On the Resonance Absorption of Rochelle Salt in Very High Frequency Region[1)]

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1. Introduction

The fact that the new absorption lines different from the pure nuclear quadrupole resonance lines were found in very high frequency region was reported by Shoji Kojima, Kineo Tsukada, Akira Shimauchi and myself(1). These absorption lines were observed when substances such as silver iodide, quartz, zinc sulphide and Rochelle salt were inserted in the coil of superregenerative oscillator. These substances were known to belong to the groups of piezo crystals. The differences of these resonance absorptions against pure nuclear quadrupole resonance absorptions were as follows. They were composed usually of many lines having random distribution in wide frequency range instead of a single or a few lines. They did not show the Zeeman splitting in the applied static magnetic field, moreover the intensity of these lines was stronger when the sample was placed on the transmission lines or near the oscillator tubes where the high frequency electric field was mainly effective. One more easily observable difference was the behavior accompanied with tempareture variation. Large temperature gradient in a sample could not make the line diffuse, and with the rapid decrease of temperature the resonance lines displaced rapidly to higher frequency side. This indicated that the absorption lines were confined to the small region in one crystal.

The resonance absorption was investigated over the frequency range from a few megacycles to several hundreds megacycles. In a powdered material the absorption pattern composed of many lines distributed randomly, but in a single crystal the absorption spectrum showed many line series which was separated with about the same distances. The study of the resonance lines about quartz and other substances will be published(2). From the experiment on the plate of quartz oscillator it was considered, that although the absorption occured in piezo crystals and seemed to be originated from mechanical vibrations it is not the higher harmonics of ordinary piezoelectric vibration.

In this paper the study about Rochelle salt was described. It is very useful to investigate the absorption lines on a single crystal, since the spectrum seems to have equidistant series. In this respect Rochelle salt is very usefull. A large single crystal of Rochelle salt was easily

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obtained, while a single crystal of other substances hardly was manufactured. Rochelle salt has a ferroelectric property in the region between two curie temperatures. Piezoelectric property is also large in the same region. The resonance lines had very strong intensity for the observation with a superregenerative oscillator. Even in a weak field of autodyne oscillator, it presented many absorption lines. The temperature dependency of the resonance frequency revealed that these lines has each property associated with the crystal axis. The width of lines was the order of 1 kc/sec except a broad line having a width of about 20 kc/sec. This broad line was characterized with the property of the a axis. About this line detailed experiment was taken. The effect of pressure on the surface of a single crystal resulted large frequency shift of this line, which was expected from the large piezoelectric constant at the a axis compared with those of other crystal axes and those of other crystals. The electrostatic effect was also expected. The experimental results were compared with the characters of Rochelle salt so far approved. The results seemed to give the fact that the absorption phenomena originate in small volume of one crystal. This localization might be connected to crystal boundaries or dislocations naturally or artificially produced.

2. Apparatus

The resonance absorption was investigated over the frequency range from a few megacycles to several hundred megacycles. The equipment of observation of pure nuclear quadrupole resonance absorption was a superregenerative detector, which was characterized with accompanying by series of side frequencies. Hence the observed line structure was complicated by accumulation of different side frequencies because of simultaneous existence of many lines. The circuit of superregenerative oscillator was described elsewhere[3]. The wave length region was from one hundred megacycles to about six hundred megacycles. A vibrating plate set against the transmission lines changes the oscillator frequency with a frequency of 50 cycles. The horizontal sweep of oscilloscope was operated with the same frequency. The oscillator was consisted of a push pull circuit of 9002 miniature tubes and quenched through its grid resistance externally. The frequency modulated signal was rectified in its plate circuit and amplified with a two stage audio amplifier to observe on an oscilloscope. The block diagram is shown in Fig. 1.

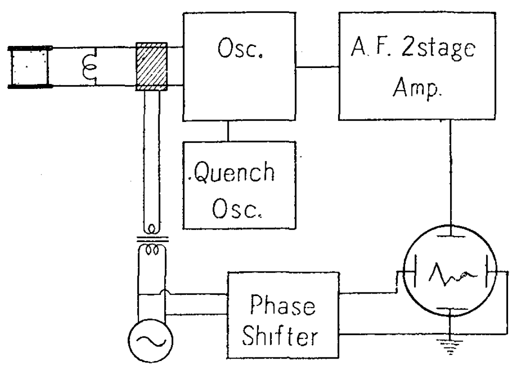

Fig. 1. The block diagram of the superregenerative oscillator.

The first detection was on silver

iodide ampled in a brawn glass tube and set in the coil of the superregenerative oscillator. However this absorption was well observed when the sample was put on the transmission lines of oscillator or between the parallel plate condenser of the *L–C* circuit instead of putting in the coil. This shows that to observe absorption lines it was not necessary magnetic flux but it need electric field.

In order to resolve the complicated spectrum which observed in the superregenerative oscillator, an autodyne oscillator was constructed. Because of low operational level of oscillation in autodyne type, the amount of detectable absorption was reduced. In this apparatus, however, Rochelle salt was mainly investigated and analysed. The operational frequency range was mainly from a few megacycles to one hundred megacycles. This circuit was taken from the circuit used in nuclear magnetic resonance absorptions. In this frequency range the oscillator units shown in block diagram were replaced with an autodyne oscillator. The circuit of autodyne oscillator is shown in Fig. 2. In this figure the parallel plate condenser to hold the sample between them was pictured. The vessel used in cooling the material was also shown.

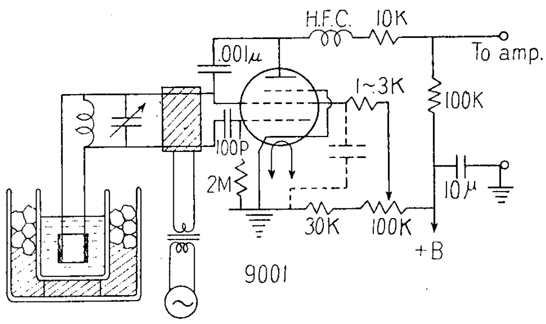

Fig. 2. The circuit of an autodyne oscillator. The cooling device is also shown.

3. The line characteristics

The resonance absorption was observed in powder and in a single crystal. In both cases the spectrum was distributed in wide frequency range. In the case of powder the spectrum of the absorption lines was complicated and no systematic properties were observed. Moreover the individual lines changed their intensities as rolling the glass tube which contained the test substances over the transmission lines. Only slight magnitude of powder sticked to the electrodes of the oscillator still exhibited the absorptions.

In 1925, E. Giebe and A. Scheibe[4] proposed the powder method. It was used to detect the materials exhibiting the piezoelectric property in a condition of grains. In their method the resonance of piezoelectric vibration was heard as noise of click whenever the oscillator frequency passed through the resonance frequencies of grains. The average value of resonance frequencies was estimated from the grain diameter by the relation

$$f = 1/2l(E/\rho)^{1/2} .$$

In this formula E is the Young's modulus, ρ the density and l the diameter of grain and they were all taken in averages. In the case of

Rochelle salt an observed frequency of one hundred megacycles was interpreted by the average diameter of only several microns provided the values of ρ and E were 1.79 gr/cm^3 and 11.6×10^{10} cm^2/dyne, respectively. The observed absorption spectrum, however, distributed in wide frequency range. Moreover the absorption exhibited in extraordinary wide frequency range even in a single crystal of large dimensions. Therefore, it could not be interpreted as the piezoelectric vibrations of whole body, but might be originated from the small portion in a single crystal. It is known that even in a perfect crystal the grain boundaries or dislocations caused by the imperfections exist naturally.

This consideration was confirmed from the following fact. In a single crystal which had the dimensions about $1.0 \times 0.5 \times 0.5$ cm^3, a strong sharp line was observed. We divided this crystal into halves. This sharp line appeared without any change in one half and did not in the other. The half containing the strong absorption line was divided again. Unfortunately this block was broken into small pieces and the line could not be observed at all. However, this was a good proof which show the resonance origin in a small volume of a single crystal.

In the case of a single crystal the absorption spectrum was different from the spectrum in powdered samples in respect of the periodical distribution. This absorption lines were consisted of many line series seemed to have a equidistant separation of about a few hundred kilocycles. In these points it is interesting to study the resonance absorption detail in single crystals. A sample was cut out from the large single crystal which three axes were known. This crystal is shown in Fig. 3. The a axis is normal to the plane of this paper, and the thickness in this direction was 1.22 cm. The sample was cut out along the dotted line which contained the contact portion of crystal growth in the direction of b and c axes.

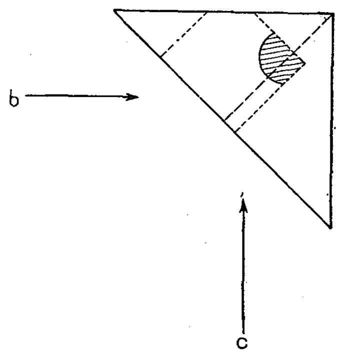

Fig. 3. A single crystal which offered the sample used in various experiments. The sample was cut out along the dotted line. It contains the surface crossed to b and c axes with an angle of 45°. The shaded part indicates the possible portion of origin of a strong broad line.

In the experimental procedure it must be noticed that the Rochelle salt has a ferroelectricity at room temperature and its dielectric constant is about 100 at those high frequencies. Thus the effective electric field at the sample was weakened if the high frequency field was applied at the direction of a axis. To eliminate the gaps between the electrodes and the sample, the aluminum foil which was applied tightly to the surface was used as electrodes. If the both surfaces were tightly contacted to the aluminum foils the oscillator frequency could not be raised to necessary high frequency. Thus the experiments were taken under the condition that only one surface was contacted to an electrode and the other had a small air gap. The obtained electric field at the sample was diminished by about a half, provided the thickness of air gap was one percent of that of the sample. The relative difference of the absorption intensity when the observation was taken at the direction of *a* axis and *b* or *c* axis might be recognized as the difference of the effective electric field at the sample. The dielectric constants of *b* and *c* axes are values as a usuall crystal.

The spectrum of the absorption lines was obtained with an autodyne oscillator. The structure in any frequency range seemed to be repeated over all range. One example of the oscilloscope display was sketched in Fig. 4. In this figure the complex spectrum at the high amplification was also recorded. The frequency width of modulation was about 200 kc/sec. At a small modulation the line seemed to have a width of several hundred cycles. The broad line shown in Fig. 4 was a exception. This was observed when the field was applied at the direction of *a* axis, and the width extended to about 20 kc/sec.

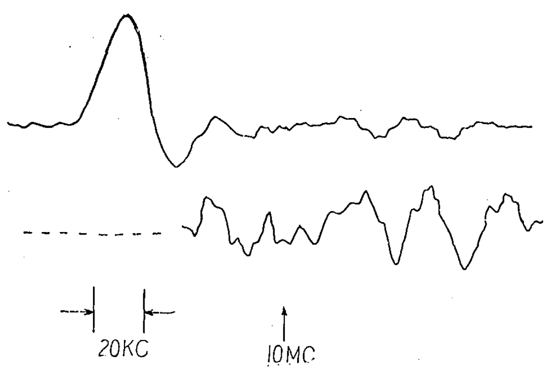

Fig. 4. An example of oscilloscope display. A strong broad line was appeared. Lower pattern shows the fine structure under a high amplification. The broad line was omitted because of saturation of amplifier.

A block of Rochelle salt with dimensions $0.965 \times 0.525 \times 1.980\,cm^3$ and a plate with dimensions $2.015 \times 1.975 \times 0.490\,cm^3$ showed very strong and sharp lines which accompanied by "wiggles". These lines dissapeared when the crystal was broken. It was also quenched when the crystal surface was wetted with liquid oil or water. When the sweep was reversed the wiggle was distinguished from the resonance line as it was damped at the opposite side to the line.

During the cause of experiment it was found that the broad line of the picture in Fig. 4 was originated in the fairly large domain remarked in Fig. 3 where the growth of crystal direction of axes *b* and *c* crossed. The use of click method above mentioned indicated some clicks about several ten kilocycles.

The spectrum over the wide frequency range is recorded in Fig. 5. In this figure small lines were omitted. It is recognized that almost all lines were periodically appeared with the separation of a few hundred kilocycles. Their intensities did not change over the frequency range measured. The series of these equidistant lines was not the higher harmonics of the fundamental body vibrations. Higher harmonic of such a type of vibration were damped very quickly and did not continue to those higher frequency. In fact it was ascertained in the case of quartz[2]. This absorption series did not reduce its intensity and moreover they seemed to have a total intensity maximum near 200 Mc/sec frequency region. The absorption line was observed as high as six hundred megacycles.

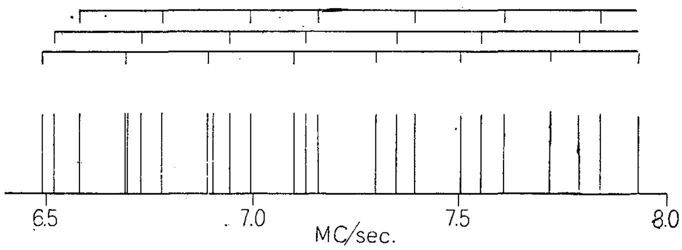

Fig. 5. A spectrum in single crystal. The lines seemed to have equidistant separation was picked up. The small lines were omitted.

4. The temperature dependency of the absorption lines.

To investigate the dependency of the absorption lines over the wide frequency range the sample was warmed or cooled. When the sample was warmed the box closing the part of the *L–C* circuit was warmed by a heater inserted in it. Later the sample was closed into a vinyl envelope and immersed in oil bath and warmed to about 40°C. The change of vapour pressure at the surface did not seem to affect in the experimental results. When the temperature was lowered cooling materials of dry ice and carbon tetrachloride were used. The changing process must be taken very slowly, since the sample was easily cracked at the rapid variation of temperature. The direct contanct of the liquid to the crystal surface caused relative diminish of the line intensity and disappearance of the wiggle mentioned above. But with the super-regenerative oscillator the intensity of the absorption in this case was strong, showing that the origin of the absorption line comes from the small internal region of the crystal.

The behavior of the broad line at the variation of temperature is shown in Fig. 6. It shows the anormalous shift of the resonance frequency to low frequency side near the two curie points 23° and −18°C. The temperature dependency of the resonance frequency at the two side of each curie point was opposite and the ratio of the coefficient was about one to two. This variation was similar to the piezoelectric vibration reported by Mason[5]. The whole dependency except this large variation seemed to have a negative temperature coefficient, though the low temperature range was not measured precisely. The behavior of sharp line at the variation of temperature was also measured. This line had not anormalies at the curie points, but the small disturbance was observed. The whole dependency except the variation near the curie points was expressed with the temperature coefficient, $(1/\nu)(d\nu/dt)$, of $-4\times10^{-4}/^{\circ}C$ in average. An example of variation of sharp line was shown in Fig. 6 together with the broad line. The measured temperature coefficients at applied electric field to b or c axes also had values between from -3 to $-8\times10^{-4}/^{\circ}C$. These values almost coincide to the value of piezoelectric temperature coefficient of Rochelle salt.

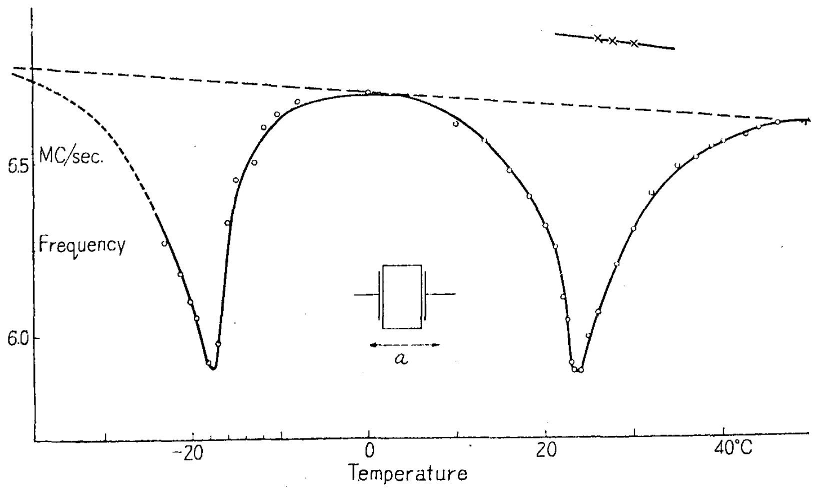

Fig. 6. The temperature versus frequency curves. The high frequency electric field was applied at a axis.

The observation with superregenerative oscillator which had high sensitivity for weak lines led the fact that at low temperature below the lower curie point the intensity of these resonance lines were weakened, the saturated strong absorption lines at the temperature between curie points reduced its intensity and that the observed line abundance was also reduced and finally became to a few weak lines comparable to background noise. This indicated the piezoelectric behavior of the absorption lines.

5. Pressure effect

If the absorption lines have piezoelectric origin they should be affected by a pressure applied externally. In order to investigate the pressure effect a lever method was used, since the direct load changes the frequency of autodyne oscillator innecessarily and disturbed the oscillation stability. The use of the lever could be removed these difficulties almost entirely. The schematic diagram of this method is shown in Fig. 7. A weight at the end of the lever was multiplied by ten times at the sample. The pressure was applied to the surface which contained the plane crossing b and c axes with an angle of 45°. In this case the pressure affected predominantly to the broad line which was characteristic to the a axis. The broad line first destroyed remarkably if a small weights was applied, and displaced in average resonance frequency to lower frequency side. One record of the frequency versus weight curve is shown in Fig. 8. The decay of the broad line was considered to be associated with the composed feature of the absorption lines. The sharp lines did not seem to shift their resonance frequencies by the load with an amount used in this experiment. In general weak lines were dissappeared into the oscilloscope background when the pressure was reached at about several kilograms per square centimeters. In addition they did not recover entirely to compose the original figure and intensity if the load was taken out. In the observation of broad line the load of large amounts made the frequency shift of the absorption line irreversible. Further repeats of measurements with a large amounts of weight became to cause only the small shift of the resonance frequency. Small recovery of frequency shift was observed at the removal of this weights. This phenomena were considered as fatigue. In this condition, if the pressure was reapplied at the normal plane to this surface, the shift was recovered producing the broad line at the initial frequency.

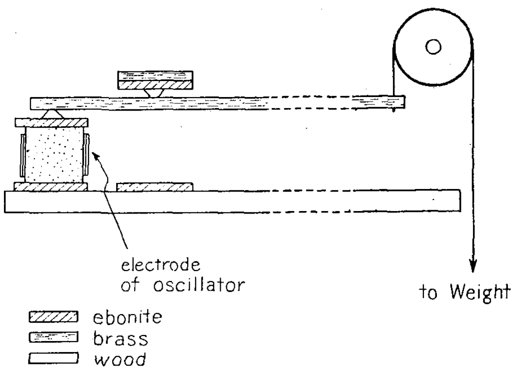

Fig. 7. The schematic diagram of the lever used in pressure effect.

In the case of ordinary vibration of piezocrystal a pressure at the direction of the a axis reduces the piezoelectric constant d_{14}. It connects to decrease the Young's modulus indirectly which lead the frequency shift of vibration to lower side. Therefore above described decay of broad line with pressure was considered to originate in the composed structure of the resonance

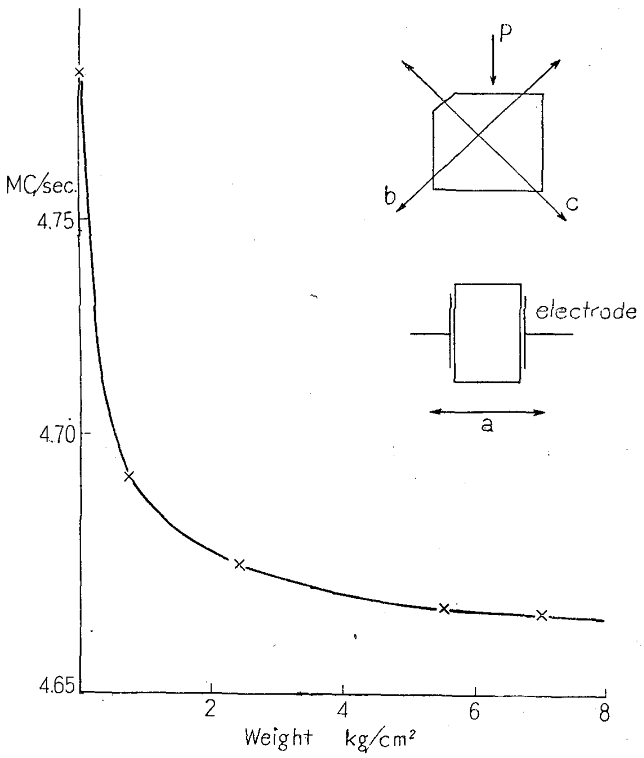

Fig. 8. Pressure versus frequency shift curve observed on the broad line. The section of the crystal is shown with the arrow which indicates the direction of pressure applied.

line. If the broad line originated from many crystal domains, the effect of pressure might cause different change in elastic constant at different domains. Thus it resulted different frequency shifts at each domain which interpreted the decay of the broad line. Later some broad lines were found, which had rather low intensities but shifted to higher frequency side.

One additional phenomenon was the relaxation for the pressure. It took times to build up new condition from the instant that the pressure was applied. The movement of the resonance absorption must be checked relative to frequency marker, since if the pressure was applied the oscillator changed the oscillation frequency a little. As the additional pressure was applied, the marker moved a little instanteneously and then the resonance absorptions moved slowly to the distance away from the previously situated position. At the removal of the additional weights this process was reversed. The marker moved to the original position at that instant leading the recovery of the resonance frequency. From the observation of movement on the oscilloscope the relaxation time was estimated as a few seconds at room temperature.

6. Electrostatic effect

In this experiment a static voltage was applied at the *a* axis. The observation was taken about the broad line. since only this line was caused by the electrostatic field. To increase the effective electrostatic field the aluminum foil was sticked at both surfaces as electrodes. Simultaneous application of high frequency oscillator in the same *a* axis restricted the area of aluminum foil in one small portion as shown in Fig. 9. In this experiment measurement could not be repeated to check the preceeding plot. After some application of static field of about 300 volts the resonance absorption was changed in its composed pattern. It also showed histeresis of resonance frequency against static voltage which could not be plotted perfectly. In Fig. 10 one example of plots is shown. Some of the lines shifted to higher frequency side and some of the other to lower with increasing static voltage. Moreover new absorption lines were appeared during the measurement. Therefore it was very perplexed to distinguish the line behavior. Above described results was considered to be the evidence that the resonance absorption lines were occurred in many localized volumes in a single crystal.

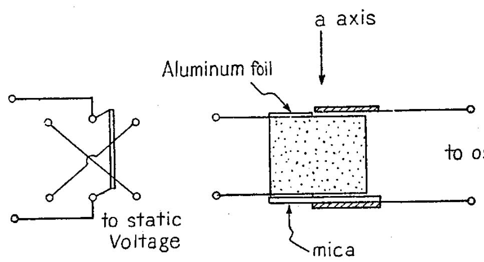

Fig. 9. The arrangement of electrodes in the electrostatic effect.

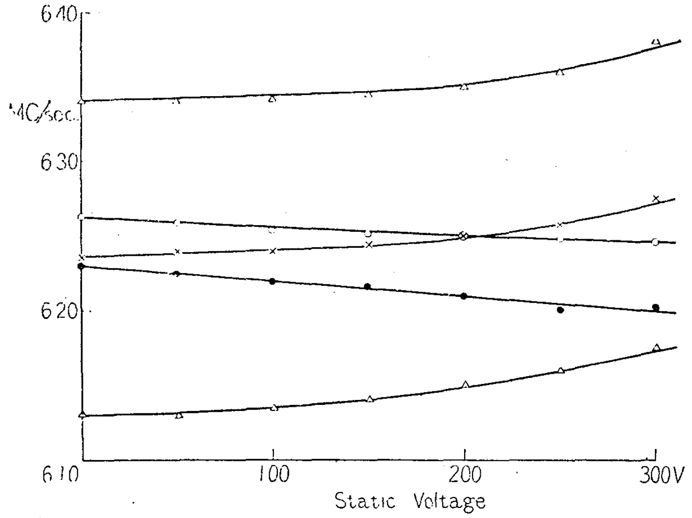

Fig. 10. The frequency shift versus static voltage curves.

7. Conclusion

The resonance absorption lines were found in some piezoelectric crystals. These absorption lines were studied about Rochelle salt. From the experimental results following facts were recognized.

The absorption lines observed from a few megacycles to several hundred megaeycles. In powdered crystal the spectrum showed no systematic distribution while in single crystals the spectrum composed of many line series which seemed to have equidistant separations. However this absorption was not the higher harmonics of ordinary piezoelectric vibration. It is a piezoelectric vibrations which resonated in those high frequencies and originated the localized portion in a single crystal. The consideration of localized vibration was confirmed. A single crystal which showed a strong sharp line was cut into halves. This line appeared in one half and did not in the other. The half containing this line was divided again. Although this block was broken into small pieces and the line could not be seen at all, this was a good proof which show the resonance origin in a small volume of a single crystal.

The absorption lines were classified roughly into two groups. Sharp lines had a width of the order of 1 kc/sec and broad lines had a width of the order of 10 kc/sec. These lines composed of each series but exhibited different behavior when the temperature was varied. This behavior was characterised with each property of crystal axis. The broad line showed the character of *a* axis. The property of *a* axis was known to have a large piezoelectric constant between two curie points. The temperature variation showed the anormalous shift of resonance frequency to low frequency near the two curie points. The sharp lines showed the simple variation which had a negative temperature coefficient agreed the data obtained ordinary piezoelectric vibration.

A pressure caused frequency shifts. This effect was predominant for the broad line. Almost of the broad lines shifted with a weight to low frequency side. This recognized from the pressure effect of the ordinary piezoelectric vibration. However, some lines moved to higher frequency side. Therefore it should be considered that the effect of pressure caused different effect at different domains in one crystal. Electrostatic field also caused the frequency shift on the broad lines. By applying the electrostatic field these lines were moved to higher or lower frequency side crossing each other. Further more new broad lines were appeared after many experimental measurements.

From these results it may be said that the absorption lines are piezoelectric vibration in crystal which resonate to a high frequency electric field applied externally. It is however not a usual resonant vibration but originates in localized portion of a single crystal. This localization are reasonably considered as crystal boundaries or dislocations which is produced naturally. It also connects to imperfections of crystals. The quantitative analysis could not yet been done. It is valuable to study this resonance absorption and to find some connection to the existence of grain boundaries ànd dislocations in single crystals.

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