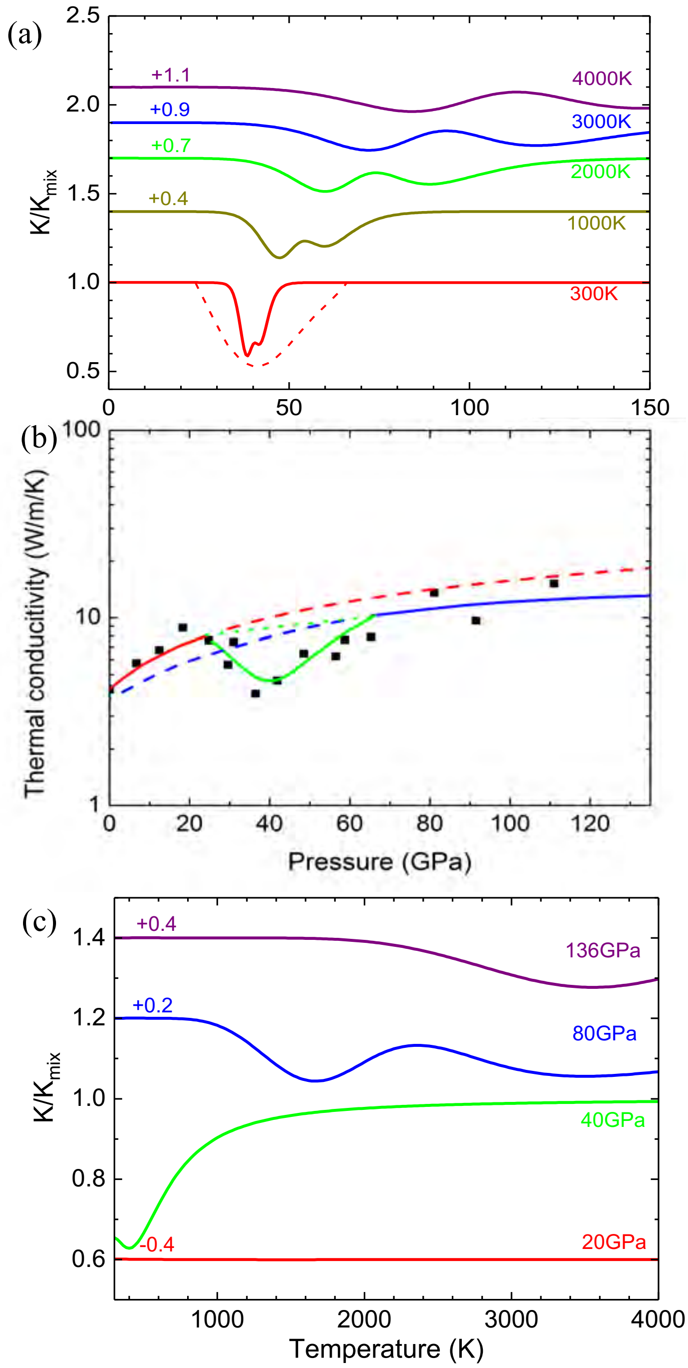

Figure 3