Possibility of modification of the ^{231}Pa Mössbauer spectra due to polarization-selective optical pumping

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(Received 11 May 2000; revised manuscript received 16 November 2000; published 18 April 2001)

The possibility of optical pumping of nuclei in solids is considered. In spite of the fact that inhomogeneous and homogeneous linewidths typically exceed the hyperfine splitting in solid hosts it is possible to redistribute the population of the hyperfine nuclear sublevels by means of polarization-selective optical pumping. Such redistribution can be detected by NMR methods or Mössbauer spectroscopic techniques. The latter case is considered in this work. The Mössbauer isotope ^{231}Pa is proposed as a candidate for possible experiment.

DOI: 10.1103/PhysRevB.63.184107 PACS number(s): 87.64.Pj

I. INTRODUCTION

Mössbauer spectroscopy has a lot of applications in chemistry and physics.[1,2] It allows one to study the nuclear surrounding in the solid host, in particular, to observe the hyperfine structure of the ions, to determine the parameters of the crystal field, to study the magnetic properties of the solids, etc. One of the most recent reviews on the subject is Ref. 3.

Recently, a new spectroscopic technique was proposed in Ref. 4 which deals with the modifications of the Mössbauer spectra under the action of optical laser radiation. It is based on the existence of the interaction between the electronic core of the atom or ion and the nuclear magnetic and quadrupole moments. As it was shown in Refs. 4,5, the Mössbauer spectra can be modified by laser radiation in many different ways. For instance, Mössbauer lines can vanish, split, change their intensity with respect to each other, etc. In this paper we take a step towards the experimental observation of the described effects. Namely, we show that optical pumping of nuclei is possible in solids, in spite of the fact that the hyperfine splitting is typically much less than the linewidths of the optical transitions in the solid hosts.

Previously several different possibilities of polarizing nuclei have been considered. In the pioneering work by Vysotskii[6] it was proposed to polarize nuclei by means of a strong magnetic field at very low temperatures. Another way of polarizing nuclei is to pump out one of the hyperfine sublevels by means of an optical field resonant to the electronic transition which involves this hyperfine sublevel. This scheme has been proposed by Karyagin.[7] However, this way of polarizing nuclei requires clearly resolved hyperfine structure in the optical spectra of atoms, which is not the case for solid state optics. Another way of optical pumping of nuclei, discussed in Appendix K of Ref. 8, is somewhat similar to what we do in our paper. It makes use of optical polarization selection rules for electronic transitions in free atoms. However, the atomic environment in solids significantly changes the selection rules for electronic transitions. Thus, it is not obvious that polarization selective optical pumping of nuclei works in solids.

In this paper we show that, indeed, very efficient polarization selective optical pumping of nuclei in solids is possible. In fact, such a possibility has been demonstrated previously in Refs. 9,10 by considering the example of $^{169}Tm^{2+}$ ion in a crystal field with octahedral symmetry. However, in these papers it has not been proposed a direct way of observation of nuclear polarization. Moreover, the efficiency of the proposed technique is rather low (the observed nuclear polarization is 12% at best) due to the fact that nonresonant broad-band polarized light was used to produce nuclear polarization and, thus, many electronic transitions with very different selection rules were involved.

In our paper we show that it is possible to obtain almost 100% nuclear polarization if one exploits the resonant character of the interaction of light with an electronic transition, i.e., if only one electronic transition is involved in the nuclear polarization process. It is proposed to use Mössbauer spectroscopy to detect nuclear polarization directly. As a particular example of the Mössbauer active ion we take $^{231}Pa^{4+}$ introduced into a solid host with octahedral symmetry. The choice of this ion has been made because of the fact that ^{231}Pa is Mössbauer active and that the corresponding ion possesses only one *f* electron in the unclosed shell. The latter simplifies calculations significantly, but does not make any restrictions on the choice of ions having 2 or more electrons in the outer shell. The magnetic hyperfine structures of $^{231}Pa^{4+}$ levels are calculated, the optical selection rules for the transitions between the hyperfine sublevels are obtained, and the changes in the Mössbauer spectra of the absorber doped with $^{231}Pa^{4+}$ ions are predicted in the rest of this paper. The estimates of the required laser intensity are made for the particular case of protactinium ion in Cs_2ZrCl_6 lattice. We also give the complete description of the experiment that can verify our predictions.

II. THEORY OF OPTICAL PUMPING

Optical pumping is a well known process in atomic physics. In order to remind one of what optical pumping is we consider a simplified model of a three-level system shown in Fig. 1. The transition $1 \leftrightarrow 2$ is coupled to the resonant optical field of Rabi frequency Ω while the transition $3 \leftrightarrow 2$ does not

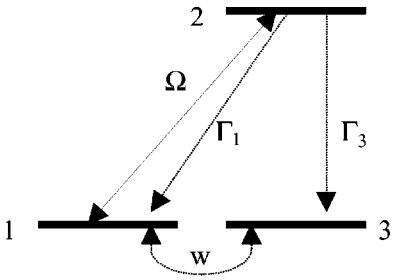

FIG. 1. Simplified scheme of optical pumping.

interact with this optical field. The levels 1 and 3 can be the hyperfine sublevels of the ground state. The population of the excited state 2 decays to levels 1 and 3 with corresponding rates Γ_1 and Γ_3. In addition, there is a population relaxation between the ground-state sublevels with rate w. The set of density matrix equations describing this system is

$$\frac{d\rho_{11}}{dt}+i(\Omega^*\sigma_{12}-\Omega\sigma_{21})=\Gamma_1\rho_{22}+w\rho_{33}-w\rho_{11}, \quad (1)$$

$$\frac{d\rho_{33}}{dt}=\Gamma_3\rho_{22}+w\rho_{11}-w\rho_{33}, \quad (2)$$

$$\rho_{11}+\rho_{22}+\rho_{33}=1, \quad (3)$$

$$\frac{d\sigma_{12}}{dt}+i\Omega(\rho_{11}-\rho_{22})=-\Gamma_{12}\sigma_{12}, \quad (4)$$

where Γ_{12} is the relaxation rate of the off-diagonal density matrix element σ_{12}. In order to simplify calculations we take $\Gamma_1=\Gamma_3=\Gamma$.

Let us now calculate the populations of the ground-state sublevels in the steady-state regime. In order to do that we set all the derivatives with respect to time equal to zero. Now, we consider two cases. First, we set $w=0$, i.e., there is no population relaxation between the ground-state sublevels. In this case all the population will be stored in level 3 under the action of an arbitrarily weak optical field. If we now introduce a small relaxation rate w, the solution of this set of equations takes the form

$$\rho_{11}=\frac{(|\Omega|^2+\Gamma\Gamma_{12})w}{2\Gamma\Gamma_{12}w+|\Omega|^2(\Gamma+3w)}, \quad (5)$$

$$\rho_{22}=\frac{|\Omega|^2 w}{2\Gamma\Gamma_{12}w+|\Omega|^2(\Gamma+3w)}, \quad (6)$$

$$\rho_{33}=\frac{\Gamma\Gamma_{12}w+|\Omega|^2(\Gamma+w)}{2\Gamma\Gamma_{12}w+|\Omega|^2(\Gamma+3w)}. \quad (7)$$

We consider the difference between ρ_{33} and 1. It can be written as

$$1-\rho_{33}=\frac{\Gamma\Gamma_{12}+2|\Omega|^2}{2\Gamma\Gamma_{12}w+|\Omega|^2(\Gamma+3w)}w. \quad (8)$$

One can see that it is proportional to the relaxation rate w, thus it can be made very small if $w\ll\Gamma,\Gamma_{12}$. Typically, in solids $w=0.01-1\ s^{-1}$, $\Gamma=10^2-10^3\ s^{-1}$ for electric dipole forbidden d-d or f-f transitions and $\Gamma=10^6-10^7\ s^{-1}$ for electric dipole allowed transitions, and $\Gamma_{12}=10^{10}-10^{13}\ s^{-1}$. Thus, the condition $w\ll\Gamma,\Gamma_{12}$ is satisfied. If $|\Omega|^2=\Gamma_{12}w$, the population of level 3 becomes 2/3. This value differs significantly from 1/2 when the optical field is not applied. Thus, if $|\Omega|^2$ is of the order of $\Gamma_{12}w$, one can expect significant population redistribution between the ground-state sublevels. If we increase the intensity of the optical field to the value of $|\Omega|^2=\Gamma\Gamma_{12}$, the difference $1-\rho_{33}$ becomes $2w/\Gamma$, i.e., a few percent in the worst case when $w=1\ s^{-1}$ and $\Gamma=10^2\ s^{-1}$. We see that all the population can be effectively stored in one of the ground-state sublevels. This is the essence of optical pumping.

In the next section we consider the possibility of realization of such a scheme in solids. In particular, we consider Pa^{4+} ions introduced into the solid host. The choice of protactinium was made due to the fact that it is Mössbauer active, so the optical pumping can be detected by observing changes in the Mössbauer spectrum of the absorber containing $^{231}Pa^{4+}$ ions due to optical pumping of the hyperfine sublevels. In addition to that fact, the Pa^{4+} ion has both f-f magnetic dipole allowed and f-d electric dipole allowed transitions, so it is possible to study both types of optical pumping schemes using one chemical element.

III. STRUCTURE OF IONIC LEVELS, SELECTION RULES, AND CHANGES IN THE MÖSSBAUER SPECTRA

In order to illustrate the possibility of optical pumping of nuclei in the solid hosts we consider two cases corresponding to the electric and the magnetic dipole allowed transitions. In both cases we choose the fourfold crystal axis to be the axis of quantization. The **k** vector of the incident laser radiation is chosen to be parallel to this axis.

A. Parity forbidden transitions

We start with the case of parity forbidden f-f transitions since this type of transitions are the most common in rare earths and actinides. In particular, we consider Cs_2ZrCl_6 doped with Pa^{4+}. This compound has been studied very extensively (see Refs. 11,12). The electronic levels of Pa^{4+} in this compound are shown in Fig. 2. The ground $5f^1$ electronic state is split due to the spin-orbit coupling

$$H_{SO}=\zeta\mathbf{L}\cdot\mathbf{S} \quad (9)$$

into two sublevels $^2F_{5/2}$ and $^2F_{7/2}$. The octahedral crystal field described by the Hamiltonian

$$H_{CF}=B^4\left(C_0^4+\sqrt{\frac{5}{14}}(C_4^4+C_{-4}^4)\right)+B^6\left(C_0^6-\sqrt{\frac{7}{2}}(C_4^6+C_{-4}^6)\right) \quad (10)$$

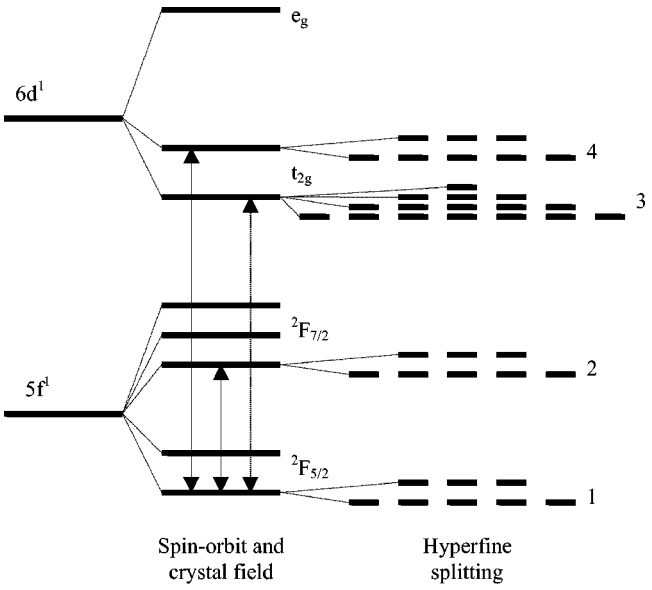

FIG. 2. Structure of electronic and hyperfine levels of $^{231}Pa^{4+}$.

splits these two states into two and three sublevels, respectively. Here we use the usual notations for the crystal field operators C_n^m which in our case are simply spherical harmonics $Y_m^n(\theta,\phi)$. The transition between the states 1 and 2 (Fig. 2) is of particular interest. Each of these two states are a Kramer's doublet. The energy of the corresponding transition is $5250\,\mathrm{cm}^{-1}$.[14]

We now consider the magnetic hyperfine splitting of the two levels mentioned above due to the interaction described by the Hamiltonian

$$H_{hf}=\lambda\,\mathbf{J}\cdot\mathbf{I},$$

where $\mathbf{J}=\mathbf{L}+\mathbf{S}$ is the total angular momentum of the electron and $\mathbf{I}$ is the nuclear spin. The structure of the hyperfine sublevels is shown on the right-hand side of Fig. 2.

We now need to determine the selection rules for the transitions between the hyperfine sublevels of the ground and excited states. As was mentioned above, these transitions are electrically dipole forbidden, so we consider the magnetic dipole allowed transitions between the states. The Hamiltonian that describes the interaction of these transitions with the optical field can be written in the form

$$H_{\mathrm{mag}}=\mu_B(\mathbf{L}+2\mathbf{S})\cdot\mathbf{B}, \tag{11}$$

where $\mathbf{B}$ is the magnetic field strength of the incident optical wave with the frequency resonant to the transition under consideration. Using this interaction Hamiltonian we can determine the selection rules for different polarizations of the optical wave. The results are given in Fig. 3. Here Ψ_n denotes the hyperfine sublevels of the $^2F_{5/2}$ ground state whereas Φ_n denotes the hyperfine sublevels of the excited $^2F_{7/2}$ state. One can see that in the cases of ''+'' or ''−'' circular polarizations there exists one hyperfine sublevel from the ground-state manifold which is not involved in any transition

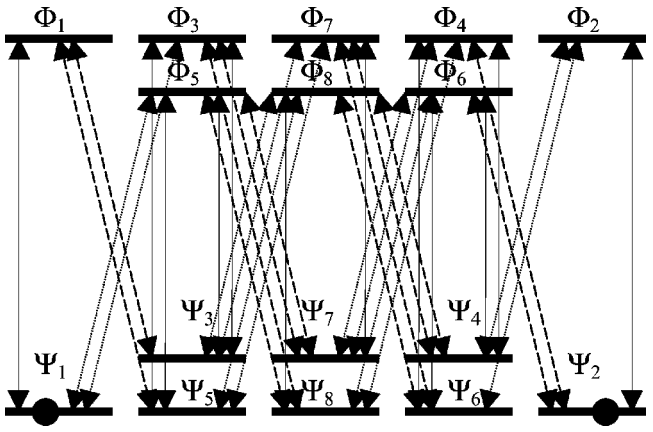

FIG. 3. Selection rules for π (solid line), σ_+ (dashed line), and σ_- (dotted line) polarizations for the transitions $1\leftrightarrow4$ and $1\leftrightarrow2$.

to the excited states. This means that this level can store all the population of the ground state as it was discussed in the previous section.

It is worth mentioning that the admixture of the even parity states to the F states due to the tetragonal or trigonal distortion of the crystal field can make f-f transitions electric dipole allowed. However, the distortion of the type

$$H_{\mathrm{dist}}=B^3(C_2^3-C_{-2}^3) \tag{12}$$

does not mix d states with the two levels that are under our consideration.

Let us now discuss the changes in the ^{231}Pa:Cs_2ZrCl_6 Mössbauer spectra that can be produced by optical pumping. The excited nuclear state is also split into two hyperfine sublevels. Therefore, the unperturbed Mössbauer spectrum consists of four lines corresponding to four transitions between the two hyperfine components of the ground state and the two hyperfine components of the excited state. When we apply the optical field, one of the ground-state hyperfine sublevels becomes empty. Therefore, two of the four Mössbauer resonances should vanish while the other two should be enhanced. The qualitative change of the Mössbauer spectrum is shown in Fig. 4. As was mentioned in the Introduction, optically resolved hyperfine structure is not required to obtain optical pumping of nuclei.

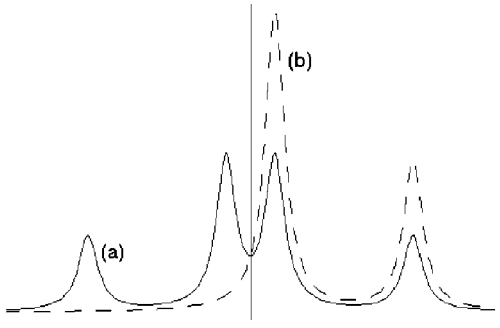

FIG. 4. Modification of the Mössbauer spectrum of protactinium: (a) unperturbed spectrum, (b) Mössbauer spectrum of optically pumped nuclei.

B. Electric dipole allowed transitions

Let us turn to the case of electric dipole allowed transitions. Again, we take a particular example of Pa^{4+} ion in Cs_2ZrCl_6. The situation is very similar to that discussed above. The absorption and emission spectra of the $5f \leftrightarrow 6d$ transition of $Cs_2ZrCl_6:Pa^{4+}$ was studied in Refs. 13,14. The excited $6d^1$ state is split into two sublevels by the octahedral crystal field

$$H_{CF}=B^4\left(C_0^4+\sqrt{\frac{5}{14}}(C_4^4+C_{-4}^4)\right). \tag{13}$$

The lowest level then is split by the spin-orbit interaction.

First, we consider the fourfold degenerate level of the $6d^1$ configuration which is the lowest one. The corresponding transition is $1 \leftrightarrow 4$ (Fig. 2). One can easily calculate the magnetic hyperfine structure of the excited level. It consists of 16 states as is shown in Fig. 2. In this case each ground-state hyperfine sublevel is involved in at least one allowed transition. Thus, optical pumping is not possible in this case since there is no hyperfine sublevel that can store the population of the ground state. The reason for this is that the excited electronic state has more hyperfine sublevels than the ground state. We claim that this is a general situation, i.e., polarization selective pumping is not possible if the excited electronic state has more hyperfine sublevels than the ground one.

In order to avoid this difficulty we consider the next state from the $6d^1$ configuration. It has eight hyperfine sublevels. The corresponding f-d transition is $1 \leftrightarrow 3$ in Fig. 2. It has an energy $24\,340\,\mathrm{cm}^{-1}$. The selection rules in this case are exactly the same as in the case of the magnetic dipole allowed f-f transition discussed in the previous subsection. They are indicated in Fig. 3. Now, Φ_n denotes the hyperfine states of the t_{2g} state. The expected modification of the Mössbauer spectrum of protactinium is exactly the same as it was in the case of the magnetic f-f transition, i.e., it is shown in Fig. 4.

IV. ESTIMATES OF LASER FIELD INTENSITY

Let us estimate the intensity of the optical field required to observe the modification of the Mössbauer spectra described above. The change in the Mössbauer spectrum can be observed if the populations of the ground-state hyperfine sublevels are changed by an order of 1. According to the estimates given in section 2, this change can be made if $|\Omega|^2$ is of the order of $\Gamma_{12}w$ (indices 1 and 2 refer to Fig. 1). For our estimates we take $w=0.1\,\mathrm{s}^{-1}$.

Let us consider first the case of the electric dipole allowed transition. In this case $\Gamma_{12} \approx 10^{13}\,\mathrm{s}^{-1}$. This means that the required Rabi frequency of the optical laser field is $10^6\,\mathrm{s}^{-1}$. The radiative lifetime of the excited $6d$ state in Pa^{4+} ion is known to be 40 ns (see Ref. 15). The required intensity can be deduced from the Rabi frequency of the optical field since $\Omega=E\mu/2\hbar$, where E is the magnitude of the electric field and μ is the magnitude of the electric dipole moment of the transition. In the case when $|\Omega|^2=\Gamma_{12}w$ the intensity of the optical field can be found as

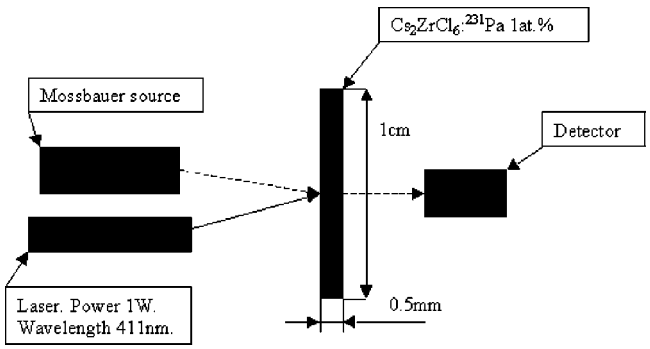

FIG. 5. The principle scheme of the experiment with protactinium.

$$I_{opt}=\frac{16\pi^2}{3}\frac{\hbar c\Gamma_{12}w}{\Gamma\lambda^3}. \tag{14}$$

Here λ is the wavelength of the optical field which in our case is $\lambda=1/24\,340$ cm$=411$ nm. The population decay rate Γ can be found as an inverse lifetime of the excited level

$$\Gamma=T_d^{-1}=2.5\times 10^7\ \mathrm{s}^{-1}. \tag{15}$$

Thus, the intensity of the optical field is $I_{opt}=10^{-4}\,\mathrm{W/cm}^2$. Such intensities can be easily achieved be modern lasers.

Now, we turn to the case of the f-f transition. We could not find the exact lifetime of the excited f state for protactinium, but we can take a typical value for such kind of transitions 4 ms which corresponds to $\Gamma=250\ \mathrm{s}^{-1}$. Typically, at low temperatures the linewidths of the f-f transitions are about $10^9-10^{10}\ \mathrm{s}^{-1}$. We take the worst value $\Gamma_{12}=10^{10}\,\mathrm{s}^{-1}$. In this case the required intensity of the optical field of wavelength $\lambda=1/5250\,\mathrm{cm}=1.9\,\mu\mathrm{m}$ is again $I_{opt}=10^{-4}\,\mathrm{W/cm}^2$. Again, such intensity is easily achievable.

The scheme of the experiment that can be proposed to verify our predictions is shown in Fig. 5. The Mössbauer absorber is illuminated by a laser. The thickness of absorber must satisfy two conditions. First, the absorber must be optically thick for γ rays. If we take the doping concentration of protactinium to be $N=10^{20}\,\mathrm{cm}^{-3}$, the linear absorption of the resonant γ rays can be calculated as follows:

$$\alpha_\gamma=N\sigma_\gamma L, \tag{16}$$

where L is the thickness of the sample and σ_γ is the resonant Mössbauer cross section. It is known that for protactinium $\sigma_\gamma=1.8\times 10^{-19}\,\mathrm{cm}^2$.[1] Thus, in order to get absorption close to 1, we need $L\approx 0.5\,\mathrm{mm}$. On the other hand, the laser light must penetrate through the whole sample. Let us estimate the absorption coefficient for the light. The population of the depleted hyperfine sublevel in the case when $|\Omega|^2 \gg \Gamma_{12}w$ can be made

$$\rho_{11}=\frac{\Gamma_{12}w}{|\Omega|^2}. \tag{17}$$

According to our estimate, $\Gamma_{12}w=|\Omega|^2$ for the intensity of the optical field $I_{opt}=10^{-4}\,\mathrm{W/cm}^2$. If we take I_{opt}

TABLE I. The parameters of the proposed experiment.

Thickness mm	Area cm^2	Density cm^{-3}	Power *W*	Wavelength nm
0.5	1	10^{20}	1	411

$=1$ W/cm^2, which is still easily achievable, the population of level 1 becomes $\rho_{11}=10^{-4}$. The absorption coefficient can be estimated as

$$\alpha_{\mathrm{opt}}=\rho_{11}N\sigma_{\mathrm{opt}}=\frac{\rho_{11}N\lambda^2\Gamma}{2\pi\Gamma_{12}}=15\ \ \mathrm{cm}^{-1} \tag{18}$$

in the case of electric-dipole allowed f-d transition in protactinium ion. Thus, the absorption length for the optical field is ≈ 0.7 mm. This value is consistent with the absorption length of resonant γ rays. Finally, we summarize the requirements for both the absorber and the laser field in Table I.

V. CONCLUSION

In conclusion we would like to say that the described effect can be observed not only for protactinium ions. In fact, it is observable for many different Mössbauer active elements, primarily rare earths and actinides, for example, ^{237}Np and ^{151,153}Eu. The choice of the Pa^{4+} ion has been made only for simplicity of calculations. The described effect of optical polarization of nuclei in solids can have a lot of applications in solid state physics and chemistry since it widens significantly the possibilities of Mössbauer spectroscopy. In addition to that, it can help in the resolution of the gamma-ray laser problem as was mentioned in Ref. 16.

ACKNOWLEDGMENTS

The authors are grateful to Olga Kocharovskaya, Alexey Belyanin, Vitaly Kocharovsky, and Yuri Rostovtsev for valuable discussions.

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