Effect of Non-resonant Impurity Atom Substitution on the ^{35}Cl NQR Spectrum of $HgCl_2$

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Doping of $HgCl_2$ with small amounts of $HgBr_2$ or HgI_2 affects the ^{35}Cl NQR line intensity very markedly, the effect being greater with the latter impurity. The large magnitude of these impurity effects probably arises from substitution of the ^{35}Cl atom by the non-resonant Br or I atom.

The effect of impurities on the ^{35}Cl nuclear quadrupole resonance is known from studies on *p*-dichlorobenzene crystals containing other *p*-disubstituted benzenes as impurity molecules[1-3]. With the incorporation of impurities the ^{35}Cl NQR line height decreases markedly. This effect has been attributed to the disturbance of the electric field gradient (efg) by the volume difference between the resonance- and impurity-molecule[1, 2]. The magnitude of the decrease has been expressed by the equation

$$I/I_0 = \exp\{-N\,C\} \qquad (1)$$

where I_0 and I are the heights of the resonance lines of a pure resonant molecule and an impurity molecule, respectively. C is the molar fraction of the impurity and N a characteristic number representing the number of resonant nuclei per impurity molecule whose resonances have been so shifted that they can no longer contribute to the central portion of the line. Besides the relative line intensity, the linewidth is also known to vary with the amount of impurity, the width increasing with C. The integrated intensity apparently remains constant when C is small, but decreases when C is increased further. Recent studies of Hamada[3] seem to whow that the volume difference alone is not sufficient to explain the impurity effect on the relative line intensity. Hamada suggests that the substitution effect caused by replacing the resonant atom in the host molecule with a non-resonant atom may be very intense while only an indirect disturbance is caused by the formation of a solid solution. In order to understand this amazing effect of impurities on ^{35}Cl NQR spectra, I have studied the effect of $HgBr_2$ and HgI_2 impurities on the spectrum of $HgCl_2$ where atomic substitution of Cl by Br or I is expected to occur[4, 5].

$HgCl_2$ samples doped with $HgBr_2$ and HgI_2 were prepared by fusion. Incorporation of $HgBr_2$ in $HgCl_2$ by fusion gives rise to HgClBr. The ^{35}Cl NQR spectra of these samples were recorded at 300 K with an SRO based NQR spectrometer constructed in this laboratory.

The spectra clearly showed that the relative line height of the ^{35}Cl NQR line of $HgCl_2$ decreases markedly and the line-width increases with increase in the non-resonant impurity ($HgBr_2$ or HgI_2) concentration. HgI_2 causes a more drastic effect than $HgBr_2$. I must point out here that mechanical mixtures of $HgCl_2$ and $HgBr_2$ (or HgI_2) of the same composition do not show such effects. Plots of the logarithm of the relative intensity of the NQR line against the impurity concentration are shown in Figure 1. The plots give fairly good straight lines with very large slopes unlike in the case of *p*-dichlorobenzene + impurity systems. Thus, even when the impurity concentration is only one mole per cent (approximately one impurity atom per 12 unit cells of $HgCl_2$), the resonance completely disappears.

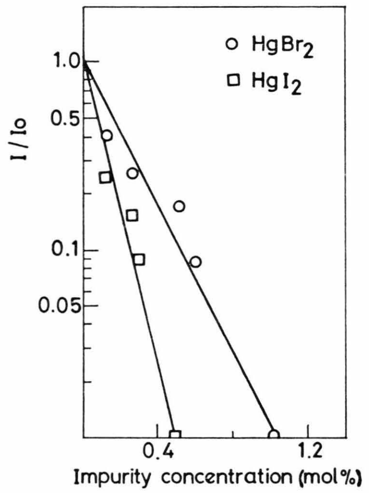

Fig. 1. Plots of relative line hight of ^{35}Cl NQR spectra of $HgCl_2$ against concentration of $HgBr_2$ and HgI_2 impurities.

The values of N, calculated from Fig. 1 for HgI_2 and $HgBr_2$ are 930 and 400 respectively, values which are considerably larger than those generally found in the *p*-dichlorobenzene system[1]. It is interesting that N is greater for HgI_2 than for $HgBr_2$ as would be expected on the basis of the volumes of these molecules.

The relative linewidth has been plotted against the concentration of impurity in Figure 2. These data can be fitted to the equation,

$$(T - T_0)/T_0 = N'\,C \qquad (2)$$

where N' is a characteristic number representing the number of resonant nuclei whose resonance has been

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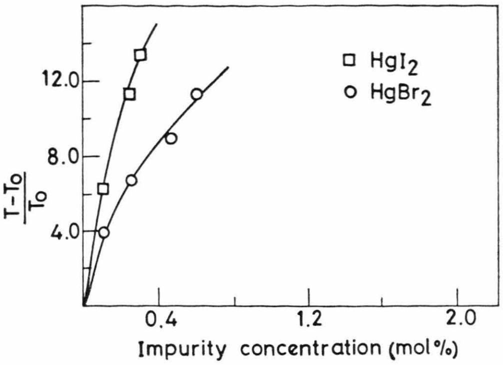

Fig. 2. Plots of relative broadening of the resonance line against impurity concentration.

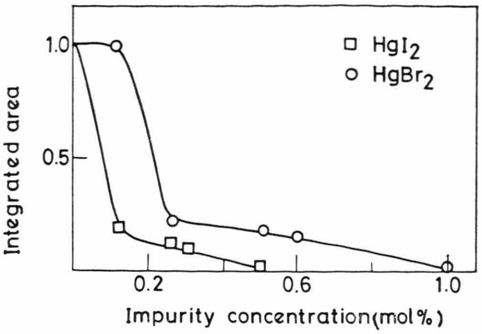

Fig. 3. Plots of integrated intensity against impurity concentration.

shifted to produce observable broadening. The approximate values of N' determined from the curves are 4000 and 2100 for HgI_2 and $HgBr_2$ respectively, again values much larger than those found in the *p*-dichlorobenzene system[1].

The integrated intensity of the line is plotted against impurity concentration in Figure 3. The impurities have a marked effect on the integrated intensities as well; the effect is much greater with the larger HgI_2 impurity. All these results clearly establish that incorporation of non-resonant impurities (even at low concentrations) markedly affects the NQR parameters, the effect being much more pronounced when atomic substitution occurs, as in the systems reported here.

The decrease in relative intensity with increase in impurity concentration in the systems reported here is somewhat similar to the effect of dislocations and other defects on NQR spectra[2]. For example, grinding a sample has been shown to decrease the relative intensity of the NQR signals. It was found that grinding $HgCl_2$ for extended periods in an agate-vial is sufficient to decrease the intensity. This is attributed to the introduction of dislocations in the crystal which causes a random distribution of efg's.

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