Muon-induced luminescence in KBr

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The energy spectrum of the luminescence induced by positive muons stopped in KBr has been obtained. This spectrum shows a Gaussian line shape with the peak located at 2.82(2) eV [FWHM, 0.56(5) eV], which is shifted considerably from the 2.28-eV luminescence line due to the lowest triplet state of self-trapped excitons (STE's). This result, together with the temperature dependences of its lifetime and yield, strongly suggests that the initial state of the observed luminescence is a triplet STE state that is specific to the muon(ium)-KBr system.

Ion-implantation techniques are of basic importance to the study of condensed matter for applications in which radiative nuclei (including muons) are used as microscopic probes: they greatly facilitate the use of these probes for a wide range of materials, without limitations due to surface effects, their solubility, the interaction between probes, and so on. Relatively little is known, however, about the deexcitation process of the implanted energetic probes in solids near or at the final stage when they might be affected by the presence of excitons or defects induced by the probe ions themselves. In most cases it has been commonly assumed that the probe ions are instantaneously degraded to thermal energy in solid specimens and that the associated excitations in crystalline solids are short-lived or dilute enough for such a radiolysis effect to be negligible.

In a previous report we showed that there is a strong correlation between the existence of so-called "anomalous muonium center (Mu^I)" and that of the relaxed excited state causing a luminescence in KBr.[1] This result suggests that, contrary to the above-stated presumptions, the implanted positive muon in the final state may interact with radiolysis products such as self-trapped excitons (STE) in alkali halides. Knowledge of the luminescence energy spectrum undoubtedly will help further elucidate this correlation and the origin of muon-induced luminescence.

We report on the energy spectrum of the luminescence observed in coincidence with the Mu^I center. The obtained spectrum, which is quite similar in line shape to that of the intrinsic π luminescence, exhibits a large blueshift from the latter. This result, together with other properties, indicates that the luminescence is caused by a triplet STE state which has a modified electronic or hole configuration compared with the initial state of the intrinsic π luminescence.

Muonium centers (i.e., the muonic analog of neutral hydrogen atoms), which are ubiquitous in semiconductors and ionic crystals after positive muon implantation, have been serving as sensitive probes to study the structure and dynamics of the simplest hydrogenlike atomic defects in those materials. In particular, much of the data have been accumulated for the muonium centers in alkali halides since the development of the muon-spin-rotation technique under high transverse magnetic field (HTF-μSR).[2] A systematic study of the hyperfine (hf) parameters brought by HTF-μSR has revealed the existence of an anomalous muonium center (Mu^I) in KBr which was observed only below 50 K with a slightly reduced hf parameter in place of the normal muonium center (Mu^{II}) seen at higher temperatures.[3] The latter has been identified as a muonic analog of the neutral hydrogen interstitial center[4] (U_2 or H_i^0 center) based on the hf and nuclear hyperfine parameters,[3,5] whereas the origin of the former state has remained unknown.

An important feature of the Mu^I center is that it exhibits rapid spin relaxation (corresponding to the spin correlation time of $\sim 10^{-10}$ s).[5] This suggests that the missing amplitude of the μSR signal in other alkali halides at lower temperatures[6,7] might be attributed to the formation of a Mu^I-like state which undergoes unobservably fast depolarization. The observation of muon-induced luminescence in KBr in coincidence with the Mu^I center immediately leads us to postulate that the fast depolarization of Mu^I or the loss of μSR signal is due to the paramagnetic interaction between muonium and self-trapped excitons produced by muon radiolysis: In the conventional μSR experiment positive muons are implanted into the specimen with an energy of 4 MeV, which is determined by the kinematics of pion decay at rest for the "surface muon" beam.

The reported difference of the decay time τ_p between the muon-induced luminescence ($=13.3$ μs) and the intrinsic π luminescence ($\simeq 100$ μs) also suggests that muon or muonium might be responsible for the formation of the modified STE state for the former luminescence.[1] However, the fact that the lifetime of the modified STE state ($=\tau_p$) is longer than the muonium lifetime τ_μ ($=2.2$ μs), which justifies the postulation that Mu^{I} is induced by muonium-STE interaction on the one hand, implies on the other that the modified STE structure cannot be directly ascribed to the coupling between STE and muonium center at their *final states.*

To improve our understanding of the relation between the muon-induced STE and the formation of Mu^{I} centers, we have measured the luminescence energy spectrum under muon irradiation of KBr. The experiment was performed at Meson Science Laboratory, University of Tokyo (UTMSL), where a pulsed surface muon beam was provided with 50-ns width at a rate of 20 Hz. As schematically shown in Fig. 1, a monochromator (Jobin Yvon Model H-10) was installed in the previous setup with a photomultiplier (Hamamatsu model R955) for the photon counting. The time-resolved photon spectra were measured over a range of wavelength from 350 to 600 nm with 16-nm resolution. Additional details of the experiment have been reported elsewhere.[1] The photon time spectra were analyzed by the form

$$n(t)=n_\mu e^{-t/\tau_\mu}+n_p e^{-t/\tau_p}+b \;, \qquad (1)$$

where τ_μ and τ_p are the decay times of positrons and photons, n_μ and n_p the counting rates at time origin respectively, and b is the time-independent background; the first component arises from the muon decay positrons directly irradiating the photomultiplier. Because of the small solid angle, the number of photon events was not enough to deduce both τ_p and n_p as free parameters in fitting the obtained time spectra with Eq. (1), therefore τ_p was fixed to 13.3 μs as obtained from the previous experiment.

Figure 2 shows the photon energy spectrum, i.e., $n_p\tau_p$ versus energy in KBr at 25 K. The best fit of the spectrum with a Gaussian line shape $\exp[-\frac{1}{2}(E-E_0/\sigma)^2]$ yields the mean energy $E_0=2.82(2)$ eV and the linewidth $\sigma=0.24(2)$ eV (i.e., FWHM$=0.56(5)$ eV). The total photon yield at this energy is consistent with that for the 13.3-μs luminescence estimated from the previous experiment. While the line shape is similar to that of the intrinsic luminescence from the lowest triplet STE state [i.e., π luminescence, shown by the dashed curve in Fig. 2, where

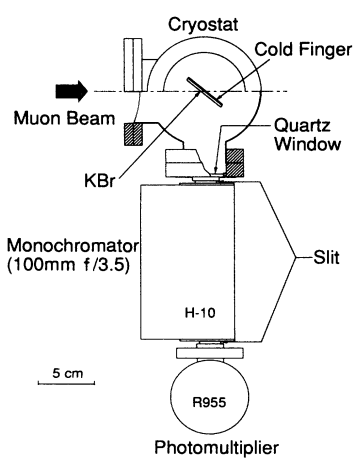

FIG. 1. A schematic diagram of the apparatus for the measurement of muon-induced luminescence spectrum. The cryostat vessel is connected to the monochromator through a quartz window.

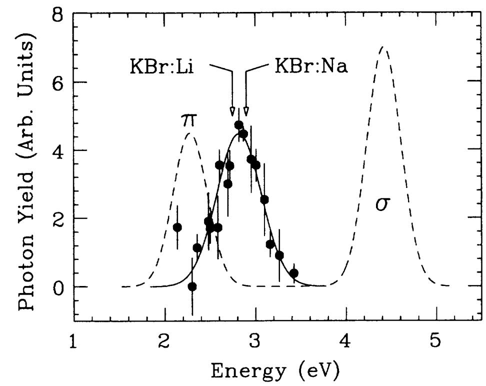

FIG. 2. The energy spectrum of muon-induced luminescence (lifetime=13.3 μsec) in KBr at 25 K. The intrinsic luminescence spectrum is shown by a dashed curve where the peak denoted by π or σ is associated with the triplet or singlet STE state (after Ref. 8). The peak energies of impurity-related luminescences are shown by arrows (after Ref. 10).

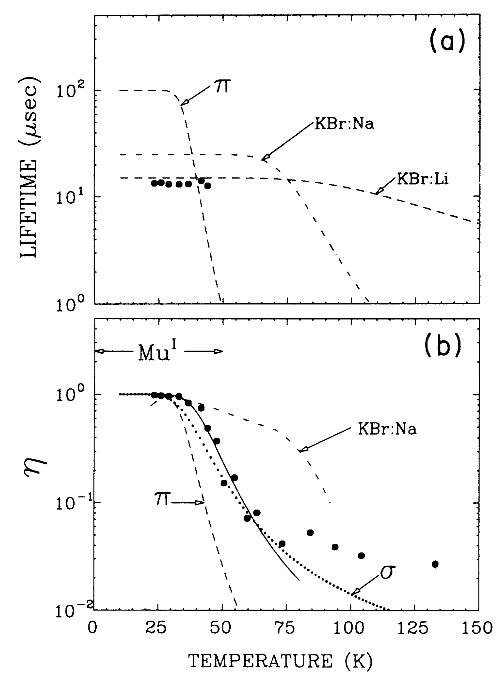

FIG. 3. Temperature dependences of the lifetime (a) and relative yield (b) of the luminescence of various origins in KBr, where the filled circles indicate the data of muon-induced luminescence (Ref. 1). Solid curve in (b) represents the best fit of the data by a form $1/\tau_0+\nu\exp(-E/kT)$. The intrinsic luminescences are, respectively, denoted by π and σ as in Fig. 2 (after Refs. 8 and 10).

$E_0 = 2.28$ eV and FWHM$=0.44$ eV at 10–50 K (Refs. 8 and 9)], the mean energy shows a large blueshift from that of the π luminescence with a slight increase of the linewidth. As is noticeable in Fig. 2, the peak energy is rather close to that associated with substitutional Li or Na impurities.[10] There is no such luminescence around this energy reported on halogen-substituted specimens (e.g., KBr:Cl, KBr:I).[11,12]

The possibility for the muon-induced luminescence to be simply attributed to those impurities is eliminated by comparing the temperature dependences of decay times or relative yields which are summarized in Fig. 3. As represented by the case of KBr:Na, the temperature range for the π luminescence from the triplet STE state perturbed by alkaline impurity is considerably extended to higher temperatures compared with that for the intrinsic π luminescence.[10] This is in marked contrast with that of the muon-induced luminescence which coincides rather with the intrinsic π or σ luminescence [see Fig. 3(b)].[1] Moreover, the lifetime of the muon-induced luminescence at this temperature range (i.e., 20–50 K) does not agree with any of the reported values of the intrinsic or impurity-related π luminescences. [In Fig. 3(a) the luminescence lifetime in KBr:Li is 15 μs below $\sim$70 K (Ref. 10)]. From these comparisons in various characteristics of the known luminescences we are led to conclude that the initial state of the observed luminescence is not the isolated STE associated with impurities.

The energy and lifetime of the muon-induced luminescence indicates that the initial state is a triplet STE state. It is suggested from the analogous case of alkali iodides, where two π-luminescence bands π_1 (E_X) and π_2 are observed, that the initial STE state of the muon-induced luminescence is either (i) an excited state, e.g., $\sigma_g 2s\ ^3\Sigma_u^+$ (Ref. 13) [or its equivalent for off-center STE (Ref. 14)], or (ii) a lowest triplet STE with modified ionic configuration for the hole, e.g., Br_3^{2-}.[15] In the former case the high-energy muons might help to populate the excited state, while they might induce a metastable ion configuration in the latter case where even a catalytic role for muonium at an early time range ($\ll 10^{-6}$ s) might be considered.[16]. In both cases the interaction between muon (or muonium) and free excitons (i.e., the precursor state of STE) during their deexitation may play an important role in deriving such a modified STE state.

In summary, the muon-induced luminescence shows a large blueshift ($\sim$0.5eV) from the intrinsic π luminescence in KBr. The energy spectrum suggests that the initial STE state of this luminescence is a triplet STE state which is in an electronically excited state or in a different ionic configuration compared with the intrinsic STE.

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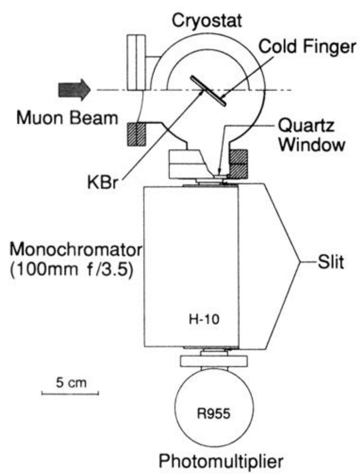

FIG. 1. A schematic diagram of the apparatus for the measurement of muon-induced luminescence spectrum. The cryostat vessel is connected to the monochromator through a quartz window.