Muonium Fluorescence: Anomalous Muonium Center and Relaxed Excited State in KBr

R. Kadono,[1] A. Matsushita,[1] and K. Nagamine[1,2]
[1]*Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan*
[2]*Meson Science Laboratory, Faculty of Science, University of Tokyo, Tokyo 113, Japan*
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A slowly decaying fluorescence [lifetime $\simeq 13.3(5)$ μs] induced by implanted positive muons has been observed in KBr by using the time-resolved direct-photon-counting method with a total yield of one photon per four incident muons below 30 K. The temperature dependence of the fluorescence yield shows a remarkable coincidence with that of the amplitude of the anomalous muonium center in KBr observed by the muon-spin-rotation method, strongly suggesting a coupled state between muonium centers and radiation-induced relaxed excited states as a model for the anomalous muonium centers.

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The relaxation process of energetic charged particles implanted into crystalline solids is one of the central issues both for radiation physics and for radiation detector applications. It is widely believed that the energetic particles are instantaneously ($< 10^{-12}$ s) degraded into thermal energy in solids due to energy dispersion predominantly by ionization of the host materials. While mounting experimental and theoretical works have been accumulated for the energy-transfer processes of the radiation particles at high energy, relatively little is known about the deexcitation of the implanted particles near the end of the process which must be largely dependent on the properties of the host crystal.

In this Letter we report the first successful measurement of the time-resolved luminescence spectrum associated with implanted positive muons which are known to form anomalous muonium ($\mu^+ e^-$) centers at low temperatures in KBr. The temperature dependence of the luminescence yield in KBr has a strong correlation with the amplitude of the anomalous muonium center: Both are observed only below ~ 50 K. This correlation as well as the relatively long lifetime of the luminescence (i.e., fluorescence) compared with that of muons strongly suggests a coupled state between muonium centers and relaxed excited states (e.g., self-trapped excitons) induced by radiation as a model for the anomalous muonium centers.

Muonium defect centers provide a unique opportunity to compare the electronic structures of simple defects in a wide range of materials which now include elemental and compound semiconductors [1], solid noble gases [2], and ionic insulators [3]. The muon-spin-rotation (μSR) spectroscopy under high transverse field has revealed two types of muonium centers distinguished by the hyperfine (hf) parameters in some crystalline solids, i.e., "normal" muonium (Mu) and anomalous muonium. Mu is a state analogous to the neutral interstitial hydrogen centers (e.g., H_i^0 or U_2 center in alkali halides [4]) characterized by a large isotropic hf interaction. While in semiconductors the anomalous center (Mu*) with highly anisotropic hf interaction has been identified as located in the bond center of the host crystal [5,6], the structure of the low-temperature centers (Mu^{I}) in KBr [3] or in copper halides [7] is still unclear, except for the known isotropic hf parameter which is either reduced (in KBr) or enhanced (in copper halides) compared with that of the high-temperature center (Mu^{II}). The striking similarity of the nuclear hyperfine (nhf) structure between Mu^{I} and Mu^{II} in CuCl, demonstrated recently by means of level-crossing resonance (LCR), indicates that both centers are in the same tetrahedral interstitial site [8]. Thus, the difference between those two centers in CuCl lies only in the relative shift of the electron spin density between the muonium center and the neighboring Cu and Cl shells.

Unfortunately, the extremely high LCR field prevents us from applying this technique to either Mu^{I} or Mu^{II} in KBr. However, the very recent development of the muonium spin T_1 relaxation technique has provided both dynamical and structural information on muonium centers in various host crystals including those in ionic insulators [9] and in compound semiconductors [10]. In particular, the average nhf coupling constants deduced by this technique have confirmed that in KBr the Mu^{II} center is a state analogous to the H_i^0 center [9] (corresponding to the "normal" Mu in other alkali halides) as suggested previously by a systematic study of muonium hf parameters in various alkali halides [3]. In comparison to Mu^{II} the enhanced spin density at the four nearest-neighbor anion sites together with the reduced hf coupling [3] strongly suggests that Mu^{I} is in an extended state which is stable only at lower temperatures.

In order to further investigate the structure and dynamics of the anomalous muonium centers from the standpoint of the host crystal excitation, we have measured the time-resolved luminescence in three alkali halide crystals including KBr under muon irradiation. The present experiment was conducted at Meson Science Laboratory, University of Tokyo (UTMSL, located at KEK) which provides a pulsed beam of $\sim 10^3$ positive muons per pulse with 50 ns width coming at a rate of 20 Hz. The single-crystal samples of KCl, NaCl, and KBr ([100] plane, 40 mm in diameter by 3 mm thick) were

obtained from Rare Metallic Co. Ltd. Muons of momentum 29 MeV/c ($\simeq$4 MeV in energy) were stopped in those samples and photons with 185–850 nm wavelength were measured directly by using a photomultiplier (Hamamatsu Co. model R2027). The arrival time of the discriminated signals from the photomultiplier relative to the incident muon beam pulse was recorded by a multistop time-to-digital converter (40 μs range) developed at UTMSL [11].

Typical examples of photon time spectra from KBr are shown in Fig. 1. The initial 10 μs of the spectra is dominated by the background events due to energetic positrons from muon decay with a lifetime of 2.2 μs. The second component with a longer decay time emerges in the spectra below 50 K. We also found that the second component is absent in the spectra for either KCl or NaCl at 20–300 K, where no state like Mu^I is reported. These spectra in Fig. 1 demonstrate that the pulsed muon beam is well suited to measure this kind of delayed rare event because of the low background level ($<10^{-4}$) during the pulse intervals. The solid curves in Fig. 1 are the best-fit results of the photon counting rate $n(t)$ by the form

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

where τ_μ ($=2.2$ μs) and τ_p are the decay times of positron and photon events, and n_μ and n_p are the respective counting rates at time origin. The excellent agreement between the data and Eq. (1) implies that the spectrum consists of a single component for the photons in this time range.

Since the detection efficiencies of the present photomultiplier including the solid angle are approximately equal for the photons and the high-energy positrons (mean energy $\sim$37 MeV) the positron component in the time spectra can be used to estimate the photon yield relative to the number of incident muons. Figure 2 shows the temperature dependence of the ratio $N_p/N_\mu \equiv n_p\tau_p/n_\mu\tau_\mu$ which is regarded as the total photon yield normalized by the muon dose. The yield in KBr shows a stepwise increase below 50 K in coincidence with that for the Mu^I centers [3], whereas no such behavior is observed, for example, in KCl. A relative yield of about one photon per four incident muons was observed in KBr below 30 K. Since more than 75% of the incident muons are known to form the Mu^I state in KBr below 50 K [12] the observed photon yield corresponds to one photon per three to four Mu^I centers. The lifetime of the luminescence was uniquely deduced from the fit analysis for the data below 45 K. As seen in the inset of Fig. 2, τ_p is almost independent of temperature, yielding an average $\tau_p=13.3(5)$ μs. The relatively small yield (i.e., $N_p/N_\mu<1$) and the long lifetime of the luminescence imply that those photons do not come directly from the initial excitations (e.g., free excitons) but rather from a relaxed excited state like a self-trapped exciton (STE).

It has been shown in a detailed study of the intrinsic luminescence under excitation by a pulsed electron or laser beam that the yield of the dominant π luminescence (2.28 eV) from the self-trapped exciton in KBr shows a temperature dependence similar to that of the muon-induced luminescence in Fig. 2 [13]. However, the lifetime of the π luminescence is $\sim$100 μs below 35 K which is far longer than that of the muon-induced luminescence, thereby indicating that the latter is not associated with the isolated STE. This, together with the missing muon-induced luminescence in KCl or NaCl in which only the normal muonium center is observed, suggests that the observed luminescence is strongly correlated with the existence of Mu^I, i.e., the muonium fluorescence.

We conclude from the current knowledge of the muonium and hydrogen centers that (a) Mu^I is not the ground state of a charged interstitial center (Mu^- or μ^+) which

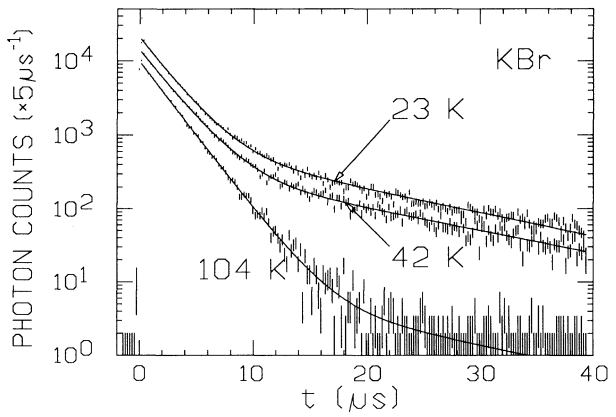

FIG. 1. Time spectra of photons from KBr after muon implantation at 23, 42, and 104 K.

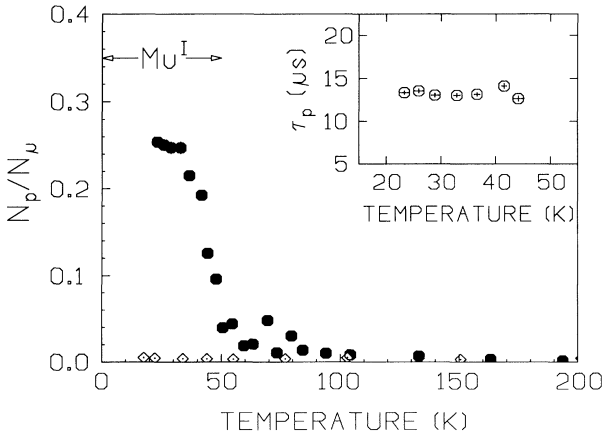

FIG. 2. Temperature dependence of the relative photon yield for the slow-decay component: filled circle, KBr; diamond, KCl. Inset: The lifetime for the photon component in KBr below 50 K.

would lead to a far smaller hf parameter, and (b) neither is it a substitutional center for which we would expect a shift of hf and nhf parameters in the opposite direction from those for the normal muonium as observed in the case for the hydrogen centers [14,15]. Meanwhile, the dynamical property of the normal muonium centers in alkali halides implies that they are in a small-polaron state which is highly mobile [9]. A van der Waals–type attractive interaction between polarons and excitons is generally expected in ionic crystals [16]. The marked coincidence of the temperature dependence between the photon yield and the Mu^I amplitude suggests that this polaron(muonium)-exciton interaction is responsible for the electronic structure for the low-temperature muonium center. The long τ_p compared with τ_μ implies that the relaxed excited state is weakly coupled with the muonium centers; otherwise we would have seen the shorter τ_p compared with the lifetime of the muonium center itself ($=\tau_\mu$). However, we note that this argument is not valid if the relaxation occurs in two (or more) steps where the photons are from the later step(s).

The explicit structure of the Mu^I center as a complex of muonium and relaxed excited states is still an open question. A hint is that fluorescence has been observed from the interstitial hydrogen centers in alkali halides doped with I^-, where the spin quartet of the charge-transfer-type relaxed excited states (i.e., $H_i^- + I^0$) are responsible for the long radiative lifetime ($\sim 10^{-6}$ s) [17]. One of the possible analogs for the Mu^I is then the spin multiplet of the charged states coupled with surrounding halogen atoms [18,19], though the observed small shift for the Mu^I hf parameter might be hard to explain by this model. More probably it may include some neutral defect centers near the muonium, e.g., Mu associated with STE or H centers. In this case the luminescence may be attributed to the STE perturbed by the nearby muonium. Spectroscopic information on the fluorescence would certainly be helpful in identifying the structure.

In conclusion, we have measured the time spectrum of the fluorescence from KBr immediately after positive muon implantation. The correlation between the fluorescence yield and the Mu^I amplitude strongly suggests the interaction between muonium centers and relaxed excited states as the origin of the anomalous muonium center in KBr. The present result also demonstrates the feasibility of combined spectroscopy between μSR and optical methods which has potentially many applications in materials research.

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[1] For a recent review see, for example, B. D. Patterson, Rev. Mod. Phys. **60**, 69 (1988).
[2] R. F. Kiefl, J. B. Warren, G. M. Marshall, C. J. Oram, and C. W. Clawson, J. Chem. Phys. **74**, 308 (1981).
[3] Hp. Baumeler *et al.*, Hyperfine Interact. **32**, 659 (1986); Hp. Baumeler, Ph.D. thesis, University of Zurich, 1988 (unpublished).
[4] J. M. Spaeth and M. Sturm, Phys. Status Solidi **42**, 739 (1970).
[5] R. F. Kiefl, M. Celio, T. L. Estle, G. M. Luke, S. R. Kreitzman, J. H. Brewer, D. R. Noakes, E. J. Ansaldo, and K. Nishiyama, Phys. Rev. Lett. **58**, 1780 (1987).
[6] R. F. Kiefl, M. Celio, T. L. Estle, S. R. Kreitzman, G. M. Luke, T. M. Riseman, and E. J. Ansaldo, Phys. Rev. Lett. **60**, 224 (1988).
[7] R. F. Kiefl, W. Odermatt, Hp. Baumeler, J. Felber, H. Keller, W. Kündig, P. F. Meier, B. D. Patterson, J. W. Schneider, K. W. Blazey, T. L. Estle, and C. Schwab, Phys. Rev. B **34**, 1474 (1986).
[8] J. W. Schneider, H. Keller, W. Odermatt, B. Pümpin, I. M. Savic, H. Simmler, S. A. Dodds, T. L. Estle, R. C. Duvarney, K. Chow, R. Kadono, R. F. Kiefl, Q. Li, T. M. Riseman, H. Zhou, R. L. Lichti, and C. Schwab, Hyperfine Interact. **64**, 543 (1990).
[9] For a recent review see, for example, R. Kadono, Hyperfine Interact. **64**, 615 (1990).
[10] R. Kadono, R. F. Kiefl, J. H. Brewer, G.M. Luke, T. Pfiz, T. M. Riseman, and B. J. Sternlieb, Hyperfine Interact. **64**, 635 (1990).
[11] F. Shimokoshi, Y. Kuno, K. Nagamine, and T. Yamazaki, Nucl. Instrum. Methods Phys. Res., Sect. A **297**, 103 (1990).
[12] R. F. Kiefl *et al.*, (unpublished).
[13] T. Karasawa and M. Hirai, J. Phys. Soc. Jpn. **40**, 128 (1976).
[14] Ch. Hoentzsch and J. M. Spaeth, Phys. Status Solidi B **88**, 581 (1978).
[15] G. Heder, J. R. Niklas, and J. M. Spaeth, Phys. Status Solidi B **100**, 567 (1980).
[16] T. Masumi, in *Physics of Polarons and Excitons in Polar Semiconductors and Ionic Crystals,* Proceedings of the Antwerp International Advanced Study Institute, edited by J. T. Devreese and F. Peeters (Plenum, New York, 1984).
[17] F. Lohse and J. M. Spaeth, Phys. Status Solidi B **93**, 153 (1979).
[18] J. M. Spaeth, Hyperfine Interact. **32**, 641 (1986).
[19] G. Kurz, Phys. Status Solidi **31**, 93 (1969).