ESR Study of Hot Ions in Solid Solutions of $K_2[(Zn,Cd,Hg)(CN)_4]$

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The ESR spectra of Cd(I) hot ions produced in solid solutions of $K_2[(Zn, Cd, Hg)(CN)_4]$ indicate that there are paramagnetic species of hot-ion molecules characteristic of the single phase of $K_2[Zn(CN)_4]$ and of the solid solution. The total contribution from the s and p orbitals to the spin density of the Cd(I) hot ions is constant, although the relative contributions from these two orbitals vary. It is shown that the mother lattice surrounding the hot ions determines the electronic structure and stability of the hot ions. These results suggest that the investigation of hot ions in a solid solution is useful for the study of microstructure of the solid solution.

Electron spin resonance (ESR) is useful for the investigation of the "hot ions"[1] which are produced by the X-ray or γ-ray irradiation of diamagnetic complexes. A large number of investigations have been carried out on various species of central metal ions.[2-5] An unpaired electron in a hot-ion molecule of Zn(I), Cd(I), Hg(I) can be described in terms of a ground state with a large s-orbital character. As a matter of fact, a considerable contribution of the s-orbital to the ground state of the metal ions has been experimentally evidenced by the large isotropic hyperfine coupling constants.[3-6]

This paper will report on the effect of a "solid solution" on the character of hot ions. It will be shown how the mother lattice of hot ions affects the electronic state of the latter, particularly with respect to their stabilities. Two different kinds of metal ions were mixed together, thus being made into cyanide complexes, where each of the metal ions produces hot ions with the unpaired electron in the s-orbital. By the γ-ray irradiation of the cyanide complexes, hot ions were produced therein. ESR was observed in the products. The ESR spectra thus obtained were compared to those of the hot ions produced in the complex compound of one of the composing metal ions (which will be referred to, hereafter, as the single-phase compound). It was found that the solid-solution sample presented new lines besides the lines of the latter which were found in the single-phase compound. This result seems to refer to the fact that the components of the sample of a solid solution are not homogenous with respect to the distribution of the components; rather each component exists in two forms, one surrounded by the metal ions of the same kind, and the other, by those of other species. The lifetimes of the hot ions differ from each other according to the type. The observed results will be discussed in correlation with the electronic structures of the hot ions.

Experimental

Samples of the cyanides of the mixed metal ions were prepared by the evaporation of a mixed aqueous solution of $K_2[M(CN)_4]$ and $K_2[M'(CN)_4]$, where M and M′ are one of three combinations; Zn and Cd, Zn and Hg, and Cd and Hg. The samples were sealed *in vacuo* (10^{-6} mmHg) and irradiated by γ-rays from a ^{60}Co source at the temperature of liquid nitrogen. After the irradiation, the ESR spectra of the samples were recorded with a JELCO 3BSX spectrometer at the temperature of liquid nitrogen.

Results

The ESR spectra of the γ-ray irradiated solid solutions are shown in Figs. 1—4. All the spectra were almost symmetrical with respect to the center of $g=2$, presenting a structure of very large hyperfine coupling constants. (In order to save space, each figure shows only half of each spectrum.) The ratios which can be seen in the figures refer to the compositions of the mother solutions, not to the compositions of the solid samples. However, we assume that this fact will not disturb any of the discussions to be given below. In the case of the $K_2[(Zn,Cd)(CN)_4]$ system (Fig. 1), one can distinguish three lines, I, II, and III. All these lines are

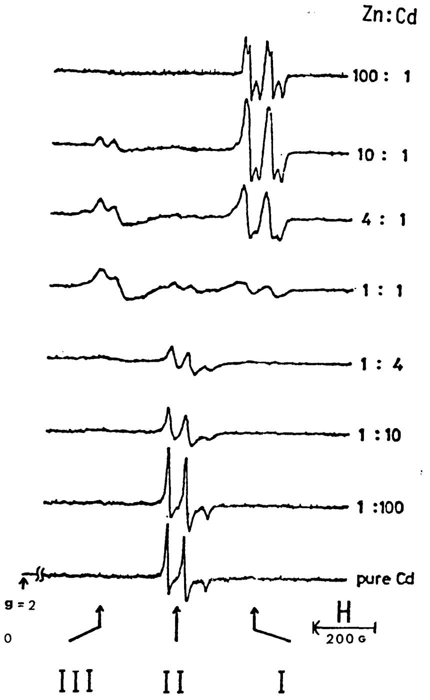

Fig. 1. ESR spectra of the Cd(I) hot ion in the $K_2[Zn(CN)_4]$-$K_2[Cd(CN)_4]$ solid solution. ($F=0$, $m_F=0$) ($F=1$, $m_F=+1$) transition for the ^{111}Cd and ^{113}Cd isotopes. The spectrum in the figure represents a half of the lower-field side of the hfs of Cd(I).

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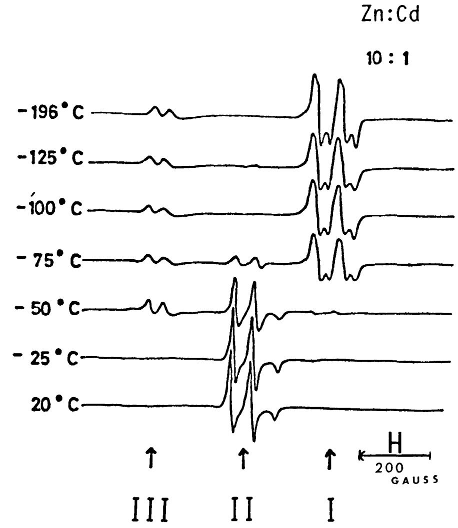

Fig. 2. ESR spectra of the Cd(I) hot ion in the $K_2[Zn(CN)_4]$-$K_2[Cd(CN)_4]$ solid solution with the molar ratio of 10 : 1. The spectra were measured at 77 K after the solution has been annealed at the temperatures indicated in the figure.

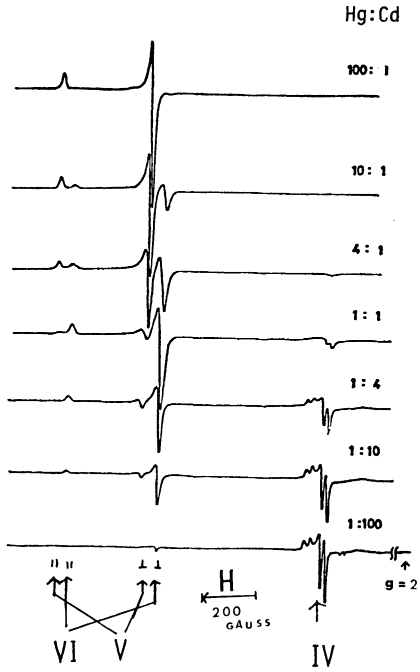

Fig. 3. ESR spectra $((F=1, m_F=-1)\ (F=1, m_F=0))$ of the Cd(I) (high field) and Hg(I) hot ions in the $K_2[Hg(CN)_4]$-$K_2[Cd(CN)_4]$ solid solution. Only the high-field side of the hf line is shown.

formed of two lines which have already been recognized as those of Cd(I) in the single-phase compound of cadmium. Those two lines are attributable to the isotopes of ^{111}Cd and ^{113}Cd. Each of the two lines shows a composite structure attributable to the contribution of the anisotropic nature of the electron. A comparison of the spectrum of Fig. 1 to that of the Cd(I) hot ion in the single-phase compound shows that Line II is attributable to Cd(I), which is surrounded by Cd(I), whereas Lines I and III are new lines of Cd(I) which have appeared in the solid-solution sample. Both of them are stable at the temperature of liquid nitrogen. However, they show an appreciable temperature dependence when they are annealed for 15 min at some elevated temperature and then cooled to the temperature of liquid nitrogen for the performance of the ESR measurements. Figure 2 shows the spectra at the temperature of liquid nitrogen after annealing at different temperatures. Lines I and III vanish with the elevation of the temperature. It is remarkable that the intensity of II increases parallel with the decreses in I and III. This seems to suggest that the unpaired electrons in I and III are transferrable to II. As may be seen in Fig. 3, similar results are also observed with the system of $K_2[(Cd,Hg)(CN)_4]$, where the lines of VI refer to Hg(I), characteristic of a solid-solution system; the V lines, to Hg(I) in $K_2[Hg(CN)_4]$, and the IV lines, to Cd(I) in $K_2[Cd(CN)_4]$. In the case of $K_2[(Zn,Hg)(CN)_4]$, it is noted that the position of Line VIII, which can be assigned to Hg(I) in the solid solution, is close to that of Hg(I) in the single-phase compound, VII (*cf.* Fig. 4). The solid-solution signals of Hg(I) in $K_2[(Cd,Hg)(CN)_4]$ become observable upon slight warming, even if they cannot be detected immediately just after irradiation. The observed results can be summarized as follows: 1) the hot ions are produced in the γ-ray irradiated mixed solid solutions, $K_2[(M,M')(CN)_4]$; 2) they are classified into two types, one characteristic of the mixed solution (Signals I, III in Fig. 1, VI in Fig. 3, and VIII in Fig. 4), and the other the same as that produced in the single-phase compound (to be referred to as the pure sample hereafter), $K_2[M(CN)_4]$ (II in Fig. 1, IV and V in Fig. 3, and VII in Fig. 4). Spin Hamiltonian parameters

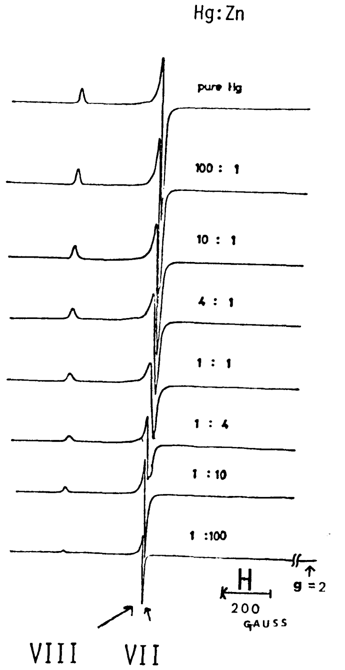

Fig. 4. ESR spectra of the Hg(I) hot ion in the $K_2[Hg(CN)_4]$-$K_2[Zn(CN)_4]$ solid solution. $(F=1, m_F=-1)$, $(F=1, m_F=0)$ transition of the ^{199}Hg isotope.

TABLE 1. ESR PARAMETERS FOR Cd(I) IONS IN THE $K_2[Zn(CN)_4]$ LATTICE

T [K]	Isotope	A (G)	g
liq N_2	113	$A_z=1815$	$g_1=1.978$
		$A_y=1745$	$g_2=1.996$
		$A_x=1718$	$g_3=1.998$
		$A_{av}=1759$	$g_{av}=1.990$
	111	$A_z=1735$	$g_1=1.979$
		$A_y=1668$	$g_2=1.995$
		$A_x=1642$	$g_{av}=1.990$
143	113	$A_{av}=1790$	$g_{av}=1.991$
	111	$A_{av}=1714$	$g_{av}=1.990$
163	113	$A_{av}=1811$	$g_{av}=1.991$
	111	$A_{av}=1731$	$g_{av}=1.991$
183	113	$A_{av}=1833$	$g_{av}=1.992$
	111	$A_{av}=1745$	$g_{av}=1.992$
Pure salt : Cd(I) in the $K_2[Cd(CN)_4]$ lattice			
liq N_2	113	$A_{av}=1510$	$g_{av}=1.989$
	111	$A_{av}=1440$	

were obtained for the Cd(I) hot ions, Species I in the $K_2[Zn(CN)_4]$ lattice, and Species II in the $K_2[Cd(CN)_4]$ lattice. All these results are shown in Table 1.

Discussion

The aforementioned results refer to the effect of a solid solution—that the hot ions differ depending on their surroundings, whether they are embedded in a lattice of metal ions of same kind or in one of ions of a different kind. The difference in the electronic natures of these two cases can be derived from the ESR parameters below.

A $K_2[Cd(CN)_4]$ molecule has a Td symmetry. Assuming that the Cd(I) hot ion still holds the position of Cd(II) in the mother lattice, the ground state may be expressed as

$$\phi^\circ = c_i\phi_{ns} + \sum_j K_j\phi_{j,\mathrm{lig}}, \tag{1}$$

where ϕ_{ns} is the s-orbital of the metal ion and where $\phi_{j,\mathrm{lig}}$ are the wave functions of the ligand; the symmetry of this state is A_1. In Cd(I) hot ions, however, the symmetries of the g and A tensors are C_{3v} in the pure salt[3] and orthorhombic in the $K_2[Zn(CN)_4]$ lattice. Therefore, the contribution from the np and the nd orbitals must be added to the ground state in the case of Cd(I) hot ions. The energy of the nd orbitals is assumed to be much higher than that of ns. Hence, it seems reasonable to represent a ground-state function as

$$\phi^\circ = c_1\phi_{ns} + c_2\phi_{np_z} + \sum_j K_j\phi_{j,\mathrm{lig}}. \tag{2}$$

The np_z orbital is assumed to have an A_1 symmetry as ns. Accordingly, the two orbitals of np_z and ns are assumed to be able to mix with each other. The spin-orbit interaction between the ground state and the np_x and np_y orbitals contributes to the g anisotropy. Neglecting the overlap integrals with ligands, the g-shift at the axial component is given by

$$\Delta g = -\frac{2\xi_{np}}{\Delta E}c_2^2, \tag{3}$$

where ξ_{np} is a spin-orbit coupling constant and where ΔE is the energy difference between the ground state and the $np_{x,y}$ orbitals.[7] This equation enables us to estimate the contribution of the p_z orbital to the ground state.

Using these values: $\xi_{np}=1000$ and $4000\ \mathrm{cm}^{-1}$, and $\Delta E=33000$ and $40000\ \mathrm{cm}^{-1}$ for Cd(I) and Hg(I) ions respectively,[8] the values of c_2^2 for the pure salt are obtained, with the use of the g-values reported in a previous paper,[3] to be as shown in parentheses in

TABLE 2a. MOLECULAR ORBITAL PARAMETERS FOR HOT ION AT THE TEMPERATURE OF LIQUID NITROGEN

Type of hot ion	c_1^2	c_2^2	$c_1^2+c_2^2$
Species II of			
Cd(I)	0.33	0.24(0.23)[a)]	0.57
Hg(I)	0.38	0.19(0.21)[a)]	0.57

a) Values in parentheses were obtained from the Δg values.

TABLE 2b. TEMPERATURE DEPENDENCE OF THE MOLECULAR ORBITAL OF THE SPECIES I OF Cd(I), Cd(I) IN $K_2[Zn(CN)_4]$

T	c_1^2	c_1^2	$c_1^2+c_2^2$
liq N_2	0.38	0.18	0.56
143 K	0.39		
183 K	0.40		

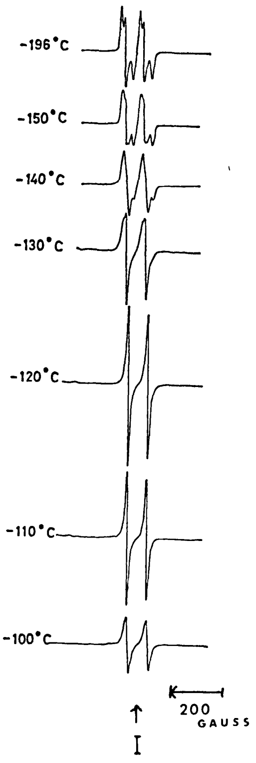

Fig. 5. Temperature dependence of the ESR spectra of the Cd(I) hot ion (Species I) in the $K_2[Zn(CN)_4]$ lattice.

Table 2. With the use of the A tensor components, the contributions from the s-orbital, c_1^2, and those of the p orbital, c_2^2, to the graund state are also calculated (*cf.* Table 2). The good agreement between the two c_2^2 values obtained from the g and A tensors justifies the formerly presented assumption that the overlap integral is negligible. In Fig. 5, the temperature dependence of the ESR spectra of Species I is presented. The spectra in the figure were measured at the temperatures cited. For the Cd(I) hot ion (Species I) in the $K_2[Zn(CN)_4]$ lattice, the values of c_1^2 and c_2^2 can be evaluated from the values of the A tensor, as is shown in Table 2. From the axial spectra at rather high temperatures, only c_1^2 can be determined. This value increases with the temperature; the averaged g value also increases slightly. From Table 2 it can be seen that, for the Cd(I) ion, the total contribution from the s and p_z orbitals is almost constant in all the cases examined, even if the relative contributions from the s and p_z orbitals vary. This may also refer to the fact that all of the ESR spectra arise from the same chemical species, which are little different with respect to the nature of the symmetry of the ion. The magnitude of the ratio of the s- and p-orbital contributions may serve as a measure of the distortion of the symmetry. The increase in the c_1^2 and g values suggests that the symmetry of the molecule becomes higher with an increase in the temperature. For a better understanding of this dynamic phenomenon, though, a further study of the ESR on a single crystal is necessary.

From a comparison between the pure salt and the solid-solution data for the Cd(I) ion, it is concluded that the symmetry of the hot ion in the $K_2[Zn(CN)_4]$ lattice (Species I) is higher than that of any other species in the pure salts.

In order to interpret the fact that Species II appear along with the decay of Species I and III (*cf.* Fig. 2), we have to assume that some aggregates of the Cd(II)-ion molecules exist in the sample. When Species I and III dacay, excess electrons are transferred to those aggregates and produce Cd(I) hot ions in the lattice of $K_2[Cd(CN)_4]$, which has been produced locally. As a result, this kind of species is relatively stable and can be observed even at higher temperatures. As to the exact nature of Species III, a further investigation of the single-crystal sample will be needed.

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