



^{207}Pb nuclear magnetic resonance study in $\text{PbWO}_4\text{:Mn}^{2+}$ and $\text{PbWO}_4\text{:Dy}^{3+}$ single crystals

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Abstract In this exploration, the nuclear magnetic resonance of the ^{207}Pb nucleus in $\text{PbWO}_4\text{:Mn}^{2+}$ and $\text{PbWO}_4\text{:Dy}^{3+}$ Single Crystals using FT-NMR spectrometer is investigated. The line width of the resonance line for the ^{207}Pb nucleus decreases as temperature increases due to motional narrowing. The chemical shift of ^{207}Pb NMR spectra also increases as temperature decreases for both crystals. The spin-lattice relaxation times T_1 of ^{39}K nucleus were calculated as a function of temperature (180 K~400 K). The T_1 of ^{207}Pb nucleus decreases as temperature increases. The dominant relaxation mechanism at the studied temperature range can be deduced as the Raman process, which is the coupling between lattice vibrations and the nuclear spins. This deduction is substantiated by the fact that the nuclear spin-lattice relaxation rate $1/T_1$ of the ^{207}Pb nucleus in $\text{PbWO}_4\text{:Mn}^{2+}$ and $\text{PbWO}_4\text{:Dy}^{3+}$ single crystal is proportional to T^2 , or temperature squared. The activation energies for the ^{207}Pb nucleus in $\text{PbWO}_4\text{:Mn}^{2+}$ and $\text{PbWO}_4\text{:Dy}^{3+}$ single crystals are $E_a = 49 \pm 1$ meV and $E_a = 47 \pm 2$ meV, respectively.

Keywords PbWO_4 single crystal, Mn^{2+} and Dy^{3+} impurities, ^{207}Pb NMR, spin-lattice relaxation time, activation energy

Introduction

Lead tungstate (PbWO_4) crystals have been intensively studied for the application of high-density scintillator with an inherent luminescence, which has been successfully applied in calorimetric detectors of the Large Hadron Collider (LHC) in CERN^{1,2} and have known as heavy scintillation materials in high-energy physics.³⁻⁶ Lead tungstate nano- and macro-crystals have been attracting increasing attention due to their interesting excitonic luminescence, thermoluminescence, and stimulated Raman scattering behavior.⁷ The researches on PbWO_4 focused on the light yield increase^{8,9} and various doping schemes.¹⁰⁻¹² In the most recent applications in high-energy physics, the crystals are used at a low temperature around 250 K, which considerably changes their radiation damage characteristics,¹³ and its mechanism is further explored.¹⁴

On the other side, PbWO_4 crystals also have several laser advantages such as stability, wide infrared transmittance, high thermal conductivity, and high laser damage threshold. PbWO_4 is a type of Raman matrix with high qualities and good application prospect in Raman materials.¹⁵ After being doped with rare earth ions, PbWO_4 could be a self-stimulated Raman laser material based on its frequency shifting action on the fluorescence of rare earth ions. Several works have been carried out on the Raman laser properties of doped PbWO_4 crystals.^{16,17} Characteristics of the PbWO_4 emission may be slightly different for various samples. They depend on

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growth conditions, quality and impurity composition of the crystals, and mechanical or chemical polishing of the samples.¹⁸ To improve the optical transmittance, decay time, and radiation hardness of PbWO₄ scintillating crystals, many researches including doping and annealing treatments have been carried out.¹⁹⁻²¹ Several studies on the structural characterization of PbWO₄ by X-ray and neutron diffraction techniques have been performed to illustrate the presence of defects in PbWO₄ crystals.^{22,23} The majority of dopants in PbWO₄ are considered to replace the Pb²⁺ ions and compensate the Pb²⁺ deficiency. Kobayashi et al. reported that the scintillating properties could be significantly improved by doping trivalent ions.²⁴ They considered that these ions could compensate the Pb²⁺ deficiency, thus reducing the defects.

PbWO₄ crystal doped with Dy³⁺ exhibit improved transmittance in the short wavelength region. In Dy:PbWO₄, the WO₄²⁻ group can absorb excitation energy and transfer part of the energy to the Dy³⁺ ions, followed by the strong luminescence of Dy³⁺.²⁵ Mn²⁺ is also frequently used as a dopant to improve phosphors. The conjectured Pb²⁺ deficiency due to evaporation can occur not only during crystal growth but also during annealing.²⁶ Nuclear magnetic resonance (NMR) method is very suitable for investigating microscopic information of materials. The spin-lattice relaxation time of the nuclei in host single crystals reflects the dynamics of the sample crystals, for instance the spin-phonon interaction, and shows how easily the excited state energy of the nuclear spin system can be transferred into the lattice. The NMR studies of PbWO₄ single crystals doped with Mn²⁺ and Dy³⁺ are not reported so far. In this paper, the ²⁰⁷Pb NMR spectra in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals at the temperature range 180 K~410 K are obtained. The chemical shift, linewidth, and intensity of the ²⁰⁷Pb NMR spectra are also discussed. The spin-lattice relaxation time of ²⁰⁷Pb nuclei in both crystals were measured using Fourier transform (FT) NMR spectrometer in order to obtain specific information regarding the dynamics of PbWO₄ crystals doped with paramagnetic impurities. The activation energy of ²⁰⁷Pb nuclei are calculated.

This investigation that studies the NMR of the PbWO₄ single crystals doped with Mn²⁺ and Dy³⁺ impurity ions have not been previously reported.

Crystal Structure and Experimental Aspects

The scheelite PbWO₄ crystal structure is tetragonal with space group *I41/a*. The lattice constants of the unit-cell are $a = b = 0.5456$ nm and $c = 1.2020$ nm.²⁷ The unit cell consists of four molecules. The W and Pb sites in PbWO₄ single crystal have S4 point symmetry. The Pb²⁺ and W⁶⁺ ions are surrounded by eight oxygen atoms and four oxygen atoms, respectively. The W ions in PbWO₄ crystals are located in two types of oxygen tetrahedra, which are slightly rotated with respect to each other.²⁸ The melting point of PbWO₄ single crystal is 1123 °C.

The NMR spectra of ²⁰⁷Pb in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals were measured by the Bruker Solid-state NMR spectrometer (DSX 400 MHz) at the Korea Basic Science Institute. The static magnetic field was 9.4 T and the Larmor frequency (central radio frequency) was set to $\omega_0/2\pi = 83.538$ MHz for the ²⁰⁷Pb nucleus. The spin-lattice relaxation time T_1 was measured using the saturation recovery pulse sequence ($\pi/2$ - τ - π) for the ²⁰⁷Pb nucleus. The delay times for the measurement of T_1 and for Fourier transform NMR resonance line of ²⁰⁷Pb nucleus are 1 s and 10 s, respectively. The temperature-dependent ²⁰⁷Pb nuclei resonance lines in the crystals were obtained within the temperature range of 180-410 K. The sample temperatures were maintained constant by adjusting the nitrogen gas flow and heater current. The saturation recovery traces of the ²⁰⁷Pb nucleus in a PbWO₄:Dy³⁺ single crystal were obtained as a function of delay time and the results are shown in Figure 1.

Analysis and Discussion

The temperature dependence of the ²⁰⁷Pb NMR spectrum in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals was measured at 13 different temperatures in

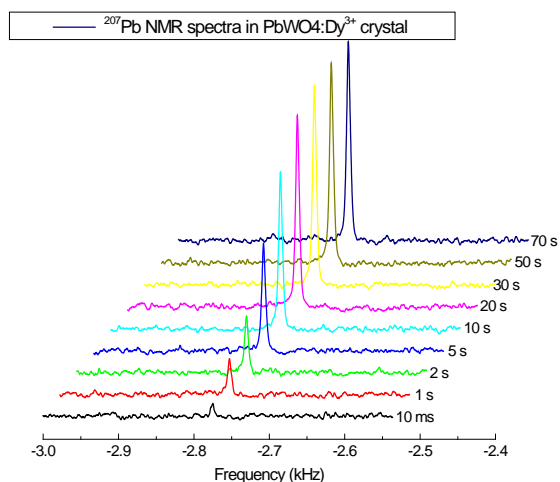


Figure 1. Saturation recovery traces of the ^{207}Pb nucleus in a $\text{PbWO}_4:\text{Dy}^{3+}$ single crystal as a function of delay time at 300 K.

the range 180 K~410 K. The typical FT NMR spectra for the ^{207}Pb nuclei in both single crystals at several temperatures are shown in Figure 2. This spectrum is obtained by a Fourier transform of the free induction decay for ^{207}Pb NMR. Only one resonance line is measured as expected from the nuclear spin $I = 1/2$ for ^{207}Pb . This single resonance line shows that there is only one chemically and magnetically equivalent ^{207}Pb site in the PbWO_4 crystal. All ^{207}Pb resonance frequencies of $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals in Figure 2 (a) and (b) are shifted from the zero point of the frequency ($= 83.538$ MHz) of the bare ^{207}Pb NMR. In general, the resonance frequency of nucleus in the crystal is different for a nucleus embedded in crystal from that of a 'bare' nucleus. These frequency shifts are originated from the chemical shift.²⁹ The spectra in Figure 2(a) and in Figure 2(b) at 300 K are shifted by -2.868 kHz for the $\text{PbWO}_4:\text{Mn}^{2+}$ crystal and by -2.777 kHz for the $\text{PbWO}_4:\text{Dy}^{3+}$ crystal from the operating frequency $\omega_0/2\pi = 83.538$ MHz, respectively, due to the chemical shift.

The temperature dependence of resonance frequency for the ^{207}Pb nuclei in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals is shown in Figure 3. The resonance frequency of the ^{207}Pb nuclei in both crystals is closer

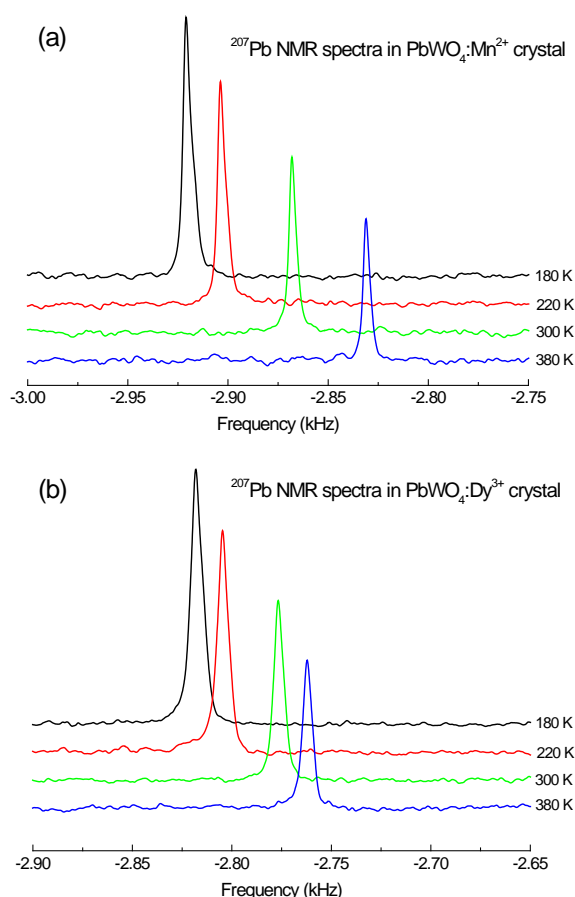


Figure 2. Typical NMR spectra of the ^{207}Pb nucleus (a) in $\text{PbWO}_4:\text{Mn}^{2+}$ (b) in $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals at several temperatures operating at $\omega_0/2\pi = 83.538$ MHz.

to the zero point of the frequency when temperature increases. The solid lines in Figure 3 are the linear fit of the resonance frequencies of the ^{207}Pb nuclei with increasing temperature for both crystals. The chemical shift of the ^{207}Pb nucleus in the $\text{PbWO}_4:\text{Mn}^{2+}$ crystal is stronger than that in the $\text{PbWO}_4:\text{Dy}^{3+}$ crystal at all temperatures within the range investigated. The chemical shifts of ^{207}Pb NMR lines in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals linearly decrease when temperature increases.

The peak to peak intensities of the ^{207}Pb NMR spectra in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals decreased with increasing temperature for all temperature range as shown in Figure 4. The

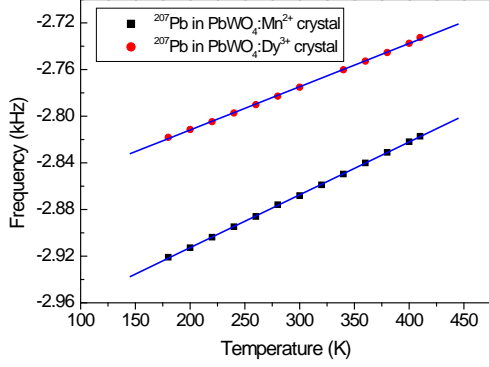


Figure 3. Resonance frequency of the ²⁰⁷Pb nuclei in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals as a function of temperature. The zero point is the Larmor frequency 83.538 MHz.

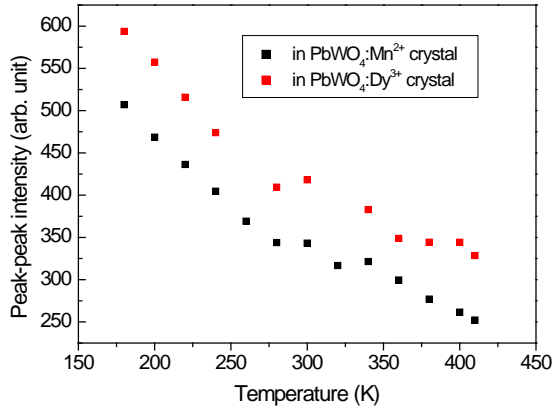


Figure 4. Peak to peak intensity of the ²⁰⁷Pb NMR line in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals as a function of temperature.

linewidths of the ²⁰⁷Pb nuclei in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals are $(\Delta\nu)_{FWHM} = 4.2$ Hz and $(\Delta\nu)_{FWHM} = 6.0$ Hz at 300 K (see Figure 5). The linewidth at FWHM (full width at half maximum) of the resonance line for the ²⁰⁷Pb NMR decreases with increasing temperature due to motional narrowing. The linewidth of the ²⁰⁷Pb nucleus in PbWO₄:Mn²⁺ is smaller than that in PbWO₄:Dy³⁺ single crystals. The differences of chemical shift and FWHM for ²⁰⁷Pb NMR spectra in two different PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ crystals may originate from the crystal growing conditions rather than different impurities

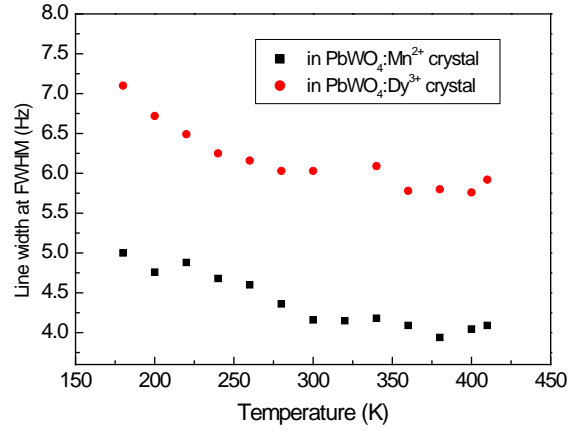


Figure 5. Linewidth (FWHM) of the ²⁰⁷Pb NMR line in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals as a function of temperature.

because both impurity concentrations in the crystals are not high.

The saturation recovery traces of the nuclear magnetization were measured at the temperature range 180~410 K for the ²⁰⁷Pb nucleus. The obtained magnetization recoveries $[M(\infty) - M(t)]/2M(\infty)$ for ²⁰⁷Pb ($I = 1/2$, natural abundance 22.6%) nucleus were found to fit a single exponential function with the following equation:³⁰⁻³²

$$[M(\infty) - M(t)]/2M(\infty) = \exp(-t/T_1) \quad (1)$$

where $M(\infty)$ denotes the nuclear magnetization at thermal equilibrium, $M(t)$ the magnetization of the transition for ²⁰⁷Pb nucleus at time t , and T_1 the spin-lattice relaxation time. The magnetization recovery traces at several temperature are shown in Figure 6.

The coupling between the lattice vibrations and the spins can be generally be written using a spin-lattice Hamiltonian.²⁹ Lattice operator can be expanded as a function of the stress. At the temperature far below the melting point of the single crystal, we can reasonably presume that the thermal stress is small and only the first few terms of lattice operator are important. The first order term shows the direct process, which is the absorption or emission of a single phonon. However, this term is negligibly small. The physical reason for the inefficiency of the direct process is that only phonons in the neighborhood of the frequency

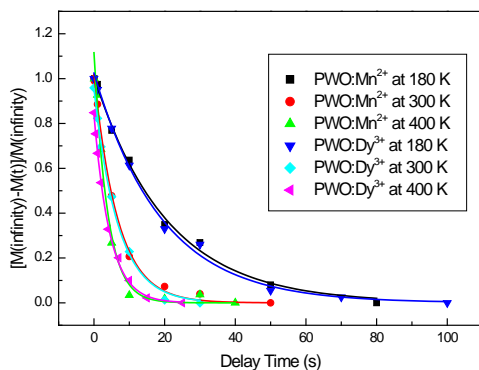


Figure 6. Magnetization recovery traces for ^{207}Pb nuclei in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ crystals. The curves are fitted with eq. (1).

contribute to the relaxation and that the corresponding spectral density of thermal energy is very small. The succeeding second order term is the two-phonon processes (Raman process). The absorption of one phonon and the emission of the other is overwhelmingly more important than the emission or absorption of two phonons. The Raman Process shows the relaxation rate, $1/T_1$, is proportional to the square of the temperature in the high temperature limit.^{29,33,34} Another two-phonon process is the Orbach process. However, this process shows an exponential relationship between the relaxation rate and temperature.²⁹

From the magnetization of the ^{207}Pb nuclei in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals, spin-relaxation times were calculated with eq. (1) in the temperature range 180 K ~ 410 K. The temperature dependence of the nuclear spin-lattice relaxation rate $1/T_1$ for ^{207}Pb nuclei was obtained and shown in Figure 7. The relaxation time of the ^{207}Pb nuclei shows no abrupt changes in the experimental temperature range, which means that no physical abrupt changes occur. The $1/T_1$ values of the ^{207}Pb nuclei in both crystals were found to increase when temperature increases. This is rational because the lattice vibration is more effective when the crystal temperature is increased, the relaxation time becomes shorter with increasing temperature.

The relaxation mechanism for the ^{207}Pb NMR in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals can be explained in terms of lattice vibration and nuclear spin. The relaxation rates of ^{207}Pb nuclei in both crystals are proportional to the square of temperature in the investigated temperature range as indicated with solid lines in Figure 7. Therefore, the temperature dependence of the ^{207}Pb relaxation rate in PbWO_4 crystals is in accordance with Raman processes. Though our measurement was made with a single crystal samples doped with Mn^{2+} and Dy^{3+} impurities, the relaxation process represents a more reliable feature of the intrinsic behavior of the $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals. Namely, the Raman process is more effective than the paramagnetic impurity effects in our experiment.

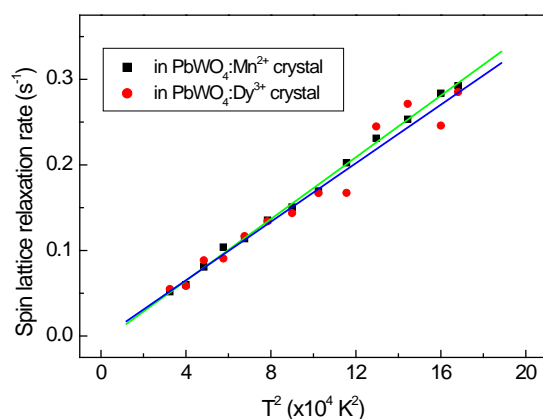


Figure 7. Temperature dependence of the spin-lattice relaxation rate $1/T_1$ for the ^{207}Pb in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals. The solid line is fits obtained by assuming Raman processes.

The activation energy of the ^{207}Pb nuclei in $\text{PbWO}_4:\text{Mn}^{2+}$ and $\text{PbWO}_4:\text{Dy}^{3+}$ single crystals was obtained from the equation $T_1 = A_o \exp(E_a/k_B T)$,^{29,35} where A_o and E_a denote the pre-exponential factor and the activation energy, respectively. The constants k_B and T denote the Boltzmann constant and the temperature, respectively. A linear plot of the natural logarithm of relaxation time T_1 as a function of inverse temperature is shown in Figure 8. The gradient of the linear fits is related to the activation energy of the ^{207}Pb nuclei. The activation energies of the ^{207}Pb nuclei

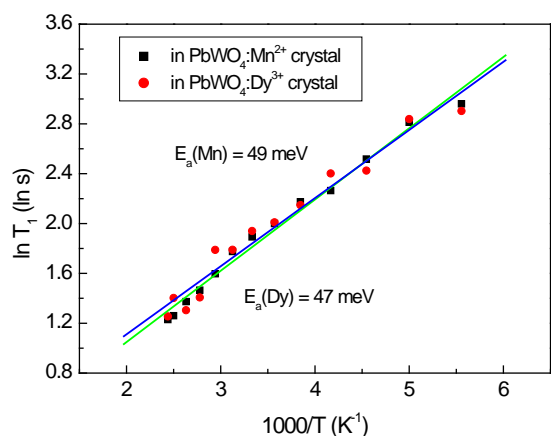


Figure 8. The spin-lattice relaxation time of the ²⁰⁷Pb nucleus vs. the reciprocal temperature in the experimental temperature region. The slope of the solid line represents the activation energy.

obtained from the slope of the graph in Figure 8 are $E_a = 49 \pm 1$ meV for PbWO₄:Mn²⁺ crystal and $E_a = 47 \pm 2$ meV for PbWO₄:Dy³⁺ single crystal, respectively. These activation energies are required to activate the nucleus and to allow the participation in the spin-lattice relaxation process of the ²⁰⁷Pb nucleus in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals. The values of activation energies of ²⁰⁷Pb nuclei in both crystals are the same within the experimental accuracy. This may show that paramagnetic impurity effects on relaxation is almost negligible because T_1 of ²⁰⁷Pb nuclei in both crystals doped with different paramagnetic ions (Mn²⁺: 3d⁵ and Dy³⁺: 4f⁹) has no difference. Only the intrinsic component is effective for the relaxation of ²⁰⁷Pb nuclei instead of paramagnetic impurities.

Summary

The NMR of the ²⁰⁷Pb nucleus in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals have been investigated by employing the FT-NMR spectrometer in the temperature range of 180 K–410 K. Only one ²⁰⁷Pb

resonance line was obtained in both crystals. This indicates that there is only one chemically and magnetically equivalent ²⁰⁷Pb site in the host crystals. The chemical shifts of ²⁰⁷Pb resonance lines in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals decrease linearly when temperature increases. The chemical shift of the ²⁰⁷Pb nucleus in PbWO₄ crystal doped with Mn²⁺ ion is stronger than that in PbWO₄ crystal doped with Dy³⁺ ion at all temperature range. The line width and peak to peak intensity of the ²⁰⁷Pb nuclei in both crystals decrease with increasing temperature.

The relaxation mechanism of the ²⁰⁷Pb nuclei was investigated by describing the spin-lattice relaxation time, T_1 , of the ²⁰⁷Pb as a function of temperature in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals. The spin-lattice relaxation time T_1 values of the ²⁰⁷Pb nuclei in PbWO₄ single crystals continuously decreased with increasing temperature. This shows that no phase transitions occurs within the experimental temperature range. The Raman process is the dominant relaxation mechanism for ²⁰⁷Pb NMR in the temperature range. This is because the spin-lattice relaxation rate $1/T_1$ of the ²⁰⁷Pb nuclei in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals is proportional to the square of temperature (T^2). The lattice vibrations in the host crystals are coupled to the nuclear spin via Raman spin-phonon coupling.

The activation energies obtained for the ²⁰⁷Pb nuclei in PbWO₄:Mn²⁺ and PbWO₄:Dy³⁺ single crystals are $E_a = 49 \pm 1$ meV and $E_a = 47 \pm 2$ meV, respectively. These activation energy of ²⁰⁷Pb nuclei for PbWO₄ doped with Mn²⁺ impurity is the same as that for PbWO₄ doped with Dy³⁺ impurity within the experimental errors. Therefore, the paramagnetic impurity effect on the relaxation of ²⁰⁷Pb in PbWO₄ crystals is almost negligible and the Raman process is dominant in the experimental temperature range investigated.

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