Electrical Properties of Gamma-Irradiated p-Type Silicon

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Electrical-conductivity and Hall-coefficient measurements have been used to investigate the production and annealing of defects which were produced in p-type silicon by Co^{60} γ irradiation at 80°K. γ irradiation reduces the carrier concentration in the sample at 80°K. Two annealing stages occurring at 175 and 350°K are observed. An illumination with white light at 82°K after irradiation reduces not only the total damage, but also the fractions of the damage recovered in both stages and the remainder after the annealing up to 500°K. Our results are consistent with the argument that the 175°K stage is due to the migration of the neutral vacancy, and the 350°K stage is due to the annealing of secondary defects, including some vacancy-impurity complexes.

1. INTRODUCTION

LITTLE work has been done on the study of radiation-induced simple defects formed at low temperatures in p-type silicon by means of the measurements of electrical properties, even though relatively extensive work has been done on n-type silicon.[1] Matsui and Hasiguti[2] studied the change of electrical properties in high purity p-type silicon caused by Co^{60} γ irradiation at 82°K. They observed an increase of hole concentration in their high-purity samples after irradiation which disappeared upon annealing between 150 and 220°K. Gregory[3] found that Co^{60} γ irradiation at 76°K on silicon solar cells fabricated from 1-Ω-cm p-type material reduced the minority carrier lifetime in the p-type region and a very prominent recovery stage occurred between 150 and 180°K. He also reported that electron injection into the p-type portion through an n-p junction reduced the lifetime degradation rate caused by irradiation, and that the recovery stage was absent in these samples. He argued that the injection-stimulated reduction in the lifetime degradation rate at 76°K was due to vacancy reordering which occurred when the injected electron density was sufficiently large to modify the vacancy charge state from neutral (mobile above 160°K)[4] to singly negative (mobile above 60°K).[5,6] Novak[7] reported briefly that two annealing stages in electrical properties occurred at 190 and 300°K in p-type silicon irradiated with 220–500 keV electrons at 100°K.

Much useful information concerning the defects in p-type silicon irradiated at low temperatures has come from the EPR work of Watkins. According to him, 1–1.5 MeV electron irradiation at 4.2 and 20.4°K on silicon produces isolated vacancies which become mobile above 60°K if their charge state is singly negative,[5] above 70°K if doubly negative,[8] and above 160°K if neutral.[4] In aluminum-doped silicon irradiated at 4.2°K, he found Al interstitials with the same production rate as isolated vacancies, from which he concluded that interstitial silicon atoms were mobile during the irradiation.[5] Recently, he reported that no significant number of isolated vacancies or aluminum interstitials were produced during 1-MeV electron irradiation at 100°K and, instead, singly positively charged divacancies and other unknown defect centers labeled Si G-12 and Si G-14 were formed. Also he reported that the total damage rate at 100°K did not change greatly in comparison with that at 4.2°K. In addition, he found that the Al interstitial production rate at room temperature was approximately the same as at 4.2°K. These striking effects of irradiation temperature on the formation of defects reflect the complexity of radiation damage in silicon. Obviously more work is needed in order to understand the nature of radiation damage in silicon. Especially, some careful studies should be done on p-type silicon irradiated at 70–120°K, because the vacancy normally stable at these temperatures in p-type silicon can become mobile after it traps a photo-excited electron created by radiation.

In this paper, we shall report some results from a study of the carrier removal in high resistivity p-type silicon by Co^{60} γ irradiation and its recovery upon isochronal annealing from 80 to 500°K. The effect of illumination with white light at 84°K on the recovery has been examined.

2. EXPERIMENTAL METHODS

The electrical conductivity and the Hall effect were measured by dc potentiometric methods on square samples (~5×5×0.8 mm).[9] Electrical contacts were made by alloying high-purity aluminum to the 4 corners on one surface of the sample. A magnetic field

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[1] H. J. Stein and F. L. Vook, Phys. Rev. **163**, 1790 (1967); in *Radiation Effects in Semiconductors*, edited by F. L. Vook (Plenum Press, Inc., New York, 1968), p. 90–123.

[2] K. Matsui and R. R. Hasiguti, J. Phys. Soc. Japan **20**, 487 (1965).

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[4] G. D. Watkins, J. Phys. Soc. Japan, Suppl. **18**, 25 (1963).

[5] G. D. Watkins, *Radiation Damage in Semiconductors* (Dunod Cie., Paris, 1965), p. 97.

[6] In his recent review (Ref. 7), he did not mention this preliminary result again. Presumably more experiments are needed on this subject.

[7] R. L. Novak, Bull. Am. Phys. Soc. **8**, 235 (1963).

[8] G. D. Watkins, in Ref. 1, p. 67.

[9] L. J. van der Pauw, Philips Tech. Rev. **20**, 220 (1958/59).

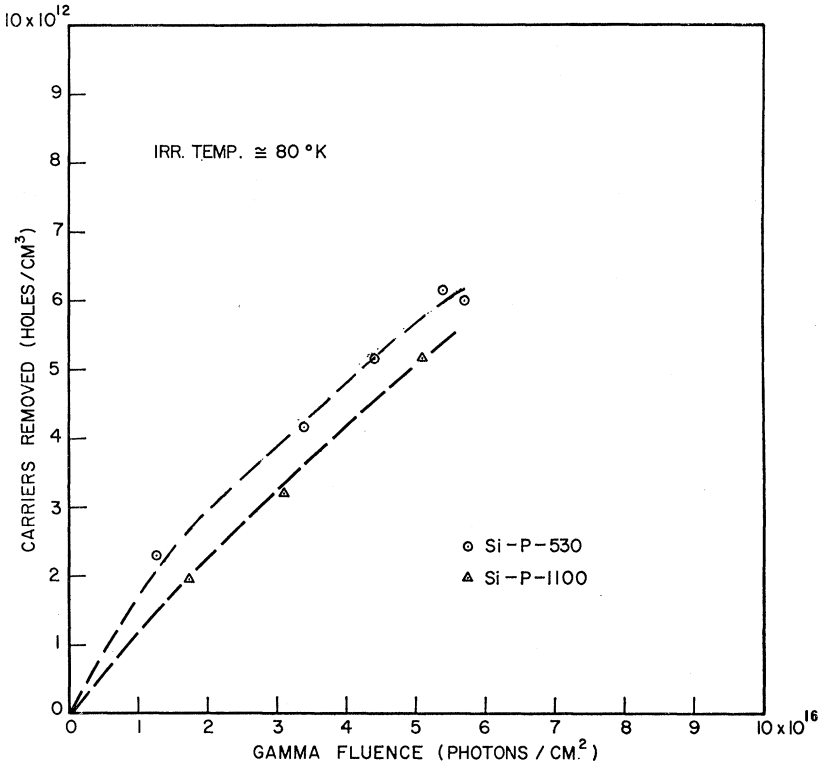

FIG. 1. Carriers removed versus Co^{60} γ fluence for Si-*P*-530 and Si-*P*-1100.

strength of 2200 G and an electric field of $\lesssim 1$ V/cm were used in the measurement. The carrier concentration p was determined from the Hall coefficient R_H through the following relation:

$$p=\frac{\mu_H/\mu_c}{eR_H},$$

where μ_H is Hall mobility, μ_c is the conductivity mobility, and e is the electronic charge. A value of 1.05 extrapolated from the work of Messier and Flores[10] was used for the ratio μ_H/μ_c at 77°K. The carrier mobility (i.e., the Hall mobility) can be obtained from the Hall coefficient and the electrical conductivity. Typical values of the carrier concentration and the Hall mobility in the samples cut from two different crystals are listed in Table I. The crystals are floating zone refined and doped with boron.

Samples were mounted on a mica-covered aluminum holder placed near the bottom of a 50-cm-long 1-cm-diam stainless-steel thin-wall tube filled with He gas. The top end of the tube was connected with electrical feedthroughs and a vacuum valve. During the experiment, the lower half of the tube was immersed in liquid nitrogen in an ordinary glass Dewar. The sample temperature was measured using a copper-constantan thermocouple pressed between the sample and the sample holder. Two miniature 6-V electric bulbs were mounted near the samples for the purpose of illumination.

Irradiations were carried out in a Co^{60} γ cell. Its γ intensity at the irradiation position was 3×10^{11} photons/cm²/sec. The sample temperatures during irradiation were $\lesssim$80°K.

3. EXPERIMENTAL RESULTS

γ irradiation at 80°K reduced hole concentrations in our *p*-type silicon samples, in contradiction to the results of Matsui and Hasiguti.[2] This effect is illustrated in Fig. 1. The data indicate that the decrease of carrier concentration is not quite linearly proportional to the γ fluence used. There is no substantial difference in carrier removal rates between the two crystals; however, the initial removal rate in the samples cut from crystal Si-*P*-1100 are slightly lower than those cut from crystal Si-*P*-530 as shown in Fig. 1. The initial carrier removal rate is found to be 1.5×10^{-4} cm^{-1} for Si-*P*-530 and 1.2×10^{-4} cm^{-1} for Si-*P*-1100.

TABLE I. Typical carrier concentration and Hall mobility measured at 77°K before irradiation.

Crystal code	Supplier	Oxygen content (cm^{-3})	p (cm^{-3})	μ_H (cm²/V sec)
Si-*P*-530	Dow Corning	$<10^{16}$	3.1×10^{13}	9500
Si-*P*-1100	Dow Corning	$<10^{16}$	1.6×10^{13}	10 700

[10] J. Messier and J. M. Flores, J. Phys. Chem. Solid, **24**, 1539 (1963).

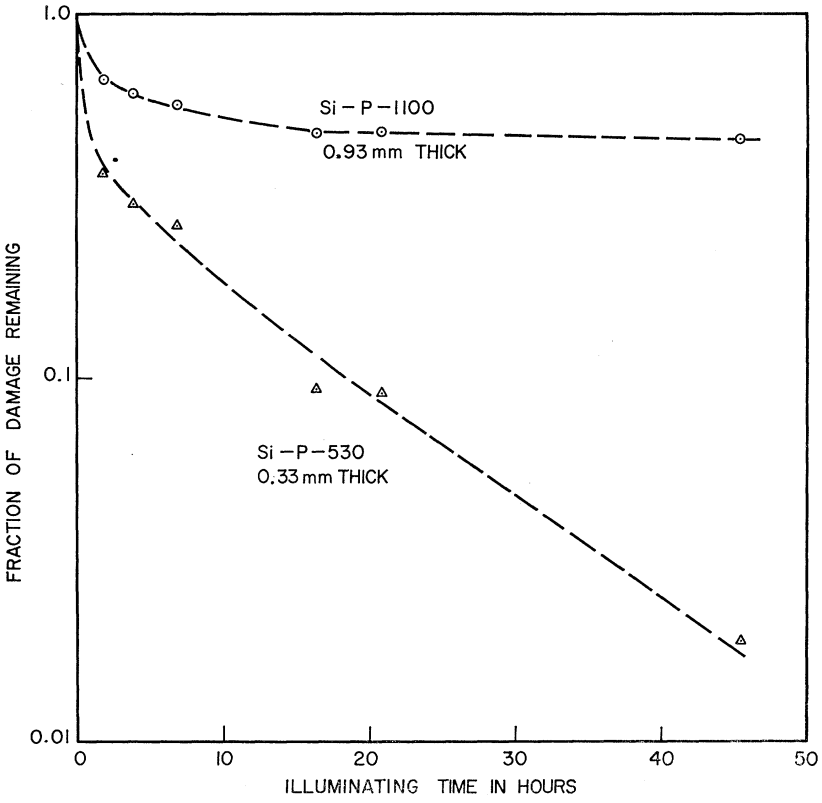

FIG. 2. Fractions of damage remaining after illumination at 82°K versus illuminating time for two samples with different thicknesses.

Illumination with white light on samples at 82°K after irradiation reduces the change in carrier concentration substantially. The effect is illustrated in Fig. 2, where the fractions of damage remaining after illumination versus illuminating time for two samples with different thicknesses are plotted. The nonexponential decay of the damage and the effect of sample thickness imply that the defects located near the surface disappear more easily upon illumination. This is consistent with the thought that the existence of the photoexcited carriers created near the surface by light causes the photo-induced recovery by changing the charge states of the defects. The data also indicate that most of the damage in carrier concentration produced by γ irradiation at 80°K can be removed by means of an illumination of long duration with white light, if the sample has a suitable thickness.

Figure 3 shows a comparison of isochronal annealing of carrier concentration for four samples: (1) without any illumination, (2) with a 4-h illumination at 82°K, (3) with a 65-h illumination at 82°K after irradiation, and (4) with a 92-h illumination at 82°K after irradiation and after isochronal annealing up to 205°K. There are two annealing stages observed. The first one is narrow and occurs at 175°K. The half-width of the annealing stage is about 15–17°K. The second stage is rather broad and occurs around 350°K with a half-width of ~55°K. Some of the damage persists up to 500°K as is evident from Fig. 3. The appearance of isochronal annealing of residual damage after various illumination conditions was roughly the same as for the sample without illumination, except that the fractional recovery of the total initial damage in each stage becomes smaller. An illumination at 82°K on a sample after irradiation and successive annealing up to 205°K can still remove considerable damage which normally disappears upon annealing at temperatures above 280°K. The fractional recovery (~27%) of the damage at the second stage in this sample after a 92-h illumination is considerably larger than that (~11%) in the sample after a 65-h illumination but without a preannealing.

Small changes ($\lesssim$1%) of the Hall mobilities in samples caused by γ irradiation were observed. Because of the inconsistency of the data, we shall not report any results on the change of the Hall mobility.

4. DISCUSSION

A. Defect Production

According to Watkins, the annealing of the vacancy occurs in the range 70–80°K in n-type silicon (presumably $V^{=}$)[8] and 150–180°K in p-type silicon (V^{0}).[4] He has mentioned some experimental evidence for V^{-} migrating around ~60°K.[5] It is important for us to determine whether or not the vacancy does exist in p-type silicon after a γ irradiation at 80°K, such as

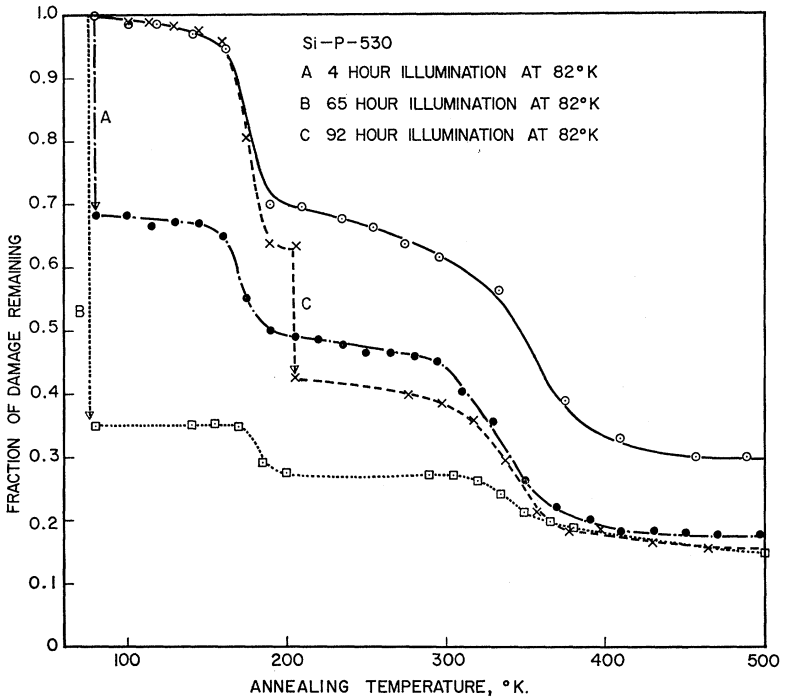

FIG. 3. Fractions of damage remaining after isochronal annealing versus annealing temperature for Si-*P*-530 samples without or with various preillumination conditions.

ours, since Watkins has recently reported that 1.5-MeV electron irradiation at 100°K on Al-doped Si after an irradiation at 20.4°K produced almost no additional vacancies or Al interstitials.[8]

First, we assume that isolated vacancies are produced during γ or electron irradiation in the temperature range from 80 to 100°K. According to Watkins, the charge state of the vacancy in p-type Si in this temperature range should be mostly neutral or singly positive. However, vacancies can become mobile and migrate to sinks during irradiation in this temperature range if they become negatively charged by trapping photo-excited electrons produced in the conduction band by radiation. The rate of change of the vacancy concentration during irradiation in this temperature range can be written approximately as

$$dN_v/dt = -\sigma_s C_s f e^{-E/kT} N_v^- + \phi \nu_v ,$$

where N_v is the vacancy concentration, t is the time, σ_s is the number of atomic trapping sites per sink, C_s is the sink concentration expressed as an atomic fraction, f is a frequency factor, E is the activation energy of motion of the singly negatively charged vacancy, k is Boltzmann's constant, T is the irradiation temperature, N_v^- is the concentration of the singly negatively charged vacancy, ϕ is the radiation flux, and ν_v is the vacancy production rate per unit flux. We have assumed that the effect of the doubly negatively charged vacancy can be neglected, since its number should be very small in comparison with the number of the singly negatively charged vacancy. It is easily seen from the equation that the production rate of the vacancy in p-type silicon becomes zero when the first term on the right-hand side is equal to the second term. This condition can be reached in some real experiments in which ionization is high and preirradiation is involved. A rough estimate has indicated some possibility that the failure to observe vacancy production at 100°K in Watkins's case is due to this reason. Thus, it should be mentioned that Watkins's result does not necessarily contradict the statement that the vacancy is formed in p-type silicon during irradiation at 80–100°K. Also the net production rate of the vacancy at 80°K might be different from that at 100°K. One decisive experiment worth doing is to irradiate fresh p-type silicon samples with a relatively small electron flux at various temperatures in the range from 70 to 120°K and to examine the production of the vacancy by the EPR method.

It is possible that a vacancy can act as a donor in p-type silicon? According to Watkins,[5] the vacancy has a level located at $<E_v+0.05$ eV. When the Fermi level of a sample is above it, the vacancy is neutral and, below it, singly positive. If the main defect responsible for the carrier removal is the vacancy, its level must be near the Fermi level or above it, which is around $E_v+0.05$ eV at 77°K in our sample. Therefore, the vacancy can act as a donor in our case. However, the actual production rate of the vacancy may be at least twice that of the observed initial carrier removal rate (1.2–1.5×10^{-4} cm^{-1}). Chan[11] has used simple displacement theory to

[11] J. H. Cahn, J. Appl. Phys. **30**, 1310 (1959).

calculate the atomic displacement cross section in silicon for γ rays of various energies. His calculated value of 0.024 cm^{-1} for 1.25-MeV Co^{60} γ photons, assuming the threshold energy for a displacement to be 15 eV, is much larger than our experimental value, even after a reasonable correction factor for occupancy is applied.

We have no explanation for the contradiction between our results and those of Matsui and Hasiguti.[2] It should be noted that the concentration of net acceptors in their samples was about ten times smaller than those in our samples.

Figure 1 shows that the carrier removal rate becomes slightly smaller as the fluence increases. The decrease may be due to three things: (1) the Fermi level of the sample increases, (2) the effect of the migration of the negative vacancy becomes important, and (3) some mobile radiation-induced defects, e.g., the interstitial, interact with imperfections originally existing in the crystal.

B. 175°K Annealing Stage

About 30–40% of the damage in carrier concentration caused by γ irradiation at 80°K disappears upon annealing in the dark in the 175°K stage. The narrowness of this stage indicates that the annealing process is a relatively simple one. Illumination with white light at 82°K reduces not only the total carrier removal but also the magnitude of this annealing stage. It is believed that the charge state of some defects in a crystal under illumination can be changed by means of trapping photo-excited carriers. One possible explanation for the illumination-induced annealing at 82°K is that the defect responsible for the 175°K stage becomes mobile under illumination at 82°K. Watkins[12] reported that enhanced annealing of the vacancy in p-type silicon was observed in EPR studies by shining light on the sample. Therefore, our results are consistent with the argument that the defect is the vacancy, which also disappears upon annealing in the dark around 160–180°K.[4] These experimental results also support the argument that γ irradiation in p-type silicon at 80°K produces the vacancy.

Watkins[7] reported that the unknown G-14 center formed in Al-doped Si during an electron irradiation at 100°K disappeared upon annealing at 180–190°K. It is unlikely that the 175°K stage is associated with the G-14 center, because of its higher annealing temperature. The 190°K stage observed in the p-type sample irradiated with electrons at 100°K by Novak might correspond to the annealing of the G-14 center. Does this really mean that the irradiation at 80°K is substantially different from that at 100°K? Obviously more work has to be done in this area before a decisive conclusion can be made.

[12] G. D. Watkins, Symposium on Radiation Effects in Semiconductor Components, Toulouse, France, 1967 (unpublished).

C. 350°K Annealing Stage

This stage is rather broad, indicating that more complex annealing processes are involved. An illumination with white light at 82°K after irradiation reduces this stage in a similar manner as it does the 175°K stage, indicating that the defects responsible for the stage might be vacancy-impurity complexes. These complexes can be formed when the vacancy is neutral. The mobile negative vacancy existing under illumination at 82°K may not be easily trapped by the particular kind of impurity, because of the Coulomb repulsion between them. One of the possible impurities is boron, since more than half of the boron atoms are negatively charged at 82°K. For checking this argument, we did an illumination at 82°K after irradiation and after isochronal annealing up to 205°K. The preannealing of the vacancy does reduce considerably the effect of illumination on the annealing stage, but does not completely eliminate it (see Fig. 3). The result is consistent with the above argument and also indicates that some defects in silicon, other than the vacancy and the interstitial, which are stable up to 280°K or higher, can be removed at 82°K by changing their charge states. Therefore, it is indicated that the 350°K stage is due to the annealing of some secondary defects, among which there are various vacancy-impurity complexes.

The above speculation has some other experimental support. Recently, Vajda[13] from the photoconductivity study on p-type silicon irradiated with 1.2-MeV electrons at 10°K found that the 3.9 μ photoconductivity band (correlated with the singly positively charged divacancy[14,15]) grew rapidly upon annealing around 350°K. Stein and Gereth[16] recently reported a recovery of carrier removal in floating zone, Lopex, and Dash-grown p-type silicon electron irradiated at 270°K occurred around 325°K where a reverse annealing was observed in crucible-grown p-type silicon. Their results are also consistent with our speculation. In addition, Swanson[17] recently found that a major annealing stage in quenched p-type silicon occurred around 310°K.

5. SUMMARY AND CONCLUSIONS

The following are the results and conclusions obtained from our experiments: (1) Co^{60} γ irradiation reduces carrier concentration in p-type silicon at 80°K. (2) Two annealing stages occurring at 175 and 350°K are observed. Some of the damage persists up to 500°K. (3) An illumination with white light at 82°K after irradiation reduces not only the total damage but also the fraction of damage recovered in both stages, and the remainder after the annealing up to 500°K. (4) In

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[14] L. J. Cheng, Phys. Letters **24A**, 729 (1967).
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[16] H. J. Stein and R. Gereth, J. Appl. Phys. **39**, 2890 (1968).
[17] M. L. Swanson, Phys. Status Solidi (to be published).

our experiments it is evident that the formation of vacancy-impurity complexes in Si depends on the charge states of the defects. (5) Our results are consistent with the argument that the 175°K stage is due to the migration of the neutral vacancy and the 350°K stage is due to the annealing of some secondary defects, among which there are various vacancy-impurity complexes.

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Far-Infrared Properties of Lattice Resonant Modes. III. Temperature Effects*

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We have measured the temperature-dependent absorption spectrum associated with resonant modes in KBr:Li^+, NaCl:Cu^+, KI:Ag^+, and MnF_2:Eu^{2+}. A comparison is given of the measured temperature dependence with that expected from a linear-coupling theory using the known static stress coupling coefficients. We find that the linear-coupling model is capable of explaining the measured temperature dependences provided the active resonant mode is coupled to another inactive resonant mode, but not if the coupling is to a Debye spectrum of lattice modes.

I. INTRODUCTION

TEMPERATURE-DEPENDENCE studies of the far-infrared absorption spectra from low-lying resonant modes can be used to measure the anharmonic nature of weakly bound impurities in crystals. In the harmonic approximation, the normal modes of a lattice containing a heavy mass defect can be considered to consist of a resonant mode Q and a set of other lattice modes q. Strictly speaking, the resonance is not a single mode, but when it occurs at low frequency as a sharp peak in the density of states, it is a reasonable approach to regard the resonance as being in a single mode. If only the mode Q is infrared-active, the absorption spectrum consists of a single sharp line at frequency Ω which is temperature independent.

Previously, we have used this approach to characterize the isotope shift[1] and stress shift[2] experiments on infrared active resonant modes associated with impurities which are weakly coupled to the host lattice (hereafter referred to as I and II, respectively). In this paper we describe temperature-dependent properties observed in practice and attempt to explain their presence in terms of various anharmonic effects.

The first investigations of the temperature-dependent properties of resonant modes presented some puzzling results. With increasing temperature, the center frequency of the impurity-induced absorption line decreased, the linewidth increased and the integrated absorption intensity decreased for both KI:Ag^+ and KBr:Li^+.[3] On the other hand, for NaCl:Cu^+ although similar temperature dependences were observed for the center frequency and the linewidth, the integrated absorption intensity was almost independent of temperature.[4] Attention then focused on the most dramatic effect, the temperature dependence of the integrated absorption and a great deal of confusion followed because it was not clear how much of the absorption spectrum was being considered in each experiment.

In discussing the intensity of the integrated absorption due to the resonant mode it is important to be quite clear as to how much of the absorption spectrum is being discussed. As stated previously if the potential energy is purely harmonic the spectrum consists of a sharp single line at Ω. When anharmonic terms are included this line may shift, broaden, and change in strength, but in general the anharmonicity would also induce other lines to appear elsewhere in the spectrum. These may be described in the language of molecular spectroscopy as combination bands, overtones, etc., or in solid-state terms as sidebands, two-phonon transi-

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