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^{11}B NMR in the layered diborides OsB_2 and RuB_2

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^{11}B nuclear magnetic resonance (NMR) measurements have been performed on ^{11}B enriched OsB_2 and RuB_2 polycrystalline powder samples in an external field of 4.7 T and in the temperature range, $4.2\ \mathrm{K} < T < 300\ \mathrm{K}$. The spectra for both samples show similar quadrupole powder patterns that are typical for a nonaxial symmetry. The Knight shifts K in both samples are very small and constant in temperature. The nuclear spin-lattice relaxation rate T_1^{-1} follows a Korringa law in the whole temperature range investigated with $T_1T = 600$ and 680 sK for OsB_2 and RuB_2, respectively. The experimental results indicate that a p character dominates the conduction electron wave function at the B site with a negligibly small s character in both compounds.

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I. INTRODUCTION

Right after the discovery of superconductivity in MgB_2 at a high temperature $T_c = 39$ K,[1] a number of subsequent experiments,[2,3] in particular, isotope effects measurements[4,5] confirmed that MgB_2 belongs to the conventional BCS superconductor. Theoretical studies using band structure calculations also found that in MgB_2, the Fermi level (E_F) is located at the shoulder of the density of states (DOS) curve in which B $2p$ states are dominant.[6–8] It seems to be generally accepted that the B $2p$ band plays a crucial role for the high T_c in MgB_2. On the other hand, many structurally-related metal diborides TB_2 (T=Ti,Zr,Hf,V,Cr,Nb,Ta,Mo) have been studied,[9–13] some of which had already been studied in the past,[14] but the role of the B $2p$ band for the superconductivity in other metal diborides TB_2 is not clearly understood yet.

There is also an interesting metal-diboride family, OsB_2 and RuB_2, which crystallize in an orthorhombic structure (*Pmmn*) containing deformed boron sheets instead of a planar boron array as in the hexagonal MgB_2. They have been known to be superconductors with $T_c = 2.1$ K for OsB_2 and 1.6 K for RuB_2 since 1975,[15] but other physical properties besides T_c have not been reported until the recent studies related to their unusually high bulk modulus.[16–18]

Note that the difference between T_c's for two compounds, $\delta T_c = 0.5$ K, which is 24% of $T_c = 2.1$ K of OsB_2, is sufficiently large but no noticeable difference between the properties related to the superconductivity has been reported yet. OsB_2 and RuB_2 are isostructural, where the difference between the lattice constants is less than 1%.[19,20] Band structure calculations suggest that the relevant DOS's at the Fermi level are even identical for both compounds as summarized in Table I.[17] From a recent comprehensive study by some of us, no considerable difference between their thermodynamic properties was observed except for the Debye temperatures, $\Theta_D = 550$ K for OsB_2 and $\Theta_D = 701$ K for RuB_2, which are consistent with their relative molar masses but are not helpful to explain the higher T_c in OsB_2.[20]

Nuclear magnetic resonance (NMR) is a microscopic tool to investigate the electronic structure in a nonmagnetic metal. The NMR parameters, the Knight shift (K) and the nuclear spin-lattice relaxation rate (T_1^{-1}) are related to the partial DOS's at the site of probing nuclei. As demonstrated from a number of ^{11}B NMR studies in MgB_2 and related materials, ^{11}B NMR is a suitable probe of the B s and/or B p states selectively in metal diborides.[21–24] We have applied ^{11}B NMR to investigate the structural and electronic properties of OsB_2 and RuB_2. The experimental results for the spectra, Knight shifts, and relaxation rates in the two compounds have been compared and discussed in relation to the local structure or to the partial DOS's at the B site.

II. EXPERIMENTAL

^{11}B enriched polycrystalline samples of OsB_2 and RuB_2 were prepared by arc-melting using ultrahigh purity Os (99.995%, Sigma Aldrich), Ru (99.995%, MV labs), and ^{11}B (99.999%, Eagle Pitcher). Details for the preparation, and the structural and thermodynamic properties of OsB_2 and RuB_2 are described elsewhere.[20] ^{11}B (nuclear spin $I = 3/2$) NMR and relaxation measurements were carried on the powdered samples with a standard Fourier transform (FT) pulse NMR spectrometer in the temperature range $4.2\ \mathrm{K} < T < 294$ K and in an external magnetic field $H = 4.7$ T corresponding to the Larmor frequency $\nu_L = 64.17837$ MHz for ^{11}B in a $NaBH_4$ aqueous solution. The $\pi/2$ radio frequency (rf) pulse

TABLE I. Summary of various information on OsB_2 and RuB_2. The densities of states N at the Fermi level (E_F) are theoretically calculated values in units of states/(eV f.u.) for the total $N(E_F)$ (both spin directions) and of states/(eV B atom) for the partial s- and p-type densities of states, respectively, where "f.u." means formula unit.

	OsB_2	RuB_2	Reference
T_c in K	2.1	1.6	15 and 20
Θ_D in K	550	701	20
$N(E_F)$	0.551	0.548	17
$N_{Bs}(E_F)$	0.007	0.006	17
$N_{Bp}(E_F)$	0.098	0.097	17

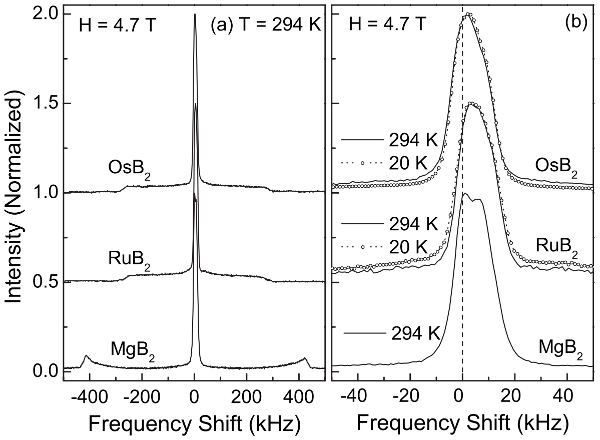

FIG. 1. ^{11}B ($I=3/2$) NMR spectra in ^{11}B enriched OsB$_2$ and RuB$_2$ powder samples at $H=4.7$ T corresponding to $\nu_L=64.178\,37$ MHz: (a) The whole spectra at room temperature and (b) the central line transition at two representative temperatures. The spectrum for MgB$_2$ is also plotted for comparison (Ref. 25).

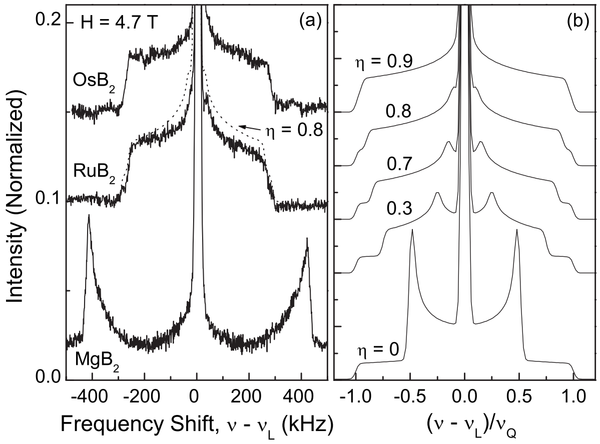

FIG. 2. Comparison of the ^{11}B ($I=3/2$) NMR spectra in OsB$_2$ and RuB$_2$ with theoretical simulations: (a) The experimental results and (b) the theoretical simulations for $I=3/2$ and several representative values of the asymmetry parameter η with a line broadening $\delta\nu/\nu_Q=0.03$. Data for MgB$_2$ are shown in (a) for comparison.

length was typically 2.4 μs. The ^{11}B spectrum was obtained from the Fourier transform of half of the echo following a $(\pi/2)_0-(\pi/2)_{90}$ pulse sequence. In order to cover the whole spectrum, separate spectra were recorded at every 100 kHz in the frequency range $-400 \leqslant \nu-\nu_L \leqslant 400$ kHz and added together. The ^{11}B T_1^{-1} was measured by monitoring the recovery of the nuclear magnetization following a long sequence of saturating rf pulses. Following this sequence, the entire spectrum becomes saturated, and the recovery of the nuclear magnetization was observed to be exponential in the whole temperature investigated.

III. RESULTS AND DISCUSSION

Figure 1 shows representative spectra for OsB$_2$ and RuB$_2$, consisting of a central line and a broad background with steps at $\nu-\nu_L \approx \pm 285$ kHz. The spectra for both compounds are quite similar to each other except for the small relative shift of the central line transition, which will be discussed later. Since the background is of quadrupolar origin and, hence, sensitive to the local symmetry including the local charge distribution at the site of probing nuclei, the observation of nearly identical spectra for both compounds is consistent with their isostructural nature.

On the other hand, the spectra [see the enlarged plots in Fig. 2(a)] are quite different from the one for hexagonal MgB$_2$ that shows two singularities of the distribution of satellite transitions typical for $I=3/2$ with an uniaxial symmetry.[25,26] The rounded quadrupolar background indicates that the local symmetry at the B site in OsB$_2$ and RuB$_2$ is far from being uniaxial,[26] reflecting the low point symmetry (the m symmetry with a mirror in the ac-plane) of the B sites which occupy the 4f Wyckoff sites in the orthorhombic lattice ($Pmmn$).[18] Compared with theoretical simulations of the NMR spectrum for $I=3/2$ with a nonaxial symmetry as shown in Fig. 2(b), the observed spectra for both compounds correspond to the ones with the asymmetry parameter $\eta \equiv |V_{xx}-V_{yy}|/|V_{zz}|=0.8-0.9$. Moreover, for such a large value of η, the rounded edge of the quadrupolar background roughly corresponds to the quadupole frequency ν_Q as can be seen from the simulations in Fig. 2(b). Thus, we estimate $\nu_Q=285\pm10$ kHz for both compounds, which is much smaller than $\nu_Q=835$ kHz for MgB$_2$.

As shown separately in Fig. 1(b), the central line transition is observed to be asymmetric and quite broad with a linewidth $\delta\nu \simeq 14$ kHz [FWHM (full width at half maximum)] and to be constant in temperature for both OsB$_2$ and RuB$_2$. In the presence of the second order quadrupole effects, the separation between the two singularities in the central line is given by[26]

$$\Delta\nu = \frac{\nu_Q^2}{48\nu_L}\left[I(I+1)-\frac{3}{4}\right](\eta^2+22\eta+25). \qquad (1)$$

Using $I=3/2$, $\nu_L=64.178\,37$ MHz, $\nu_Q \simeq 285$ kHz, and $\eta \approx 0.9$, we obtain $\Delta\nu \approx 1.2$ kHz, which is too small to explain the observed linewidth, $\delta\nu \simeq 14$ kHz. Such a broad central line cannot be explained by the quadrupole effects. As compared in Fig. 1(b), the anomalously broad line (with a split structure) has also been observed in MgB$_2$[21,24,25] and explained excellently by dipolar doublets from systematic measurements at various external fields.[24] From the calculation of the second moment $\langle\Delta\omega^2\rangle$ for the ^{11}B enriched OsB$_2$ using the lattice parameters in Ref. 20, we obtained $\langle\Delta\omega^2\rangle \simeq 1800$ (rad^2 kHz^2), which corresponds to $\Delta\nu \simeq 15$ kHz for a Gaussian line shape. Thus we conclude that the broad and temperature-independent linewidth in OsB$_2$ and RuB$_2$ is also dominated by the dipole-dipole interaction between ^{11}B nuclei similarly to the MgB$_2$ case. The rather rounded and asymmetric shape of the central line without the split structure seems to be related to the anisotropic dipole interaction and/or to the nonaxial symmetry in OsB$_2$ and RuB$_2$. We note that the dipolar interaction is very sensitive to the B-B distance, d, between the nearest neighbors.[24] Therefore, the ob-

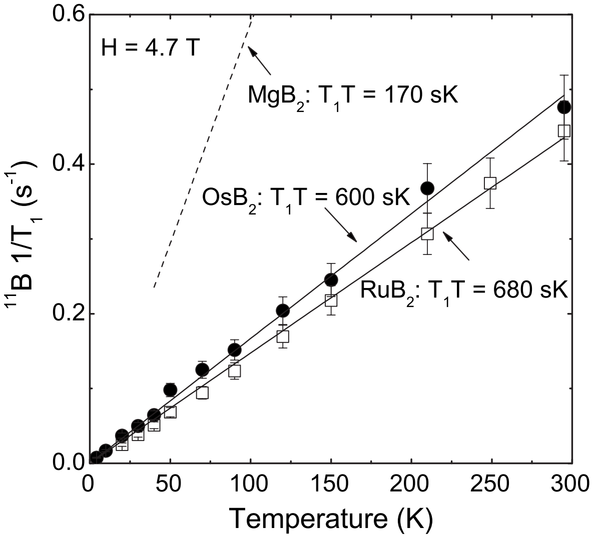

FIG. 3. Temperature dependence of the ^{11}B nuclear spin-lattice relaxation rate T_1^{-1} in OsB$_2$ and RuB$_2$ powder samples. The solid lines are fits to the Korringa relation T_1T=const. The dashed line represents the results for MgB$_2$ from Ref. 24.

servation of the nearly identical linewidth, which implies that d in both compounds is qualitatively similar to each other, is also consistent with their isostructural nature.

Since the central line is asymmetric, the position of the center of gravity $\nu_{\rm cg}$ instead of the peak position was used to determine the Knight shift K. Thus, the K values obtained here represent the isotropic Knight shift. From the central part with the intensity (normalized with respect to the maximum value) higher than 0.05 which is chosen to exclude the background contribution, we obtain $\nu_{\rm cg}-\nu_{\rm L}\approx 3$ kHz and ≈ 5 kHz, yielding $K\equiv(\nu_{\rm cg}-\nu_{\rm L})/\nu_{\rm L}\approx 50$ ppm for OsB$_2$ and $K\approx 80$ ppm for RuB$_2$ with respect to a NaBH$_4$ aqueous solution. If the Knight shift is referred to the BF$_3$ solution that is used as the "zero chemical shift,"[27] we obtain $K\approx 10$ ppm for OsB$_2$ and $K\approx 40$ ppm for RuB$_2$. The small and temperature-independent K indicates that the s-component of the wave function at the B site at the Fermi level is negligibly small in both compounds,[26] which is in good agreement with the theoretical calculations summarized in Table I (Ref. 17) and similar to the situation of MgB$_2$.[23,24]

We turn now to the behavior of the ^{11}B nuclear spin-lattice relaxation rate, T_1^{-1}. As mentioned earlier, with a sufficiently long sequence of saturating rf pulses, the recovery of the nuclear magnetization was observed to be exponential. This is ascribed to the relatively narrow quadrupolar background in OsB$_2$ and RuB$_2$. The experimental results of ^{11}B T_1^{-1} obtained by fitting the recovery data to a single exponential function are shown in Fig. 3. The ^{11}B T_1^{-1} follows a linear temperature dependence, the so-called Korringa law, with $T_1T=600\pm 30$ sK for OsB$_2$ and 680 ± 35 sK for RuB$_2$ in the whole temperature range investigated. Using the values for the isotropic Knight shift K and the value $S=2.57\times 10^{-6}$ sK for ^{11}B $[S\equiv(\gamma_e/\gamma_n)^2(h/8\pi^2k_B)$, and γ_e and γ_n are the gyromagnetic ratios for electron and nucleus, respectively], we obtain the Korringa ratio, $R\equiv K^2T_1T/S\approx 0.02$ and ≈ 0.4 for OsB$_2$ and for RuB$_2$, respectively. Note that the Korringa ratio for both compounds is much smaller than the ideal value of unity for the case where the contact interaction with s electrons causes both K and T_1^{-1}.[26] This indicates that the T_1^{-1} is partially driven by a mechanism different from scattering with s-type conduction electrons at the Fermi level, such as the orbital contribution from the p electrons. This orbital contribution is expected to be roughly proportional to the density of p states at the Fermi level and to temperature. On the other hand, this orbital contribution is quenched for the isotropic Knight shift and does not obey the Korringa ratio. In fact, from band structure calculations, $N_{{\rm B}p}(E_F)\approx 0.1$ states/(eV B atom) is obtained to be much larger than $N_{{\rm B}s}(E_F)\approx 0.01$ states/(eV B atom) for both compounds (see Table I),[17] in qualitative agreement with our observations.

TABLE II. Summary of the experimental ^{11}B NMR parameters for OsB$_2$ and RuB$_2$. The results for MgB$_2$ from Ref. 24 are presented for comparison.

	OsB$_2$	RuB$_2$	MgB$_2$ (Ref. 24)
ν_Q (kHz)	285(10)	285(10)	835
K (ppm)[a]	$\approx$10	$\approx$40	40
T_1T (sK)	600(30)	680(35)	170
R	$\approx$0.02	$\approx$0.4	0.102

[a] Corrected with respect to the reference solution BF$_3$ as described in text.

Finally, we note that the Korringa ratio R and the values of T_1T are observed to be clearly different in the two compounds. Although the partial DOS's, $N_{{\rm B}p}$ and $N_{{\rm B}s}$, were reported to be almost the same for both compounds on the basis of band structure calculations,[17] our observation indicates that there exists a noticeable difference between the partial DOS's in the two compounds, whereby $N_{{\rm B}p}$ is considerably larger in OsB$_2$ than in RuB$_2$. The B p-band contribution to the DOS at the Fermi level is believed to be the key for the superconductivity in MgB$_2$[6–8] and to be relevant to the superconductivity even in other metal diborides TB$_2$.[12,13] In this scenario, the larger B p-band contribution is expected for the higher T_c in OsB$_2$ as we observed here from ^{11}B NMR relaxation measurements.

IV. CONCLUSIONS

We have presented a complete set of ^{11}B NMR data in the layered diborides OsB$_2$ and RuB$_2$ and representative results are summarized in Table II. All the experimental results have been understood qualitatively in relation to the local structure or to the partial DOS's. We find that, at the B site, the p character is dominant for the DOS at the Fermi level for both compounds similarly to the MgB$_2$ case. A noticeable difference between the Korringa ratio R for the two compounds has been observed, which seems to be relevant to the different T_c's for two compounds. In discussion about the mechanism of the ^{11}B T_1^{-1}, the contribution of the fluctuating dipolar field from the B p character at the Fermi surface is overlooked due to the lack of theoretical support.[23,24] In order to understand better the microscopic origin of the difference between the NMR parameters in the two compounds and its relevance to the superconductivity, a comparison of our experimental results with *ab initio* calculated values for Knight shifts and relaxations is highly desirable.[23,24]

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