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Ab-initio study of the effects of pressure and chemistry on the electron-capture radioactive decay constants of ^{7}Be, ^{22}Na and ^{40}K

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Abstract

Using state-of-the-art ab-initio computations, we find that pressure and chemical environment have a small effect on the electron-capture component of the decay constants of isotopes of ^{7}Be, ^{22}Na and ^{40}K. As expected, ^{7}Be shows the greatest amount of change with ~0.1–0.2% increase in the decay constant at 25 GPa as a metal, chloride or oxide. In their metallic forms, ^{22}Na and ^{40}K show an increase of 0.06% and 0.025% change, respectively, at 25 GPa. Upon further compression, potassium and sodium undergo an s-to-d electronic transition of their valence electron, causing a significant change in the charge density at the nucleus. Our results suggest that the effect of pressure and chemistry on ^{40}K, combined with the opposing effects of high temperatures, will have little, discernible effect on the heat production in the deep Earth as our predicted changes are smaller than the uncertainties in the total decay constant for ^{40}K.

Keywords: electron-capture radioactivity; beta decay; beryllium; sodium; potassium; high pressure

1. Introduction

Radioactive decay plays a central role in planetary science as appropriate decay schemes are used to date geological and astronomical processes at all time and length scales (Dickin, 1995), and radioactivity provides an important source of heat in planetary bodies, both in their early history during accretion and differentiation (Dickin, 1995; Urey, 1955, 1956; Urey and Donn, 1956) and also over geological times (Fowler, 2005). In the Earth, approximately 21 TW (Fowler, 2005) of heat is currently thought to be produced by the decay of four isotopes, ^{40}K, ^{232}Th, ^{235}U and ^{238}U, almost half of the ~44 TW heat measured at the surface (Pollack et al., 1993). Roughly 20% of that heating is estimated to be generated in the crust ($<10^{-7}$ of the Earth's volume), and as much as 8 TW could be produced by ^{40}K decay in the core alone (Lee and Jeanloz, 2003; Lee et al., 2004). Despite the small natural abundance of ^{40}K (~0.01% of total potassium, averaged over the entire Earth: ~100–1000 ppm K (Verhoogen, 1980)) and the other isotopes (~80–100 ppb Th and ~15–25 ppb U averaged over the entire Earth (Fowler, 2005)), they are important in determining the thermal and tectonic evolution of the Earth.

There are two primary decay types: α and β. Many naturally occurring heavy nuclei, including ^{232}Th, ^{235}U and ^{238}U, decay by emission of α-particles (Dickin, 1995). In contrast, β decay isotopes correct a single proton (p) or neutron (n) excess by directly converting a proton into a neutron or a neutron into a proton,

$$\begin{array}{ll} n \rightarrow p + e^- & \beta^- \text{ decay} \\ p \rightarrow n + e^+ & \beta^+ \text{ decay} \\ p + e^- \rightarrow n & \text{electron capture} \end{array} \qquad (1)$$

In the positive and negative β decays, an electron (e^-) or positron (e^+) respectively is produced inside the nucleus and

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Table 1
Electron-capture parent isotopes and daughter isotopes, total half-life values, electron-capture half-life, percent of decay scheme that are electron capture, characteristic gamma ray energies emitted with each decay. Values are from Krane (1988), Dickin (1995) and from additional sources as noted in the table

Parent	Daughter	$\tau_{1/2}$	$\tau_{1/2,\mathrm{ec}}$	Percent EC decay	γ-ray energy (MeV)	Additional references
^{7}Be	^{7}Li	53.3 days	53.3 days	100%	0.478	Norman et al. (2001)
^{22}Na	^{22}Ne	2.6 yr	28 yr	~9.4%, rest β^{+}	1.275	Firestone et al. (1978)
^{40}K	^{40}Ar	1.25 Gyr	10.4 Gyr	~12%, rest β^{-}, β^{+}	1.461	(Norman et al., 2001; Steiger and Jager, 1977)

immediately ejected. Another particle, either a neutrino or anti-neutrino, is also emitted during β decays. The electron-capture decay process occurs when an orbital electron is captured by a proton in the nucleus to form a neutron, neutrino and often a γ-ray (Krane, 1988). Table 1 shows the relative amount of electron-capture decay and respective total half-life $\tau_{1/2,\mathrm{ec}}$ and $\tau_{1/2}$ for investigated isotopes ^{7}Be, ^{22}Na and ^{40}K.

Since radioactive decay is a nuclear process, it is often considered to be insensitive to external factors, such as ionization, temperature, pressure, or chemical environment. This is due to screening provided by the orbital electrons surrounding the nucleus and has been shown to be essentially true for α- and positive and negative β decays (see references within Hahn et al., 1976). However, for electron-capture processes, external forces can influence the stability of an unstable nuclide because the decay rate is directly related to total electron charge density ρ_{e} at the nucleus (Daudel, 1947; Segre, 1947; Emery, 1972). ρ_{e} is affected by the shape of the orbital: only s atomic orbitals, or s-like states in condensed phases, have finite electronic densities at the nucleus. Therefore the electron-capture decay constant, $\lambda_{\mathrm{ec}}\left(=\frac{\ln 2}{\tau_{1/2,\mathrm{ec}}}\right)$, can be influenced by external factors that affect the s-like components of the electronic wave functions such as ionization (Bosch, 1999), temperature (Emery, 1972; Hahn et al., 1976), pressure (Gogarty et al., 1963; Mukoyama and Shimizu, 1974; Bukowinski, 1979a; Liu and Huh, 2000; Tossell, 2002), physical state (Norman et al., 2001) and chemical state (Daudel, 1947; Huh, 1999; Tossell, 2002). Of these, only the effects of chemical and physical (e.g., solid versus aqueous solution) state and pressure have been explored in detail for ^{7}Be, with a few studies on other very short-lived electron-capture isotopes: ^{64}Cu, ^{97}Ru, ^{85}Sr and ^{89}Zr (see references in Hahn et al., 1976).

The change in electron-capture decay constant, $\delta\lambda_{\mathrm{ec}}$ is given by (Bukowinski, 1979a; Tossell, 2002):

$$\delta\lambda_{\mathrm{ec}}=\left[\frac{\rho_{\mathrm{e}}}{\rho_{\mathrm{e,ref}}}-1\right]\lambda_{\mathrm{ec,ref}} \tag{2}$$

where $\lambda_{\mathrm{ec,ref}}$ is the reference decay constant for electron-capture decays and $\rho_{\mathrm{e,ref}}$ is the reference electronic charge density, both at 0 GPa (Table 2).

Here we investigate the effects of pressure and chemistry on the electron-capture portion of the decay constants of ^{7}Be, ^{22}Na and ^{40}K (Table 1) by means of ab-initio computations of the electron charge density ρ_{e} at the nucleus. We add new estimates of $\delta\lambda_{\mathrm{ec}}$ for ^{7}Be, ^{22}Na and ^{40}K as metals, oxides and chlorides and compare to existing estimates of $\delta\lambda_{\mathrm{ec}}$ due to pressure for metallic ^{40}K (Bukowinski, 1979a) and crystalline ^{7}BeO (Hensley et al., 1973). We also compare effects due to the chemical environment on ^{7}Be compounds.

2. Previous work

2.1. ^{7}Be

^{7}Be is naturally produced by cosmic ray bombardment of atmospheric nitrogen and oxygen and decays completely by electron capture to ^{7}Li (Table 1). Once formed, ^{7}Be is removed from the atmosphere and is incorporated into sedimentary material and water. The short half-life, rapid removal from the atmosphere and affinity for sediments make this nuclide useful in determining recent sediment formation. The external environment is expected to have the largest effect on the decay constant of ^{7}Be due to its simple electronic structure that offers little electronic shielding of the nucleus. Experiments indicate

Table 2
The reference total electron charge density $\rho_{\mathrm{e,ref}}$ for metal and simple compound forms of Be, Na and K at zero pressure for this study unless otherwise indicated. The structures used are those stable at zero pressure. R_{MT} values (in Bohr) are kept constant through compression and are 1.23 for beryllium, 1.39 for sodium and 1.96 for potassium compounds. Uncertainties, where available, are given in parentheses

Isotope	Compound	Structure	$\rho_{\mathrm{e,ref}}$ (electrons/Bohr^{3})	Predicted difference in λ_{ec} at 0 GPa from metal form (%)
^{7}Be	Be	hcp	35.3901	
	$BeCl_2$	orth	35.3672	−0.065
	BeO	hcp	35.4017	+0.033
	BeO [a]			+0.091
	BeO [b]			−0.991
	BeO [c]			−0.037 (0.008)
	BeO [d]			−0.030 (0.018)
^{22}Na	Na	bcc	888.388	
	NaCl	fcc	887.970	−0.047
	Na_2O	fcc	888.180	−0.023
^{40}K	K	bcc	5393.79	
	KCl	fcc	5393.14	−0.012
	K_2O	fcc	5393.45	−0.006
	$Fe_{31}K$ [e]	hcp		+0.029

[a] For a model of BeO and with respect to the $\rho_{\mathrm{e,ref}}$ for $Be(OH_2)_4^{2+}$ (Tossell, 2002).

[b] Experimental value for difference between BeO and $Be(OH_2)_4^{2+}$ (Huh, 1999).

[c] Experimental value for difference between BeO and $Be(OH_2)_4^{2+}$ (Johlige et al., 1970).

[d] Experimental value for difference between BeO and Be (Segre and Wiegand, 1949).

[e] These computations used a different R_0 than the other computations, thus the absolute values of $\rho_{\mathrm{e,ref}}$ cannot be directly compared with that listed for K in the bcc structure. Instead, we compare $\rho_{\mathrm{e,ref}}$ (bcc K: 5220.71 e/Bohr^{3}, $Fe_{31}K$: 5222.22 e/Bohr^{3}) for the same value of R_0.

that the decay constant of ^{7}Be changes up to ~1.5% for chemically different compounds, including $Be(OH)_2$, BeO and BeF_2 (Johlige et al., 1970; Mukoyama and Shimizu, 1974; Huh, 1999; Ray et al., 1999; Norman et al., 2001; Tossell, 2002). Additionally, a few studies have also predicted a decrease in half-life of ^{7}Be with the application of pressure (Mukoyama and Shimizu, 1974; Tossell, 2002) and measured up to ~1% decrease in the half-life with the application of a pressure of ~40 GPa (Hensley et al., 1973; Liu and Huh, 2000).

2.2. ^{40}K

^{40}K is of central significance in Earth science as it is the only electron-capture isotope that continues to heat the Earth to any significant degree at present (Fowler, 2005). Additionally, potassium, as an alkali metal, has been shown to undergo a pressure-induced electronic transition whereby the initially unoccupied d-like electronic states are filled (Bukowinski, 1976; Takemura and Syassen, 1983; Lee et al., 2004). Because of the difference in shape between s-like and d-like states, it is likely that this will also influence the decay constant of ^{40}K. For metallic K, the electronic transition occurs at a pressure of ~25–35 GPa, also evidenced by the solid solution formed between potassium and transition metal iron, $Fe_xK_{(1-x)}$, under compression (Lee and Jeanloz, 2003; Lee et al., 2004).

2.3. ^{22}Na

^{22}Na decays primarily by β^+ emission, however approximately 9.4% decays by electron capture (Table 1). We choose to investigate the pressure and chemical effects on sodium as it is an alkali metal like potassium with similar electronic structure also predicted to undergo an s→d electronic transition at high pressure (Young, 1991). With its short half-life and commercially available isotope-enriched samples, our predictions can be tested with experiments directly and will serve as a test to the success of our predictions for longer-lived isotopes such as ^{40}K.

3. Methods

In order to accurately model the electronic charge density ρ_e with density-functional theory (DFT) we employ state-of-the-art all-electron first-principles computations. We use the linearized augmented plane wave (LAPW) method as implemented in the Wien2k package (Blaha et al., 2001; Schwarz and Blaha, 2003) with a spherical harmonic basis set around the nuclei in the muffin tin sphere (with a radius R_{MT}), providing an atomic-orbital-like description of the charge density near the nuclei. In order to minimize changes due to the basis set expansion we keep R_{MT} constant for a given atomic system (all crystals based on Be, Na, and K, respectively); R_{MT} in each system is chosen as one-half of the shortest nearest-neighbor distance investigated of the respective atomic system, which in all cases is the oxide at the highest compression considered (see Table 2 for R_{MT} values). As a test, we have also tried varying the R_{MT} within an atomic system and find that although the absolute values of ρ_e differ, the relative changes are negligible (see online Supplementary material). The electron charge density at the nucleus ρ_e is also influenced by the value of the first radial mesh point (R_0) at which the electron charge density is computed. Here we use $R_0 = 1\times10^{-5}$ Bohr. Although we find that the absolute values of ρ_e increase when varying R_0 from 5×10^{-4} to 10^{-6} Bohr, relative changes of ρ_e within a system are negligible. The size of the basis set was set by $R_{MT}*K_{max}=9.0$ for all Na and K compounds; for the Be system $R_{MT}*K_{max}$ was set to 7.0. Reciprocal space sampling for body-centered cubic (bcc), face-centered cubic (fcc), simple cubic (sc) and orthorhombic (orth) structures, was performed with a $16\times16\times16$ *k*-point mesh, while for hexagonal-close packed (hcp) structure, a $16\times16\times9$ mesh was used. With this choice of $R_{MT}*K_{max}$ and *k*-point sampling total energies are converged to better than 1 meV/atom and ρ_e at the nucleus to less than 10^{-3} e^-/Bohr^3. The electron density convergence corresponds to differences in a respective ρ_e of less than 1 part in 10^5 for Be, 1 part in 10^6 for Na and 1 part in 10^7 for K.

We have used both the generalized-gradient (Perdew et al., 1996) and local-density approximations (Perdew and Wang, 1992) (GGA and LDA respectively) to determine ρ_e and find that although the absolute charge densities are different, the relative differences used to determine $\delta\lambda_{ec}$ are small: less than 1/10 of the total difference. Because the differences between GGA and LDA are small, we present only our GGA results.

We have calculated the total electron charge density ρ_e of pure metals Be, Na and K; oxides BeO, Na_2O and K_2O; and chlorides $BeCl_2$, NaCl and KCl in low- and high-pressure crystal structures where known (Tables 3 and 4). In order to accurately and efficiently determine atomic positions and cell shape in structures with internal and external degrees of freedom, we relaxed in the structures at constant volume with the Vienna Ab-initio Simulation Package (VASP) (Kresse and Hafner, 1993; Kresse and Furthmuller, 1996), using the projector-augmented plane wave method (Blochl, 1994; Kresse and Joubert, 1999). The resulting structures and atom positions

Table 3
Metals and simple compounds with Be, Na and K chemistry investigated. Isotope and compounds are listed along with possible structure types and the predicted change in λ_{ec} at 25 GPa. Structure types investigated are listed and include simple cubic (sc), body-centered cubic (bcc), face-centered cubic (fcc), orthorhombic (orth) and hexagonal-close packed (hcp). The computed stable structure of those investigated at 25 GPa is given in bold face

Isotope	Compound	Structure	Predicted change in λ_{ec} at 25 GPa (%)
^{7}Be	Be	**hcp**, fcc, bcc	+0.1
	$BeCl_2$	**orth**	+0.2
	BeO	**hcp**	+0.1
^{22}Na	Na	**bcc**, fcc, hcp	+0.06
	NaCl	**fcc**, sc	+0.02
	Na_2O	**fcc**	+0.015
^{40}K	K	bcc, **fcc**	+0.025
	KCl	fcc, **sc**	+0.004
	K_2O	**fcc**	+0.004

Table 4
Equation of state parameters for Be, Na and K metals, oxides and chlorides determined by Wien2k using GGA for this study, unless explicitly stated otherwise. Uncertainties, when available, are given in parentheses

	Compound	Structure	V_0 (Å^3)	K_0 (GPa)	K'_0
^{7}Be	Be, this study	hcp	15.7 (0.1)	123 (2.3)	3.5 (0.1)
	Be, experiment (Evans et al., 2005)	hcp	NG [a]	109.88 (1.05)	3.584 (0.027)
	Be, theory (Sinko and Smirnov, 2005)	hcp	15.84	122	3.3
	$BeCl_2$, this study	orth	338.4 (4.3)	1.1 (0.2)	11.2 (1.2)
	BeO, this study	hcp	28.16 (0.04)	207.6 (0.4)	3.8 (0.1)
	BeO, experiment (Mori et al., 2004)	hcp	NG [a]	223 (4)	4.0 [b]
	BeO, theory (Milman and Warren, 2001)	hcp	27.7	206 (1)	3.3 (0.1)
^{22}Na	Na, this study	bcc	36.4 (0.5)	8.4 (0.7)	3.8 (0.1)
	Na, experiment [c], (Hanfland et al., 2002)	bcc	39.5 [d]	6.31 (0.08)	3.886 (0.020)
	Na, theory (Hanfland et al., 2002)	bcc	37.7 (0.2)	6.81 (0.16)	3.93 (0.01)
	Na, this study	fcc	36.6 (0.4)	8.1 (0.8)	3.8 (0.1)
	Na, experiment [c], (Hanfland et al., 2002)	fcc	39.5 [d]	6.433 (0.030)	3.83 (0.08)
	Na, theory (Hanfland et al., 2002)	fcc	37.7 (0.2)	6.85 (0.18)	3.92 (0.01)
	NaCl, this study	fcc	46.4 (0.1)	23.3 (0.2)	4.6 (0.1)
	NaCl, experiment (Sato-Sorensen, 1983)	fcc	44.9 (0.1)	23.8 (7.5)	4.0 (3.9)
	NaCl, this study	sc	43.3 (0.1)	26.5 (0.2)	4.4 (0.1)
	NaCl, experiment (Heinz and Jeanloz, 1984)	sc	41.67 [e]	36.2 (4.2)	4 [b]
	Na_2O, this study	fcc	43.29 (0.16)	50.8 (1.0)	4.1 (0.1)
^{40}K	K, this study	bcc	74.2 (1.4)	3.7 (0.5)	3.7 (0.2)
	K, experiment (Winzenick et al., 1994)	bcc	75.64 [f]	2.963 (0.001)	4.06 (0.19)
	K, experiment (Liu, 1986)	bcc	75.64 [f]	2.99 (0.02)	4.15 (0.10)
	K, this study	fcc	72.7 (0.7)	4.2 (0.2)	3.5 (0.1)
	K, experiment (Winzenick et al., 1994)	fcc	71.0 (1.6)	4.2 (0.5)	3.6 (0.3)
	KCl, this study	fcc	66.5 (0.3)	11.3 (1.4)	7.3 (1.2)
	KCl, theory (Froyen and Cohen, 1986)	fcc	62.5 (0.3)	24.8 (2.5)	4.0 [b]
	KCl, this study	sc	56.0 (0.2)	22.2 (0.4)	4.3 (0.1)
	KCl, theory (Froyen and Cohen, 1986)	sc	62.5 [g] (0.3)	22.6 (2.3)	4.0 [b]
	K_2O, this study	fcc	67.9 (0.1)	28.4 (0.3)	4.2 (0.1)

[a] NG = not given.
[b] K'_0 held constant.
[c] H02 equation of state function (Holzapfel, 1991).
[d] V_0 from Barrett (1956).
[e] V_0 determined from $V_{02}/V_{01}=0.929$ as given in Heinz and Jeanloz (1984) with $V_{01}=44.86$ Å^3.
[f] V_0 from Anderson and Swenson (1983).
[g] V_0 calculated from low-pressure phase.

were then used in the charge density computation by the LAPW method as outlined above. While the different representations in the electronic wave function in Wien2k and VASP can potentially lead to different optimized structures, the VASP structures used in Wien2k typically lead to small forces (<1 mRy/Bohr) on the atoms. Furthermore, the resulting equations of state from both VASP and Wien2k are in agreement with one another and experiments (Table 4). As all of the metal, oxide and chloride forms of potassium and sodium investigated are high-symmetry structures, there are no degrees of freedom to be relaxed.

To evaluate chemical environment effects, we compare zero pressure ρ_e between pure metals and simple compounds (Table 2). We have also determined the percent change in the electron-capture decay constant λ_{ec} as a function of pressure (Eq. (2), Table 3): once the total electron charge density ρ_e was calculated at several volumes, a 4th-order polynomial was fit to the volume range of interest and used to generate the $\delta\lambda_{ec}$ at pressure using Eq. (2) and a Birch–Murnaghan equation of state fit to the calculated energies (Birch, 1952) (Table 4).

4. Computational results

4.1. Chemical effects at zero pressure

The chemical environment has been suggested to have a large effect on electron-capture isotope ^{7}Be (Daudel, 1947; Emery, 1972; Hahn et al., 1976; Ray et al., 1999; Tossell, 2002). To estimate the effects of chemistry alone, we list the reference electron charge densities at zero pressure ($\rho_{e,ref}$) for the metals and compounds investigated in Table 2. We find the effect is small: less than 0.1% change in λ_{ec} for both oxides and chlorides, with chlorides showing slightly more of an effect than the oxides.

It has been observed (Johlige et al., 1970) that the decay constant for ^{7}Be in different compounds behaves as follows: λ [Be(OH$_2$)$_4^{2+}$]$>\lambda$ [Be]$>\lambda$ [BeO]$>\lambda$ [BeF$_2$]. We find the order: λ_{ec} [BeO]$\geq\lambda_{ec}$ [Be]$>\lambda_{ec}$ [BeCl$_2$], where the difference between Be and BeO is approximately 0.03% (Table 2). While the order is somewhat different from the experiments, it is consistent with previous density-functional based

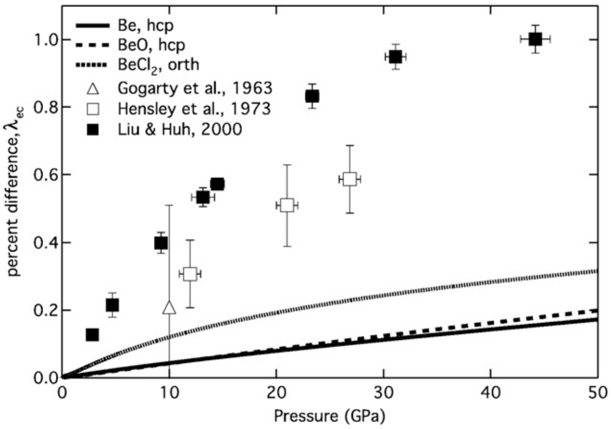

Fig. 1. Percent change λ_{ec} for hcp Be (solid line), BeO (dashed line) and BeCl$_2$ (dotted line). An increase in the decay constant λ_{ec} corresponds to a decrease in the half-life $\tau_{1/2,ec}$. Each percent difference in λ_{ec} is referenced from the zero pressure $\lambda_{ec,0}$ for either Be, BeO or BeCl$_2$ respectively. To compare, experimental determination of the change in λ_{ec} is shown for BeCO$_3$·Be(OH)$_2$ (open triangles, (Gogarty et al., 1963)), BeO (open squares, (Hensley et al., 1973)) and Be(OH)$_2$ (filled squares, (Liu and Huh, 2000)).

computations (Tossell, 2002) and may hint at experimental uncertainties. Alternatively, methods beyond DFT may also be necessary (Miyake et al., 2002) to capture the electron density completely, which we discuss in detail in Section 5 below.

The alkali-metal oxides and chlorides investigated show a negative change in ρ_{ec}, corresponding to an increase in the respective electron-capture half-lives $\tau_{1/2,ec}$ when compared to their pure metal counterparts (Table 2). In addition, we have looked at the metallic bonding between Fe–K alloys (Lee et al., 2004) and find the opposite relation at zero pressure: there is a positive change in ρ_{ec} when compared to metallic K (Table 2).

4.2. *Pressure effects*

4.2.1. *^{7}Be*

We find that Be remains stable in the hcp structure relative to other possible candidate structures such as bcc, fcc and orthorhombic for all volumes investigated, in good agreement with recent experiments of Be to near 200 GPa (Nakano et al., 2002; Evans et al., 2005) as well as a recent ab-initio study (Sinko and Smirnov, 2005). Thus for this study we only compute ρ_e for the hcp structure. We have used the hexagonal-close packed structure of BeO as this has been shown both experimentally (Mori et al., 2004) and through computations (Milman and Warren, 2001) to be the stable structure to more than 100 GPa. We find good agreement of our equations of state of Be and BeO with previous studies (Table 4). For BeCl$_2$, we calculate an equation of state assuming no pressure-induced phase transitions and using the orthorhombic structure determined by Troyanov (2000) (Table 4). This may not be a good assumption as BeCl$_2$ shows at least 4 phase transitions for temperatures between 13 and 750 K (McDonald and Oetting, 1965). However, to our knowledge, there is no experimental evidence of structural changes with pressure.

Metallic Be and BeO show an 0.2% increase in λ_{ec}, corresponding to a 0.2% decrease in the $\tau_{1/2,ec}$ at 50 GPa, both in their high-pressure hcp structures (Fig. 1). For BeCl$_2$ we predict an ~0.3% increase in λ_{ec} at 50 GPa. Although predicted changes are small, they are measurable. In comparison to experimental measurements (Hensley et al., 1973), our values for BeO are smaller by a factor of 3–6. We discuss possibilities for this discrepancy in Section 5.

4.2.2. *^{40}K*

The electron-capture decay constant λ_{ec} for ^{40}K increases with pressure up to ~25 GPa for pure K in bcc and fcc structures, the first two phases of K (U. Schwarz et al., 1999; Winzenick et al., 1994), and up to ~50 GPa for the oxide and chloride (Fig. 2). Above ~25 GPa, potassium's 4 s electron becomes 3d-like, thus changing the total electron density at the nucleus (Fig. 3). Until recently (McMahon et al., 2006), the structure of metallic K above ~25 GPa was not well known (Winzenick et al., 1994; Schwarz et al., 1999), thus limiting our ability to investigate K in the appropriate structure at much higher pressures. However we have extended the compression range for K in the fcc structure as we believe that the crystal structure will not make a large difference as is evident from a comparison of charge density in the bcc and fcc structures at low pressure (Figs. 2 and 3). The agreement between our predictions and those of a previous study on bcc K (Bukowinski, 1976; Bukowinski, 1979b) is excellent throughout the entire compression range for pure K in both bcc and fcc structures (Fig. 3). This is not unexpected as the methods used are comparable. Fig. 3 shows the total electron charge density versus volume (or compression) and reveals an inflection in the charge density above ~25 GPa (V_0/V~3), as expected for the s→d electronic transition. Upon further compression, the total electron charge density drops to below the reference charge density $\rho_{e,ref}$ at a volume of ~14 Å^3 (V_0/V~5) before

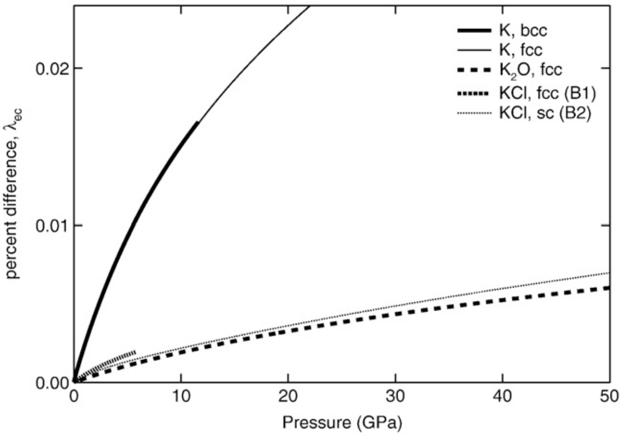

Fig. 2. Percent change in electron-capture decay constant λ_{ec} versus pressure for K (bcc: thick solid line; fcc: thin solid line), K$_2$O (thick dashed line) and KCl (fcc (B1): thick dotted line; sc (B2): thin dotted line). The changes for bcc and fcc K are similar as expected due to their nearly identical equations of state (Table 3). Each percent difference in λ_{ec} is referenced from the zero pressure $\lambda_{ec,0}$ for either K, K$_2$O or KCl respectively.

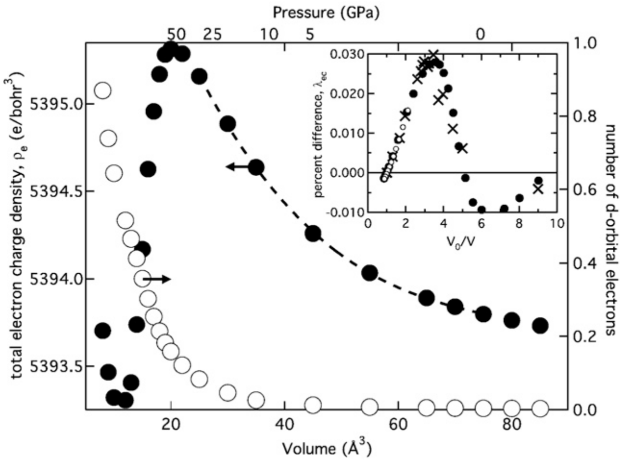

Fig. 3. Total electron density ρ_e versus volume (or corresponding pressure) for fcc K (solid circles). A 4th-order polynomial fit (dashed line) to ρ_e is shown for volumes between 25 and 75 Å^3. For volumes less than 20 Å^3, ρ_e decreases after a steady increase as expected for the pressure-induced s→d electronic transition, but then begins to increase for volumes less than 10 Å^3. Along the right axis we plot the number of d-orbital electrons (open circles) whose values go from 0 to 1 at high compression. **Inset.** Percent change in electron-capture decay constant λ_{ec} versus V_0/V for K (bcc: small open circles; fcc: large filled circles). The changes are nearly identical for bcc and fcc K as expected due to their nearly identical equations of state (Table 3). Each percent difference in λ_{ec} is referenced from the zero pressure $\lambda_{ec,0}$ for either bcc or fcc K. Earlier predictions of the percent change in λ_{ec} (Bukowinski, 1979a) are plotted as crosses.

increasing again at volumes less than 10 Å^3 (V_0/V~7). This second increase of charge density at nucleus at volumes less than 10 Å^3 can be explained by the two related effects: (1) increased band dispersion under high compression will lead to hybridization and electrons in addition to the ones in s-orbitals and will thus contribute to increased charge density at the nucleus; and (2) as a consequence the association of charge with atomic-type orbitals looses its validity at extreme compression, and the charge density analysis for orbital type should be seen as a mathematical construct in terms of spherical harmonics.

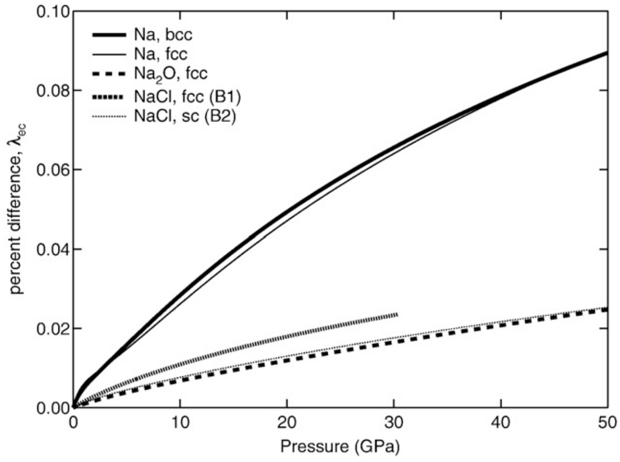

Fig. 4. Percent change in electron-capture decay constant λ_{ec} for bcc Na (bcc: thick solid line; fcc: thin solid line), Na_2O (thick dashed line) and NaCl (fcc (B1): thick dotted line; sc (B2): thin dotted line). The changes for bcc and fcc Na are similar as expected due to their nearly identical equations of state (Table 3). Each percent difference in λ_{ec} is referenced from the zero pressure $\lambda_{ec,0}$ for either Na, Na_2O or NaCl respectively.

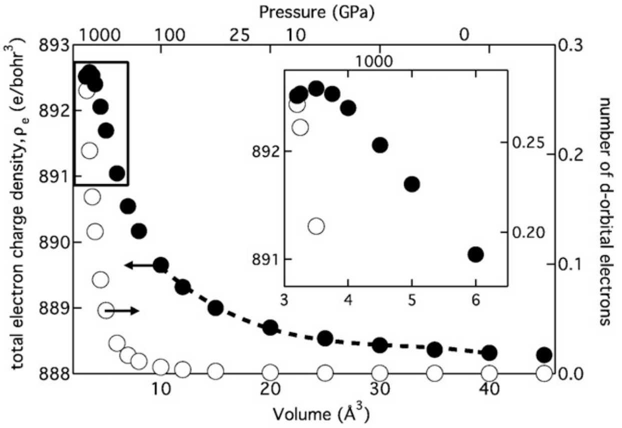

Fig. 5. Total electron density ρ_e versus volume (or corresponding pressure) for fcc Na (solid circles). A 4th-order polynomial fit (dashed line) to ρ_e is shown for volumes between 10 and 40 Å^3. Along the right axis we plot the number of d-orbital electrons (open circles). **Inset.** Enlarged outlined-boxed region shows the turnaround in the electron charge density at high compression. For volumes less than 3.5 Å^3, ρ_e decreases after a steady increase as expected for the pressure-induced s→d electronic transition.

4.2.3. ^{22}Na

Fig. 4 shows that, like potassium, the low- and high-pressure structures of sodium behave similarly, confirming that ^{22}Na may consequently be used as an analog for ^{40}K. We predict an increase of ~0.1% in the electron-capture decay constant λ_{ec} of ^{22}Na at 50 GPa as a pure metal. Like the potassium compounds, NaCl and Na_2O show a smaller pressure effect than the metallic form of Na by a factor of ~4–5. As expected, we also find that Na undergoes a turnover in the total electron charge density, corresponding to the s→d electron transition. However, this occurs at much higher compression (V_0/V~10, Fig. 5).

5. Discussion

Our results show that the pressure effect for ^{40}K, combined with the opposing effects of high temperatures, will have little discernible effect on the heat production in the Earth as the predicted changes are smaller than the experimental uncertainties (Beckinsale and Gale, 1969; Steiger and Jager, 1977) in the total decay constant for ^{40}K, in agreement with previous results (Bukowinski, 1979a). The uncertainty in the total decay constant λ is less than 1% and although much of this uncertainty stems from different measurement techniques (Beckinsale and Gale, 1969; Steiger and Jager, 1977), some of the spread may also be due to the variety of samples (hence varying chemistry) used in the measurements. The predicted chemical effects on λ_{ec} may contribute to the total decay constant uncertainties. A recent experimental study (Norman et al., 2001) investigated the influence of the physical (solid versus solution) and chemical environment and also found no change in the decay constant to within their measurement precision of ~1%. Our results support these studies.

There have been two previous theoretical studies on how pressure effects the change in decay constant of ^{7}Be; one based on a simple model for Be metal (Mukoyama and Shimizu, 1974) and a prediction based on the electronic charge density for $Be(OH)_4^{2-}$ structural groups (Tossell, 2002). Qualitatively these studies agree with the experimental results better than our results. However, the first model (Mukoyama and Shimizu, 1974) is based on the energy of the neutrino emitted during electron-capture decay and the atomic number (Z) of the isotope. Although this model seems to agree well with experimental data (Gogarty et al., 1963; Hensley et al., 1973; Liu and Huh, 2000), this may be fortuitous as it is not a good model for ^{131}Ba which is also tested. The second model (Tossell, 2002) does not specifically look at pressure effects, but rather compares volumes based on varying Be–O distances in $Be(OH)_4^{2-}$ as a proxy for pressure changes observed in experiments on $Be(OH)_2$ gel (Liu and Huh, 2000). Additionally, an appropriate equation of state is not used to determine pressure of these volumes, but rather a third-order polynomial fit. The discrepancies between the two most recent experiments on ^{7}Be decay under pressure as well as the discrepancies between recent computations (Tossell, 2002) and this study may also stem from the physical state of the materials investigated. For instance, crystalline BeO, as evidenced by X-ray diffraction, was used by Hensley et al. (1973), whereas a $Be(OH)_2$ gel, which remained amorphous under pressure, was used in the most recent experiment (Liu and Huh, 2000). The experiments using crystalline samples predict a smaller change in λ_{ec} with pressure than those using samples that remained amorphous. We use a crystalline approach for our computations: we employ periodic boundary conditions to mimic crystal structures, rather than the method used by Tossell (2002) where atomic clusters were used. The failure to reproduce large differences in electron charge density at the nucleus, thus large $\delta\lambda_{ec}$, as measured in the most recent experiments (Huh, 1999) between various chemical forms of Be, may also be due to different reference decay constants that are used: Be versus $Be(OH_2)_4^{2+}$.

At first glance, our results suggest that our methods cannot reproduce experimental measurements. If the most recent experiments investigating chemical environment changes which find large differences (up to ~1.5%) in the decay constant of ^{7}Be are correct, this hints at a fundamental problem of solid-state band structure computations, either within DFT itself, the basis set used, or the periodic boundary conditions applied. Here we have chosen a highly accurate method with a local basis set that is atomic orbital-like around the nuclei (within the R_{MT}) making the second possibility unlikely. We have also tested adjusting the values of R_{MT} and R_0, as well as the choice for the exchange and correlation potential (GGA versus LDA) and find that although absolute electron charge density values are different, the relative differences are small: less than 1 order of magnitude and up to 3 orders of magnitude smaller than the effect on the total charge density (see online Supplementary material). This, and general good agreement with previous computational studies (Bukowinski, 1979a; Tossell, 2002), gives us confidence that our predictions are accurate within the framework of DFT. This confidence is further supported by the fact that DFT can be used successfully in charge density analysis-based properties, such as valence analysis (Kirfel et al., 2005) or electrical field gradient (Bastow, 2002; Bastow et al., 2002), for a wide range of materials. However, two features in DFT may limit its use in the current context: (1) DFT is a ground state theory, representing excited electronic states incorrectly. This may contribute to the charge density at the nucleus, in particular for the metals where no band gap exists. (2) The approximations to exchange and – in particular – correlation may severely misrepresent screening in the systems considered (Osterfeld, 1992; Miyake et al., 2002). Computations beyond DFT using, for example, time-dependent DFT or the GW approximation for excited states (Aulbur et al., 2000) and the random phase approximation (RPA) (Osterfeld, 1992; Miyake et al., 2002) to account for dynamical screening should perhaps be used to further investigate the charge density at the nucleus.

Alternatively, our predictions may hint at the unreliability of the experimental measurements. To determine which of these possibilities are more likely, more advanced computations and additional experiments need to be performed on other isotopic systems and compounds.

6. Conclusions

With standard density-functional theory for crystalline materials using a local atomic-like basis set, we find that pressure and chemical state have a small effect on the decay constants of electron-capture isotopes ^{7}Be, ^{22}Na and ^{40}K. Here we have provided additional predictions on metallic, oxide and chloride forms of measurable isotopes: ^{7}Be and ^{22}Na and, although the effects predicted are small, they are potentially measurable with isotopically-enriched samples. As sodium has an electronic structure similar to that of potassium, ^{22}Na may be a good proxy to understanding how pressure, chemical environment as well as other external parameters affect much longer-lived ^{40}K, although this effect is expected to be small.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2007.12.014.

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