Spectroscopic Study of Concentration Fluctuation and Intermolecular Interaction in Liquid

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The band widths of the infrared absorption spectra were observed for binary solutions of methyl iodide, methyl cyanide, chloroform, and carbon disulfide. The observed bands are: the ν_1 fundamental of chloroform in carbon disulfide and in carbon tetrachloride; the ν_2 fundamental of methyl iodide in methyl cyanide, nitromethane, benzene, carbon disulfide, and carbon tetrachloride; the $2\nu_2$ band of methyl iodide in methyl cyanide, and the ν_8 and $2\nu_8$ bands of methyl cyanide in methyl iodide. The concentration dependence of a band width was explained in terms of the concentration fluctuation. The theory was compared with the observed band widths, together with the light-scattering data. A fluctuation volume was related with the intermolecular interactions in these binary solutions.

Gordon1) and Shimizu2) have shown that a shape of an infrared absorption band of a liquid or a solution can be interpreted as the Fourier transform of a time-correlation function of a transition dipole moment. The time-correlation function of a transition dipole moment is considered to be determined mainly by the reorientational motion of molecules. Many reports have been published which have determined the rate of molecular reorientation in liquids or solutions from measurements of the shapes of infrared-absorption bands.3–6) However, the time-correlation function of a transition moment may be affected by many other factors than the reorientational motion of molecules. Among these factors, two important factors, namely, the vibrational relaxation and the vibration-rotation interaction, have been shown to affect the observed band shape considerably in some cases.7,8) The former of the two factors is concerned with the decay of an excited vibrational level, and the latter, with the fact that a transition moment is not fixed to a molecular frame in the case of a degenerate-type vibration of a symmetric top molecule. Taking into account the effects of these factors, the present authors have succeeded in explaining the abnormal behavior of the half-band width of carbon disulfide7) and of methyl cyanide8) in liquid and in solutions. Recently, Bondarev and Mardaeva9) have suggested that the concentration fluctuation affects the half-band width of the spectra of solutions.

The present report will be concerned with the observation of the half-band widths of the infrared-absorption spectra for a few binary solutions and with the introduction of concentration fluctuation to the explanation of the band widths. A consideration of the nature of the concentration fluctuation observed from the infrared spectra will be given, together with a detailed description of the relation between the half-band width of the infrared absorption spectra and the concentration fluctuation.

Experimental

All the chemicals used in the present study were commercial products. The methyl iodide was distilled just before the observation to remove its pale yellowish color. The other samples were used without further purification, although the infrared spectra of methyl cyanide showed a small amount (about 0.5 wt %) of water in it, the presence of water in methyl cyanide seems to cause no serious error.

The binary solutions were prepared just before the observation in order to attain the appropriate concentration by measuring the weight of each component. The mole percentage was calculated by the use of the density data.10)

The infrared absorption spectra were measured with a Perkin-Elmer 112G single-beam infrared spectrometer (the ν_1 band of chloroform, and the ν_2 and $2\nu_2$ bands of methyl iodide). A Perkin-Elmer 12C single-beam infrared spectrometer mounted with a CsBr prism was used to measure the ν_8 band of methyl cyanide in a methyl iodide solution. A Hitachi EPI-G2 double-beam infrared spectrometer was used to measure the $2\nu_8$ band of methyl cyanide in a methyl iodide solution.

The spectrometers were operated under a resolution of about 1 cm^{-1} except for the case of the ν_8 and $2\nu_8$ bands of methyl cyanide, where the resolution was about 2—3 cm^{-1}. The effect of the finite slit width on the observed spectra was found to be very small. All the measurements were carried out at room temperature (25 °C). The frequencies were calibrated by the use of atmospheric water-vapor or carbon dioxide lines for the 112G spectrometer, and by the use of atmospheric water-vapor or methanol-vapor lines for the 12C spectrometer.

The observed spectra were reduced to the absorption index curve, $k(\nu)$. We fitted a Lorentzian curve to the observed $k(\nu)$ curve by the method of least-squares. The half-width and peak frequency of a band were determined as the parameters of the Lorentzian curve.

Results and Discussion

Half-band Width and Concentration Fluctuation. Consider the case where a peak frequency of a spectral line varies according to the concentration variation. We will confine our discussion to a binary solution. The two components of a binary solution will be denoted hereafter as 1 and 2. All the symbols suffixed by 1 and 2 correspond to the 1 or 2 component, respectively. When a sample of the binary solution is prepared to give a mole fraction of one component, x_1°, the actual mole fraction, x_1, is not always the same as x_1°, but has a distribution around x_1°. The difference between x_1 and x_1° is denoted as Δx_1:

$$x_1 = x_1^\circ + \Delta x_1 \tag{1}$$

Corresponding to the distribution of x_1, the peak frequency, ν_1, also has a distribution:

$$\nu_1 = \nu_1^\circ + \Delta\nu_1 \tag{2}$$

where ν_1° corresponds to a peak frequency at a mole fraction of x_1°, and where $\Delta\nu_1$ is expressed as:

$$\Delta\nu_1 = \frac{\partial\nu_1}{\partial x_1}\Delta x_1 \tag{3}$$

A spectral band of a 1 component directly reflects the distribution of $\Delta\nu_1$. If there is no broadening factor for the spectral band other than the concentration fluctuation, and if a Gaussian distribution is assumed to be the distribution of $\Delta\nu_1$, a normalized intensity distribution, $I(\Delta\nu_1)$, of the band may be expressed as:

$$I(\Delta\nu_1) = \frac{1}{\sqrt{2\pi\langle\Delta\nu_1^2\rangle}}\exp\left[-\frac{\Delta\nu_1^2}{2\langle\Delta\nu_1^2\rangle}\right] \tag{4}$$

where $<\ >$ means a statistical average. Then, a half-band width, $\Delta\nu_{1/2}$, of the band is:

$$\Delta\nu_{1/2} = 2\sqrt{2\ln 2}\sqrt{\langle\Delta\nu_1^2\rangle} = 2\sqrt{2\ln 2}\left|\frac{\partial\nu_1}{\partial x_1}\right|\sqrt{\langle\Delta x_1^2\rangle} \tag{5}$$

Let the N_1 and N_2 molecules of the components be contained in a volume in which the concentration fluctuation takes place. We call this volume the "fluctuation volume." Then, we can write:

$$x_1 = \frac{N_1}{N_1+N_2} \tag{6}$$

and:

$$\Delta x_1 = \frac{N_2}{(N_1+N_2)^2}\Delta N_1 \tag{7}$$

It is derived by the method of statistical mechanics that

$$\langle\Delta N_1^2\rangle = kT\Big/\left(\frac{\partial\mu_1}{\partial N_1}\right)_{T,P} \tag{8}$$

where k is the Boltzmann constant; T, the absolute temperature; P, the pressure, and μ_1, the chemical potential. The chemical potential is expressed as:

$$\mu_1 = kT\ln x_1 \tag{9}$$

if the solution is considered to be an ideal solution. A straightforward calculation using Eqs. (6) through (9) leads to:

$$\langle\Delta x_1^2\rangle = \frac{x_1(1-x_1)}{N_1+N_2} \tag{10}$$

which, combined with Eq. (5), gives:

$$\Delta\nu_{1/2} = \sqrt{2\ln 2}\left|\frac{\partial\nu_1}{\partial x_1}\right|\sqrt{\frac{x_1(1-x_1)}{N}} \tag{11}$$

where:

$$N = N_1 + N_2 \tag{12}$$

is the number of molecules contained in the fluctuation volume. Equation (11) tells us that the necessary conditions for the appearance of the broadening of this type are a large change in a peak frequency and a small number of molecules in the fluctuation volume. When these conditions are satisfied, the broadening appears to a measurable extent; the maximum width occurs at $x_1=0.5$.

Comparison with Observed Data. Figure 1 shows the half widths, γ's, of the infrared absorption band of the ν_1 fundamental of chloroform observed in the carbon disulfide and carbon tetrachloride solutions. It may be seen from the figure that the concentration dependence of γ is quite different in the two solutions. In the carbon disulfide solution, γ increases in magnitude as the concentration decreases down to 50 mole percent, and then it decreases as the concentration decreases. This is just the same as what the factor, $\sqrt{x_1(1-x_1)}$, of Eq. (11) predicts. In the carbon tetrachloride solution, on the other hand, γ takes an almost constant value over the whole concentration range. As is shown in Fig. 2, the concentration dependence of the peak frequency of the ν_1 band of chloroform has a strong dependency on the concentration in the carbon disulfide solution at all the concentrations. This fact is consistent with the result of Eq. (11) namely, the line broadening due to the concentration fluctuation is proportional to the magnitude of the change in the peak frequency

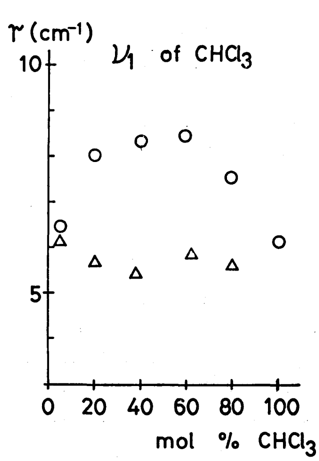

Fig. 1. Concentration dependence of the half width, γ, of the infrared absorption band of the ν_1 fundamental of chloroform. The circles and triangles correspond to those observed in carbon disulfide solutions and in carbon tetrachloride solutions, respectively.

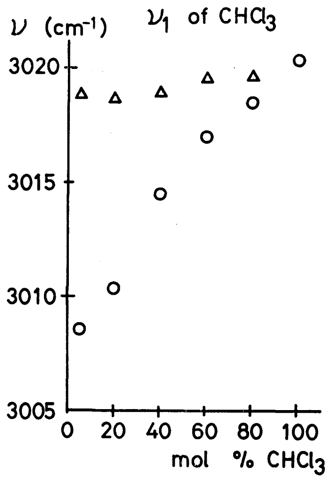

Fig. 2. Concentration dependence of the peak frequency of the infrared absorption band of the ν_1 fundamental of chloroform. The circles and triangles correspond to those observed in carbon disulfide solution and in carbon tetrachloride solution, respectively.

against the concentration. Similar phenomena were observed for the ν_2 band of methyl iodide in nitromethane, methyl cyanide, carbon tetrachloride, benzene, and carbon disulfide solutions. The results are given in Figs. 3 and 4. It may be seen from the figures that a broadening of this type is observed for the ν_2 band in methyl cyanide or nitromethane solutions, and that the shifts of the peak frequencies are very large in these solutions. Figure 4 shows that the frequency shift of the $2\nu_2$ band is about two times that of the ν_2 band in methyl cyanide solutions. In Eq. (11), all the factors except $|\partial\nu_1/\partial x_1|$ should be the same for these two absorption bands. Thence, the broadening of the $2\nu_2$ band should be about two times that of the ν_2 band, which is seen to be true in Fig. 3.

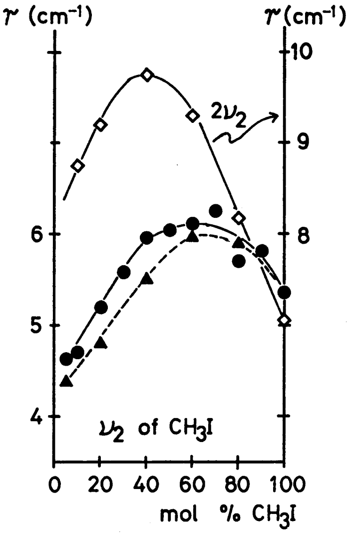

Fig. 3-a. Concentration dependence of the half width, γ, of the infrared absorption band of the ν_2 and $2\nu_2$ of methyl iodide. The open squares correspond to the $2\nu_2$ band observed in methyl cyanide solutions. The closed circles and closed triangles correspond to the ν_2 band observed in methyl cyanide solutions and in nitromethane solutions, respectively.

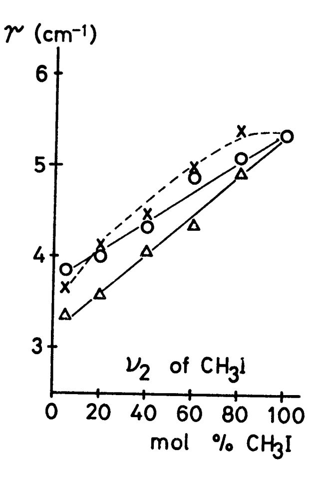

Fig. 3-b. Concentration dependence of the half-width, γ, of the infrared absorption band of the ν_2 band of methyl iodide. Used solvents are: ×; benzene, ○; carbon disulfide, △; carbon tetrachloride.

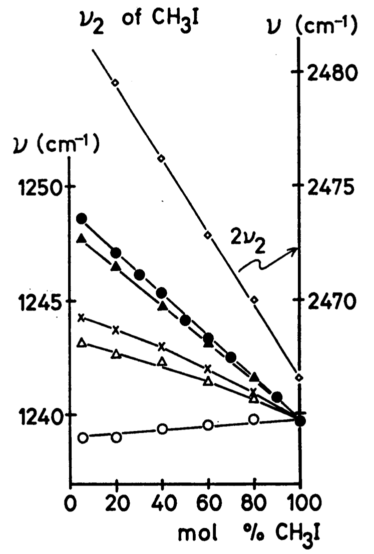

Fig. 4. Concentration dependence of the peak frequencies of the ν_2 and $2\nu_2$ infrared absorption bands of methyl iodide. The open squares correspond to the $2\nu_2$ band in methyl cyanide solutions. Used solvents are: ●; methyl cyanide, ▲; nitromethane, ×; benzene, △; carbon tetrachloride, ○; carbon disulfide.

The observed band widths are composed not only of the width due to concentration fluctuation, but also of those due to the other factors the reorientational motion of molecules, vibrational relaxations, and so on. When $|\partial\nu/\partial x|$ is small, an observed band width is thought to be independent of the concentration; an example of this is the ν_1 band of chloroform in the carbon tetrachloride solution (see Fig. 2).[11] Therefore, the part of the band-width caused by the concentration fluctuation, γ_f, is expressed as:

$$\gamma_f = \gamma - \gamma' \tag{13}$$

where γ is an observed band width, and where γ' is a width caused by the other factors. We consider that γ' is expressed as:

$$\gamma' = \gamma_0 + x(\gamma_1 - \gamma_0), \tag{14}$$

where x is a mole fraction; γ_1 and γ_0 are the observed band widths at $x=1$ and $x=0$ respectively. Thus, $\Delta\nu_{1/2}$ of Eq. (11) is defined as:

$$\Delta\nu_{1/2} = 2\gamma_f. \tag{15}$$

In the case of the $2\nu_8$ band of methyl cyanide, which is shown in Fig. 5, no reliable change in the half-band width due to concentration fluctuation was observed, although the peak-frequency change due to concentration is considerably large. This can probably be explained by the fact that the width of the band is very broad, while the width can be explained by γ' of Eq. (13). The accuracy of the band-width measurement was not satisfactory enough to detect the width change due to concentration fluctuation from γ. Fig. 5 shows the results obtained for the ν_8 and $2\nu_8$ bands of methyl cyanide in the methyl iodide solution. The $|\partial\nu/\partial x|$ values for the ν_8 and $2\nu_8$ bands are 6 and 11 cm^{-1} respectively.

Comparison with Light-scattering Data. So far the relation between the concentration fluctuation and the

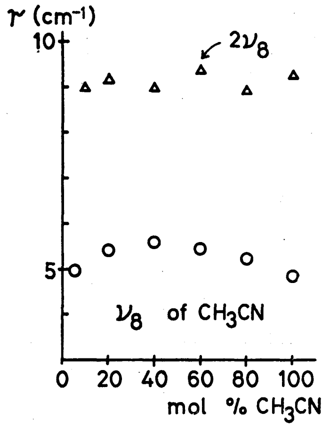

Fig. 5. Concentration dependence of the half width, γ, of the ν_8 and $2\nu_8$ infrared absorption bands of methyl cyanide observed in methyl iodide solutions.

band widths of the infrared spectra has been discussed. A light-scattering measurement is also an useful method to determine the concentration fluctuation. We cannot, however, compare the results obtained by these two methods directly. A band width affords information about the concentration fluctuation in the $<\Delta x^2>$ form. On the other hand, an intensity measurement of the Rayleigh scattering affords information about the concentration fluctuation in the form of $<\Delta x^2>\times V^*$, where V^* is the fluctuation volume, that is, the volume in which the concentration fluctuation is observed. We call this product, $<\Delta x^2>\times V^*$, the "fluctuation ability."[12]

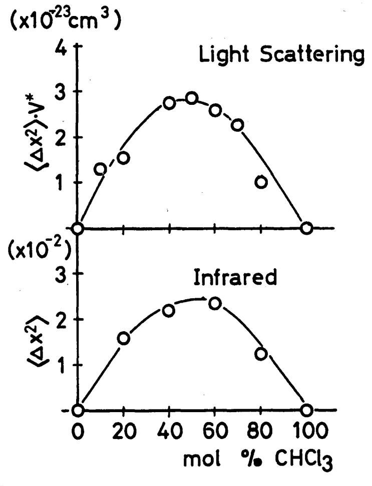

Fig. 6. Comparison of the concentration fluctuation obtained from infrared absorption spectra with that from light scattering data (chloroform–carbon disulfide system).

For the chloroform–carbon disulfide system, a fluctuation ability was observed by the intensity measurement of the Rayleigh scattering.[12] Figure 6 shows a comparison of the $<\Delta x^2>_{\mathrm{IR}}$ obtained from the infrared data with the $[<\Delta x^2>\times V^*]_{\mathrm{LS}}$ obtained from the light-scattering data. They show quite an analogous dependency on the change in concentration, indicating a qualitative consistency between the two sets of experimental results.

Attention should be paid to the fact that the $<\Delta x^2>_{\mathrm{IR}}$ values are obtained, in the case of the infrared spectra, regardless of the dimensions of the fluctuation volume. It is important, therefore, to examine the dimensions of the fluctuation volume from which a band width of the infrared spectrum receives information about the concentration fluctuation. In order to examine the fluctuation volume quantitatively, the number of molecules contained in a fluctuation volume, N, was calculated in two ways. One was to calculate N directly from Eq. (11), using the observed spectral data, $\Delta\nu_{1/2}$ and $|\partial\nu_1/\partial x_1|$. In this procedure, the system was assumed to be an ideal solution. The other way was to calculate N from the observed scattering data, $[<\Delta x^2>\times V^*]_{\mathrm{LS}}$, and the absorption spectral data, $<\Delta x^2>_{\mathrm{IR}}$, as:

$$N=\frac{[\langle\Delta x^2\rangle\times V^*]_{\mathrm{LS}}}{\langle\Delta x^2\rangle_{\mathrm{IR}}}\times\frac{N_{\mathrm{a}}}{x_1\left(\frac{M_1}{\rho_1}\right)+x_2\left(\frac{M_2}{\rho_2}\right)} \tag{16}$$

where M was the molecular weight; ρ, the density, and N_{a}, the Avogardro number. The additivity of volumes on mixing is assumed in the procedure. If the infrared data correctly reflect the concentration fluctuation of the binary solution, and if the binary solution can be regarded as an ideal solution, the N values calculated by the two different ways should be identical. The calculated results are summarized in Table 1. The agreement between these two sets of N values is quite good; this in turn indicates that the proposed mechanism of line broadening as being due to concentration fluctuation is quite reasonable.

TABLE 1. COMPARISON OF N AND $\langle\Delta x^2\rangle$ OBTAINED FROM INFRARED ABSORPTION DATA WITH THOSE FROM INFRARED AND LIGHT SCATTERING DATA, FOR CHLOROFORM–CARBON DISULFIDE SYSTEM

Mole fraction of CHCl₃	Infrared		Light scattering	
	$\langle\Delta x^2\rangle$	N	$\langle\Delta x^2\rangle\times V^*$ $\times 10^{23}$ (cm³)	N
0.0	0		0	
0.1			1.32	
0.2	0.0160	10.0	1.55	9.0
0.3				
0.4	0.0213	11.3	2.76	11.3
0.5			2.84	
0.6	0.0234	10.3	2.57	9.1
0.7			2.28	
0.8	0.0126	12.7	1.0	6.2
0.9				
1.0	0		0	

Fluctuation Volume and Intermolecular Interaction. The problem of spectral-line broadening due to concentration fluctuation has now been reduced to the problem of the shift of the peak frequency in the solutions. It is necessary, for a complete understanding of the spectral-line broadening due to concentration fluctuation, to understand why a peak frequency changes its magnitude according to the concentration variation. This is a quite difficult problem indeed, and no satisfactory answer has yet been given. The determination of the N values, however, seems to give some useful information regarding this problem.

Considering the mechanism through which the concentration fluctuation causes broadening in a spectral line, the N value or the dimensions of the fluctuation volume corresponding to $<\Delta x^2>_{IR}$ indicates the region in which the surrounding molecules are confined, which can affect the peak frequency of a central molecule through intermolecular interactions.

It is established in the preceding paragraph that N can reasonably be estimated using only the infrared spectral data and Eq. (11), if the solution can be considered to be an ideal solution. Now, let us proceed further in the calculation of N through Eq. (11) for the other absorption bands observed. The results are summarized in Table 2. It may be seen from Table 2 that the N values are almost the same for the three bands observed in the methyl iodide–methyl cyanide system. If we compare the results of Table 2 with those of Table 1, we see, however, a difference between these two sets of N values; that is the N value is larger for the methyl iodide–methyl cyanide system than for the chloroform–carbon disulfide system. The N values of Table 1 are around 10. This may indicate that the intermolecular interaction, which effectively affects the peak frequency of the ν_1 band of chloroform in the carbon disulfide solution, arises from about 10 surrounding molecules. In other words, the peak-frequency change reflects the intermolecular interaction between a given molecule and the nearest neighbor molecules. The larger N values for methyl iodide–methyl cyanide system indicate the existence of a different type of intermolecular interaction. The peak-frequency change or the band-width change, in this case, may afford information about the intermolecular interaction between a given central molecule and the nearest and next nearest neighbour molecles.

TABLE 2. N AND $\langle \Delta x^2 \rangle$ CALCULATED FROM INFRARED ABSORPTION SPECTRA

Mole Fraction of CH_3I	$\nu_2(CH_3I)^{a)}$		$2_2\nu(CH_3I)^{a)}$		$\nu_8(CH_3CN)^{a)}$		$\nu_2(CH_3I)^{b)}$	
	$\langle \Delta x^2 \rangle$	N	$\langle \Delta x^2 \rangle$	N	$\langle \Delta x^2 \rangle$	N	$\langle \Delta x^2 \rangle$	N
0.0	0		0		0		0	
0.2	0.0038		0.0022		0.0030		0.0017	
0.4	0.0118	20	0.0086	28	0.0068	35	0.0087	28
0.6	0.0129	19	0.0086	28	0.0106	23	0.0130	18
0.8	0.0027		0.0022		0.0057		0.0069	
1.0	0		0		0		0	

a) $CH_3I–CH_3CN$. b) $CH_3I–CH_3NO_2$.

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References

1) R. G. Gordon, *J. Chem. Phys.*, **43**, 1307 (1965).

2) H. Shimizu, *J. Chem. Phys.*, **43**, 2453 (1965).

3) T. Fujiyama and B. Crawford, Jr., *J. Phys. Chem.*, **72**, 2174 (1968); **73**, 4040 (1969); B. Crawford, Jr., A. C. Gilby, A. A. Clifford, and T. Fujiyama, *Pure Appl. Chem.*, **18**, 373 (1969).

4) W. G. Rothschild, *J. Chem. Phys.*, **49**, 2250 (1968), **51**, 5187 (1969), **53**, 990, 6453 (1970); *Chem. Phys. Lett.*, **9**, 149 (1971); *J. Chem. Phys.*, **55**, 1402 (1971), **56**, 4722 (1972), **57**, 991 (1972), **59**, 2498 (1973).

5) Marsault-Herail, Jean-Pierre Marsault, Maurice Chalaye, Lean-Louis Saulnier, and Georges Levi, *C. R. Acad. Sci. Paris*, **B275**, 307 (1972).

6) K. Klier, *J. Chem. Phys.*, **58**, 737 (1973).

7) M. Kakimoto and T. Fujiyama, *Bull. Chem. Soc. Jpn*, **45**, 2970 (1972).

8) M. Kakimoto and T. Fujiyama, *Bull. Chem. Soc. Jpn*, **45**, 3021 (1972).

9) A. F. Bondarev and A. I. Mardaeva, *Opt. Spectrosc.*, **35**, 167 (1973).

10) "International Critical Tables," National Research Council, McGraw-Hill, New York (1928).

11) As the intensity values of these bands are small in magnitude, band widths due to vibrational relaxation are comparatively small. Therefore, the term of vibrational relaxation is thought to be negligible, so far as the concentration dependence of band widths is considered (see Ref. 7).

12) K. Iwasaki, M. Tanaka, and T. Fujiyama, to be published.