

Hyperfine interaction as a reason for removing the forbiddenness of a phononless transition in an impurity center

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Investigation of the influence of the activator's isotopic composition on the intensity of the phononless line in the emission band of CaS-Pb²⁺ phosphorus, which corresponds to the strongly forbidden ${}^3A_{1u} \rightarrow {}^1A_{1g}$ transition, showed for the first time that this line appears because of hyperfine interaction in an impurity center.

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The normal manifestation of hyperfine interaction in optical spectra is a splitting of the spectral lines. This effect has been thoroughly investigated for free atoms, and it has also been observed in certain rare-earth ions in crystals.¹ Recently, hyperfine interaction (HFI) in impurity centers, i.e., interaction between optical electrons and the nuclear spin of an impurity ion, has been used to explain certain details in the optical spectra of mercury-like ions (ions with two outer *s* electrons) in alkali-halide crystals. Thus, the presence of a long-term component in luminescence damping ($\tau \approx 0.2\text{--}3$ msec) has been explained by HFI in Refs. 2, 3; this, however, has not been confirmed experimentally.⁴ There have also been attempts to use HFI to explain the degree of radiation polarization of these centers.⁵ The influence of nuclear spin on the polarization of impurity radiation was examined theoretically in Ref. 6.

We were able to demonstrate experimentally using Pb²⁺ ions in CaS that the phononless line (PLL) in the electron-vibrational spectrum of a forbidden transition appears because of HFI in an impurity center. It appears to us that this result has a more general meaning, since it shows presumably for the first time that 1) HFI can occur in the optical spectrum of mercury-like ions and 2) HFI may account for the removal of forbiddenness from the phononless transition in an impurity center.

The allowed ${}^3T_{1u} \rightleftharpoons {}^3A_{1g}$ transition (${}^3P_1 \rightleftharpoons {}^1S_0$ transition in the free ion) and the strongly forbidden ${}^3A_{1u} \rightarrow {}^3A_{1g}$ (${}^3P_0 \rightarrow {}^1S_0$) transition with τ of the order of 10^{-3} sec have been observed in the mercury-like Pb²⁺ and Bi³⁺ ions in cubic crystals of the oxides and sulfides of alkaline-earth metals. Studies of the vibrational structure of the spectra at 4.2 K showed^{7,8} that the latter transition is allowed because of mixing of the ${}^3A_{1u}$ and ${}^3T_{1u}$ levels by crystal vibrations of the T_{1g} type. The presence of the PLL in this radiation band cannot be attributed to electron-phonon interaction.^{7,8} We have suggested⁷ that the PLL appears in the spectrum of the ${}^3A_{1u} \rightarrow {}^3A_{1g}$ transition because of mixing of the ${}^3A_{1u}$ and ${}^3T_{1u}$ levels by the magnetic field of the impurity nucleus. The purpose of this investigation is to directly verify this hypothesis.

The experiments were performed for Pb²⁺ ions in CaS. Natural lead consists of

TABLE I

CaS-Pb Sample number	^{208}Pb	^{207}Pb	^{206}Pb	^{204}Pb
1	99.8	0	0.2	0
2	52.3	22.6	23.6	1.48
3	—	50.0	50.0	—
4	—	75.0	25.0	—
5	0.7	98.8	0.5	0

four stable isotopes, of which only ^{207}Pb has a nonzero nuclear spin ($\frac{1}{2}$) and magnetic moment ($+0.5895 \mu_N$).⁹ If the appearance of the PLL in the luminescence band corresponding to the $^3A_{1u} \rightarrow ^3A_{1g}$ transition is due to HFI, then the intensity of the PLL must increase linearly with increasing percentage (n) of the ^{207}Pb isotope in the activator.

Using the method of Ref. 10, we have synthesized five CaS-Pb²⁺ samples with different percentages of lead isotopes in the PbSO₄ activator salt (see Table I). The ^{206}Pb , ^{207}Pb , and ^{208}Pb isotopes were introduced into the CaS powder in different proportions; sample No. 2 had a natural⁹ isotopic composition of the activator. The radiation spectra of phosphorus were measured at 4.2 K using a DFS-24 spectrometer with a resolution of $\sim 2 \text{ cm}^{-1}$.

For short-wave excitation¹ only the forbidden $^3A_{1u} \rightarrow ^3A_{1g}$ transition has been observed in the radiation spectrum of CaS-Pb²⁺. The spectrum (see Fig. 1) is comprised of a weak PLL and a phonon wing (PW), which begins with a one-phonon part caused by type T_{1g} lattice vibrations; this is followed by the multiphonon part of the PW, which is attributable to the repetitions of the one-phonon part of the PW in the A_{1g} vibrations.

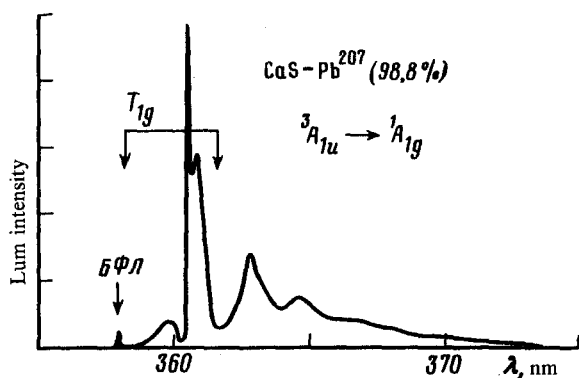


FIG. 1. Radiation spectrum for the strongly forbidden $^3A_{1u} \rightarrow ^3A_{1g}$ transition in CaS-Pb²⁺ (sample No. 5) at $T = 4.2 \text{ K}$ and for excitation by light with $\lambda = 267.5 \text{ nm}$. PLL is the phononless line; T_{1g} is the one-phonon part of the phonon wing produced by T_{1g} vibrations.

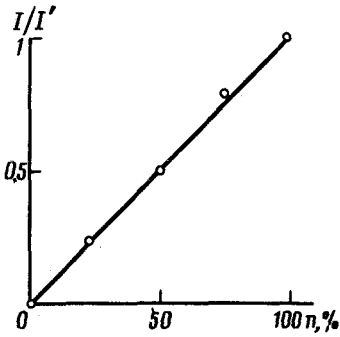


FIG. 2. Dependence of the ratio I/I' on the percentage n of the ^{207}Pb isotope in the activator. I is the normalized PLL intensity for a sample with arbitrary ^{207}Pb content and I' is the normalized PLL intensity for 100% ^{207}Pb content. The straight line represents the predicted dependence and the points denote the experimental values.

We define the normalized PLL intensity (I) as the ratio of the peak PLL intensity to the intensity of the first maximum in the one-phonon part of the PW (for $\lambda = 359.7$ nm), which did not depend in our measurements on the isotopic composition of the activator. If we denote by I' the normalized PLL intensity for $\text{CaS-}^{207}\text{Pb}(100\%)$, then we can write the predicted linear dependence in the form $I/I' = n/100$. We can see in Fig. 2 that this dependence has been obtained experimentally. The experiment shows, therefore, that the phononless $^3A_{1u} \rightarrow ^3A_{1g}$ transition in CaS-Pb^{2+} is accounted for by the HFI effect in an impurity center.

Does this conclusion also extend to other systems with a similar radiation spectrum? Table II lists the following values: τ is the lifetime of the $^3A_{1u}$ state at 70 K,¹¹ s is the ratio of the area under the PLL to the area of the one-phonon part of the PW at 4.2 K for the natural isotopic composition of the activator, and w is the probability of the phononless $^3A_{1u} \rightarrow ^3A_{1g}$ transition. The value of w was estimated from the relation $w = s/0.226 \tau$ for the Pb^{2+} centers and $w = s/\tau$ for the Bi^{3+} centers (natural bismuth consists of only one stable ^{209}Bi isotope⁹ with a nuclear spin of 9/2 and a magnetic moment of $+4.080 \mu_N$).

It can be seen in Table II that the probability of phononless transitions for Pb^{2+} centers in different base materials is approximately the same order of magnitude.

TABLE II

Sample	τ , msec	s	w , sec^{-1}
CaS - Pb	1	1/680	6.5
CaS - Bi	3	1/37	9.0
CaO - Pb	2	1/460	4.8
CaO - Bi	3.5	1/25	11.4
SrO - Pb	3	1/790	1.9
SrO - Bi	3.5	1/32	8.9

Therefore, the presence of PLL in the Pb^{2+} centers in other crystals can also be explained by HFI. The w values for Bi^{3+} centers are somewhat higher than for Pb^{2+} centers in the same base materials. Since the nuclear spin of bismuth is higher, we can assume that the PLL in the Bi^{3+} centers is attributable to HFI.

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