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ESR in Mercury(II) Iodide Thiocyanate

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Powder of mercury(II) iodide thiocyanate (HgISCN) gives a weak electron spin resonance (ESR) signal at $g=2.003$ in the dark. When the powder is irradiated, the ESR-signal intensity increases during the exposure. When the light is turned off, the intensity decreases. The ESR-signal may be due to electrons trapped by lattice defects.

Mercury(II) iodide thiocyanate (HgISCN), was prepared for the first time by Rao and Watson[1] in order to study the photochromism of this compound, but its crystal structure was not investigated. In recent years,[2,3] though, the photochromic process of HgISCN has been studied in our laboratory by the use of the radioisotopic tracer technique. When powder of labeled HgISCN with radioactive tracers is exposed to sunlight, it immediately turns from orange yellow to black, and ^{203}Hg, ^{35}S and ^{131}I atoms diffuse toward the crystal surface and escape into atmosphere. On the other hand, the ^{14}C atom does not move. The black color of this powder is somewhat bleached by keeping it in the dark at room temperature for several months. These results suggest that the electrons belonging to $(SCN)^-$ or I^- may be optically excited to the conduction band and may be trapped by the lattice defects or impurity levels. These trapped electrons must show an ESR-signal. It was found that HgISCN is, optically, a very sensitive compound, showing the ESR-signal during irradiation with light, and thermally it is an unstable compound, decomposing at 165 °C. HgISCN seems to be a molecular compound between mercury(II) iodide and mercury(II) thiocyanate. The present paper will present the results of our ESR experiments.

Experimental

Materials. The powder of mercury(II) iodide thiocyanate was prepared as reported in a previous paper.[2,3] The chemical analysis with an atomic-absorption apparatus exhibited this Hg content for HgISCN: calcd 52.02%, obsd 53%, while the chemical analysis by a fused method[4] exhibited this S content for HgISCN: calcd 8.32%, obsd 8.0%. This powder shows photochromic behavior.

ESR. ESR measurements were made in the dark by the use of ESR equipment [JEOL, X-band] at a field of 3250 ± 250 G ($1\ \text{G}=10^{-4}$ T). Then, the HgISCN powder was irradiated at room temperature with a tungsten lamp of 150 W through the window of the cavity of the ESR equipment for the appropriate length of times. The ESR-signal intensity of the powder rapidly grew and then gradually approached saturation after 30 min irradiation. When the light was switched off after saturation has been reached, the ESR-signal decayed rapidly. The excitation intensity in front of the window of the cavity was measured as 7000 lx with a Toshiba luxmeter. The rise-and-decay ESR experiments were repeated at various temperatures (*cf.* Fig. 2). The temperature was controlled at about 60, 25, −10, and −50 °C by flowing through nitrogen gas, warmed with a heater or cooled with liquid nitrogen, into the cavity: it was measured by means of a copper-constantan thermocouple.

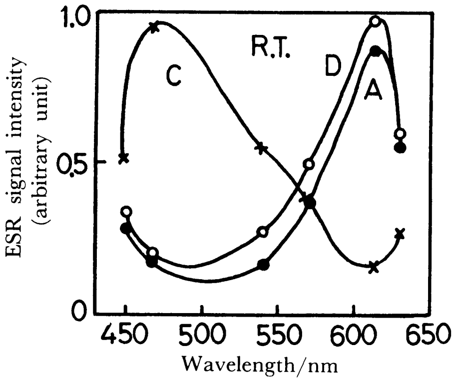

Fig. 1. Excitation spectra of the ESR signal intensity for A, C, and D. A: powder of HgISCN, C: one of the thermal decomposition products of $Hg(SCN)_2$, D: powder of $Hg(SCN)_2$ which was heated up to 155—158 °C.

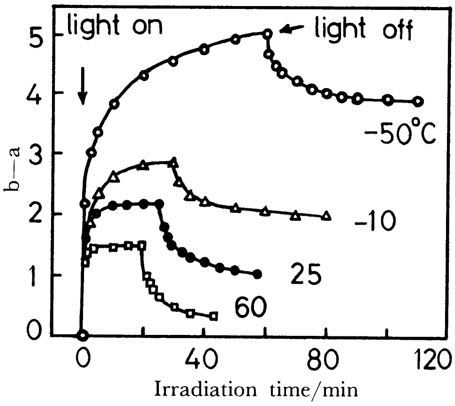

Fig. 2. The relationship between b—a and irradiation time at various temperatures. a is the ESR signal intensity of a nonirradiated HgISCN powder normalized to that of MnO. b is the ESR signal intensity of an irradiated HgISCN powder normalized to that of MnO.

Excitation Spectra of ESR-signal. Monochromatic light was obtained by the use of six filters made by the Shimadzu Co. The radiation from the tungsten lamp was selected with filters and was focussed on a capillary glass tube containing HgISCN powder (*cf.* Fig. 1).

Results and Discussion

ESR-signal of Nonirradiated Powder of HgISCN. A weak signal for the nonirradiated orange yellow powder of HgISCN, which is conveniently denoted by A, was observed at $g=2.003$. The observed ESR-signal of A is ascribed not to an impurity, but to a defect in A. This can be explained as follows. A was formed when a mixture of mercury(II) iodide and mercury(II) thiocyanate was heated at 162 °C. The mixture heated only to 150 °C gave no ESR-signal at all. When heated up to 155—158 °C, though, the mixture begins to show the ESR-signal (g=2.003). This signal may be due to mercury(II) thiocyanate, because mercury(II) thiocyanate heated to 155—158 °C, denoted by D, gives a weak ESR-signal at g=2.003, while mercury(II) iodide heated to the same temperature shows no ESR-signal. Mercury(II) thiocyanate decomposes at 165 °C into a black powder, denoted by B, and into a yellow powder, denoted by C. B and C gave weak signals at g=2.003. The signal intensity of B was not sensitive to light, but that of C was sensitive to light. B was removed from A by washing with concentrated hydrochloric acid containing pottasium chlorate. The X-ray diffraction pattern of A was different from those of B, C, and D. The patterns of B and D were similar to those of cubic mercury(II) sulfide and of mercury(I) thiocyanate respectively, while the pattern of C showed that C is a nearly amorphous material. In order to make clear the origin of the ESR-signal of A, the excitation spectra of the ESR-signal was measured. The spectra of A and D were similar to each other, while the spectrum of C was entirely different from that of A or D (*cf.* Fig. 1). Consequently, when the mixture is heated to 155—158 °C, the mixture may begin to form a structure of A, although its fraction may be small. In order to form A, the mixture must be heated to 162 °C. It is not clear, however, whether the observed ESR-signal of A is attributed to the lattice defects which are formed in A in the 155—162 °C range or to the signal of D, which exists in A as an impurity. This problem was solved by the following experiment. If A contains a small quantity of D as an impurity, the ESR-signal intensity of a mixture of A and D must become stronger than that of A when a small quantity of D is added to A. Various quantities of D were added to A, and the ESR-signals of these mixtures were measured at room temperature. Quantities of mixtures in the quartz-glass capillary tube were kept constant in order to keep the quality factor in the cavity constant. The experimental results show that the ESR-signal intensities of A containing D at 4.17, 8.30, or 12.5 wt% of D are smaller than the intensity of alone A and that they gradually decrease according to the increase in the content of D (*cf.* Fig. 3). This fact shows that the signal of A is attributed not to the signal of D in A as an impurity, but to the lattice defects in A.

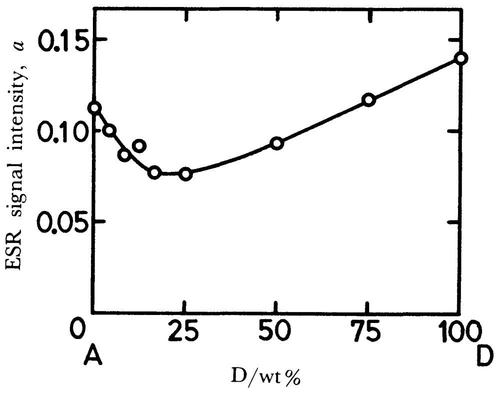

Fig. 3. The relationship between the ESR signal intensity in the dark of A containing D at various weight percents and the weight percent of D. The ESR signal intensities are normalized to that of MnO.

ESR-signal of Irradiated HgISCN. A quartz-glass capillary tube containing MnO powder was put into the cavity. The ESR of MnO was then measured as a standard of the ESR-signal at the same time as the ESR of A put into another quartz-glass capillary tube was measured. When A was irradiated with a tungsten lamp, MnO powder was irradiated at the same time. The ESR-signal intensity of MnO during the exposure did not change from that of MnO in the dark. When a is the signal intensity of A in the dark normalized to that of MnO, and b is the signal intensity of an irradiated A normalized to that of MnO, b—a means the increase in the signal intensity during exposure to the light. Figure 2 shows the b—a relationships and the irradiation times at various temperatures. The rising curves of the ESR-signal intensity during the irradiation show the speed at which the traps are filled with excited electrons. The saturation value of b—a was reached after about 10 min under the irradiation at 60 °C, but the saturation was not reached even after 60 min under the irradiation at −50 °C. The decay curves of the ESR-signal intensity show the detrapping speed of electrons from the traps. When the light was switched off at the saturation of b—a at 60 °C, the value of b—a decreased rapidly; it approached a zero value after 20 min. When the light was switched off after saturation had been reached at −50 °C, the value of b—a decreased slowly, but it was still somewhat big even after 60 min. It takes a long time at −50 °C before the value of b—a reaches zero.

Under constant excitation with light, the rising-and-decay curves of the ESR-signal intensity may be discussed by the use of a simple electron-trapping model in terms of a simple first-order reaction equation. If F is the number of photons absorbed per unit of volume per unit of time, the number of optically excited electrons may be proportional to F. It is assumed that the θ fraction of mF, where m is the proportional constant, is trapped by trap and that the $(1-\theta)$ fraction of mF is consumed by recombination or fluorescence. If p is the probability of an electron escaping from a trap with a depth of E and a cross-section for the capture of an electron, S, at a certain temperature T, the filling speed of an electron into a trap may be given by $\mathrm{d}n/\mathrm{d}t=\theta mF-np$, where n is number of trapped electrons and $p=NvS\cdot\exp(-E/kT)$.[5] N is the effective density of states in the conduction band, v is the thermal velocity of an electron, and k is the Boltzmann constant. At saturation with a value of b—a, $\mathrm{d}n/\mathrm{d}t=0$ and $\theta mF=n_0p$, where n_0 is the value of n at the saturation. Then, $\mathrm{d}n/\mathrm{d}t=p(n_0-n)$. The solution of this equation is:

$$n = n_0(1-\mathrm{e}^{-pt}). \qquad (1)$$

The rate of change of the number of trapped electrons during the decay is $-\mathrm{d}n/\mathrm{d}t=np$. The solution of this equation is:

$$n = n_0 e^{-pt}. \qquad (2)$$

The rising-and-decay curves of the ESR-signal intensity are shown by Eqs. 1 and 2 respectively. These equations contain the term of $1/e^{E/kT}$. At some time t, a value of $1/e^{pt}$ at a higher temperature may become smaller than those at a lower temperature if N, v, S, and E are independent of the temperature in the range of 60—−50 °C. Therefore, it is expected that, at 60 °C, n may rapidly increase and n_0 may be reached rapidly after irradiation. At −50 °C, n may slowly increase, and n_0 may be reached slowly after irradiation. Similarly, the decay rate may be effected to be big at 60 °C and small at −50 °C. The value of n_0 at −50 °C in Fig.2 is bigger than that at 60 °C. This comes from the fact that the lower the temperature, the greater the number of the trapped electrons. The results in Fig.2 nearly satisfy these expectations. The actual filling and detrapping speeds may be a mean of the individual speeds for the individual traps with a given depth E, because there are a number of traps with various depths.

Excitation Spectra of ESR-signal. The excitation spectra of the ESR-signal of HgISCN at room temperature are shown in Fig. 1. The most sensitive wavelength of the ESR-signal is located at about 620 nm.

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