STABILITY OF QUARTZ RESONATORS AT VERY LOW TEMPERATURES

F. P. Phelps

National Bureau of Standards

Quartz Crystals serve as the frequency determining elements in the more precise types of frequency standards, oscillators and like equipment where precise control of frequency is required. In fact, the best way at present for controlling frequency to a high degree of precision, for any protracted period of time is by means of Quartz Crystals. Atomic and molecular standards will probably be used as spot checking devices while the Quartz Crystal is used as the flywheel to carry on between checks. However, all quartz crystal units designed for frequency control are subject to the defect of "aging" i.e., the resonance frequency of the crystal changes as time elapses. For crystals fabricated with the utmost skill and care, or such as those used to control the frequency of the Standard Frequency and Time Broadcast Stations of the NBS, WWV at Washington, D.C., and WWVH at Hawaii, the residual drift is very small, being less than 1 part in 10^9 per day and after several years this may decrease to about a part in 10^{10}. To give a concrete idea of what this means, let us suppose that the crystal is used to drive a clock. Since there are approximately 10^9 seconds in 30 years, a precision of one part in 10^9 corresponds to about one second in 30 years while a precision of 1 part in 10^{10} corresponds to about one second in 300 years. However, these changes, as small as they are, need to be reduced as there are military and other applications requiring a precision of frequency measurement of about this order of magnitude (1 part in 10^9) or about that of the present primary standard of frequency. Since it is axiomatic that a primary standard should be more precise, preferably by one or more orders of magnitude, than that which is to be measured by the Standard, it has become increasingly clear that the present standard of frequency must be improved; and obviously this also means improved measuring techniques and equipment since these go hand in hand with the standard. Work with this end in view is now under way at the Boulder Laboratories of the NBS along several avenues of approach including development of atomic and molecular frequency standards as well as improvements in the performance of Quartz Crystals. This report concerns only a small part of this work.

There is evidence both theoretical and experimental that by operating the crystal at a very low temperature, such as the temperature of liquid He ($4^{o}K$) or even that of liquid nitrogen ($76^{o}K$) a reduction of several orders of magnitude will be obtained in the aging rate, together with a material improvement in Q in some instances. Naturally, crystal units designed to operate at ordinary temperatures cannot be expected to perform at their best at these very low temperatures. For a number of years our laboratory has been investigating crystal units at low temperatures and has arrived at a design suitable for use at liquid N_2 temperature. This is essentially an AT type unit, modified by changing the ZZ' or ϕ angle so as to give a "turnover point" on the f vs. t curve at or slightly above N_2 temperature ($76^{o}K$).

More recently there has been under way, for the Signal Corps, investigation of the "Stability of Quartz Resonators at Low Temperatures." This project involves the development of cryostats, the design and development of frequency measuring devices and techniques which are "capable of measuring frequencies with a precision of a few parts in 10^{10} or better" and finally, measurement of the frequency and stability of high precision units fabricated at BTL under another contract with the Signal Corps.

Certain phases of both these projects will be discussed and some of the results thus far obtained will be shown.

Cryostats for the project are being developed in the Bureau's Cryogenic Laboratory by Dr. Goodwin. Details are rather fully set forth in the various project reports and all one need say here is that a cryostat has been designed and is being built which will permit a maximum of flexibility for experimental purposes, i.e., in the application of different refrigerants, and of different methods of temperature control, applicable both to short-time studies and to protracted aging studies. Dr. Goodwin, I am sure, will be glad to answer any questions concerning this part of the work.

The problem of the development of frequency measuring equipment and techniques has been apporached along several lines:

(1) The first is dual channel frequency multiplier system paralleling the equipment used in connection with monitoring WWV and WWVH. A part of this equipment is now in operating with a resolution of 1 part in 10^9. It is planned to increase this by multiplying the beat frequency by 10 or 100 before counting it, thus obtaining a resolution of 1 in 10^{10} or 10^{11} respectively. A limiting factor determining how far we can go along this line, no doubt will be the noise level. However, we expect at least 1 in 10^{10} and hope ultimately to attain a precision of 1 part in 10^{11}.

(2) Another is the 5 MC and 2.5 MC stable oscillators with tunable multipliers so that frequencies considerably off from the nominal can be measured. Most nontunable multipliers pass only a very narrow band of frequencies. This type of equipment is for use where there are large frequency changes such as when a crystal is measured over a large temperature range. (See slide 1)

(3) A third system is a resonance method whereby a stable oscillator is tuned to the resonance frequency of the crystal, the criterion for resonance being zero phase shift in going through the crystal. Any phase shift will be translated through a servo system into dial motion returning the drive oscillator. (See slide 2)

(4) Also there are several other methods under development which are not so far along toward completion as the above three.

Further details of these methods and their circuitry will be shown later if time permits.

Crystal Measurements.

Slide 3 shows the aging rate or frequency drift of two GT type 100 kc crystals in 50-foot wells below the Radio Building. Here the temperature is about 13°C and is rising steadily at a rate of about 0.001°C per day. One has been in operation since February 5 and the other since February 20. They are used as the control element in WE type D175730 Frequency Standard oscillators. The frequency is measured and recorded with a precision better than 1 in 10^{10}. It will be noted that the drift rate is already somewhat less than 1 part in 10^9 per day.

Slide 4 is for another GT 100 kc unit which is Pt plated and the electrodes soldered directly to the platinum without benefit of Ag spots. It appears to be quite sensitive to position. It was placed in an ice bath and frequency measurements made by a resonance method. The individual measurements are precise to 1 to 10^{10}. The erratic readings recorded probably are due to changes induced by the slight movements of the crystal when the thermos is serviced with cracked ice. Although there is a good deal of scatter, yet a definite aging trend is obvious, somewhat more than 1 part in 10^9. It is planned next to put this crystal in one of the 50-foot wells at 13°C and record its aging as is being done for the two units on the previous slide.

Slide 5 represents a 5 MC 5th overtone AT type modified to have a turnover point near N_2 temperature (-7° below) R^{N2}_{S} = 45 ohms R^{He}_{S} = 20 ohms. It was put in liquid nitrogen December 21, 1956, the resolution of the measuring equipment then was only about 2 parts in 10^8. About January 23, 1957, this was increased to 1 in 10^9 by the addition of newly completed equipment. The scatter which one sees here is believed to be in part due to oscillator instability and in part to temperature changes (variation of N_2 temperature with atomspheric pressure changes). From later data taken after eliminating or at least reducing a large part of the oscillator troubles most of the variations are believed to be due to temperature changes. Note that there is no apparent continuous drift. The thin line represents what the change would have been if the frequency had drifted 1 part in 10^9 per day. In slide 6 the upper curve shows frequency changes while the lower one represents temperature changes. Note that almost one to one correspondence of the changes.

Slide 7 indicates this crystal had a turning point about 0.7° below N_2 temperature. The temperature coefficient calculated from the data on this and the previous slide is about 9×10^{-8} per 1°.0. It is operating in the region indicated. At this operating point a frequency stability of 1 part in 10^{10} would require temperature control to 0.01°K or about 2/3 of a mm pressure (1 mm pressure = 0.014°K). If the operating point were right at the turnover temperature much less precise control of temperature would suffice.

In connection with the design of a crystal unit for operation at these low temperatures such as the one described above with the expectation of attaining increased stability and reduction of aging, the frequency versus temperature characteristics of a family of crystal units have been explored over the temperature range. These units may be looked upon as modifications of the well-known AT Type. In the IRE Standard Nomenclature they would be designated yxl ($\phi = 35^\circ 15'$ to $41^\circ 30'$), length = width = diameter (round plates). Quartz has two temperature coefficients of frequency, one positive and one negative, which are tied in with the various elastic constants of quartz.

It is well known (for a limited range of temperatures only) that by cutting a quartz plate at a suitable crystallographic orientation these positive and negative coefficients may be made to neutralize or balance one another at any desired temperature within this limited range to give a crystal unit having essentially zero coefficient of frequency at that temperature.

In slide 8 that there is a point on each f vs. t plot where the curve goes through a minimum and another where it goes through a maximum. At these points the temperature coefficient of frequency is, of course, zero and also is quite small for a considerable range on each side. Note also that as the ZZ' angle (ϕ) becomes larger ($35^\circ 30'$ to $35^\circ 50'$) the upper turnover point moves toward higher temperatures and the lower one toward lower temperatures. This slide covering experimental data between about -60°C and +120°C represents the situation prior to the present work. We have extended the upper temperature limit to about 250°C and the lower to -269°C (4°K) and have summarized the data in slide 9.

Here the temperature at which the frequency-temperature coefficient is zero is plotted as a function of the angle of cut (ϕ or ZZ'). Note in the lower portion of the curve that for each value of ϕ just as on the previous slide there are two temperatures at which the "Turnover Points" (points of 0 temperature coefficient) occur and that as ϕ becomes larger these two temperatures approach one another and finally coalesce at about $\phi = 40^\circ 37'$ and produce a point of inflection at about $-228^{\circ}C$ on the f vs. t curve very much like that which you saw on the previous slide near $30^{\circ}C$. For angles greater than $\phi = 40^{\circ}37'$, no turnover points could be found showing that for angles larger than this it is not possible, by the procedures here used, to balance the positive and negative coefficients and obtain an effective zero coefficient.

This curve supplies us with the correct value of ϕ to use, that is, at what angle to cut the crystal if we wish to fabricate a crystal unit which will have a zero or very small temperature coefficient of frequency at any predetermined low temperature. Data of this kind is also of considerable theoretical interest since it is closely related to the structural and elastic constants of Quartz about which much remains to be known.

Slide 10 shows a number of f vs. t curves from which the lower portion of the curve in Slide 9 was derived.

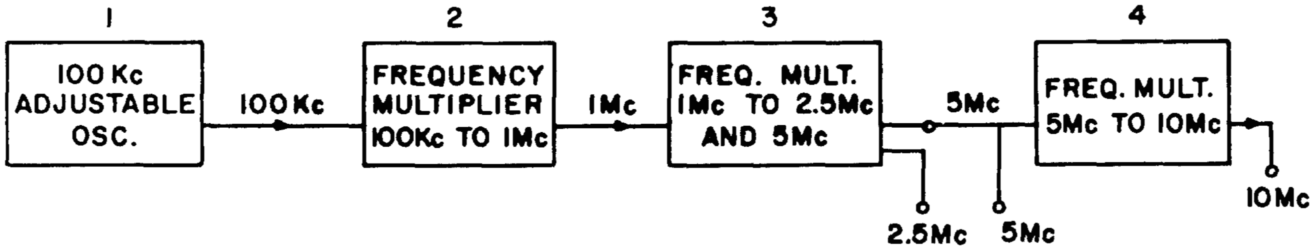
In Slide 10 an additional interesting point may also be noted. In several instances after the f vs. t curves had been obtained with the crystal unit highly evacuated (1×10^{-6}mm/Hg), a small amount of helium (about 400µ at room temperature) was introduced into the unit to eliminate the temperature lag inherent in the highly evacuated unit.

In every case it was observed that the crystal (in helium) had a lower frequency at and near the temperature of liquid helium than when it was highly evacuated. This is especially interesting in view of the fact that in vacuum the temperature-coefficient appears to be slightly negative; so the observed effect is in the wrong direction to be due to heating of the crystal by the energy put into it to drive it and the better dissipation of heat by Helium.

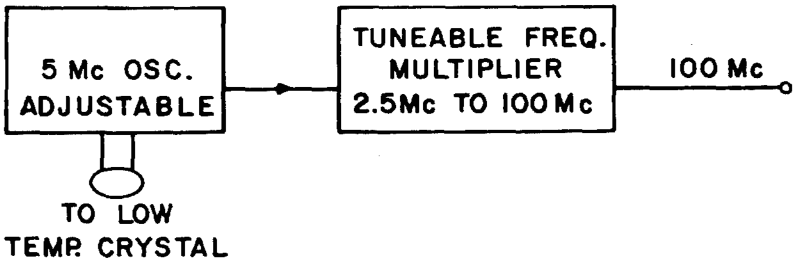
We have not as yet arrived at a satisfactory explanation for this behavior, but have been thinking on the possibility that the crystal in its vibrations may set up high frequency compressional waves in the adjacent helium of of sufficient intensity to liquefy some helium on the crystal. This would tend to "load" the crystal so that its frequency would be lowered thus explaining the effect. This idea seems to have some plausibility because the helium in the envelope at these temperatures is very close to the liquefaction temperature, and the effect becomes more pronounced as the temperature of liquid helium is approached. We would be very happy to have any comments or ideas on this subject.

Slide 11 shows a group of these plates.

Slides 12 and 13 show the f vs. t curve for a plate 1 minute beyond the limiting angle of 40°37' and 1 minute below this angle respectively.

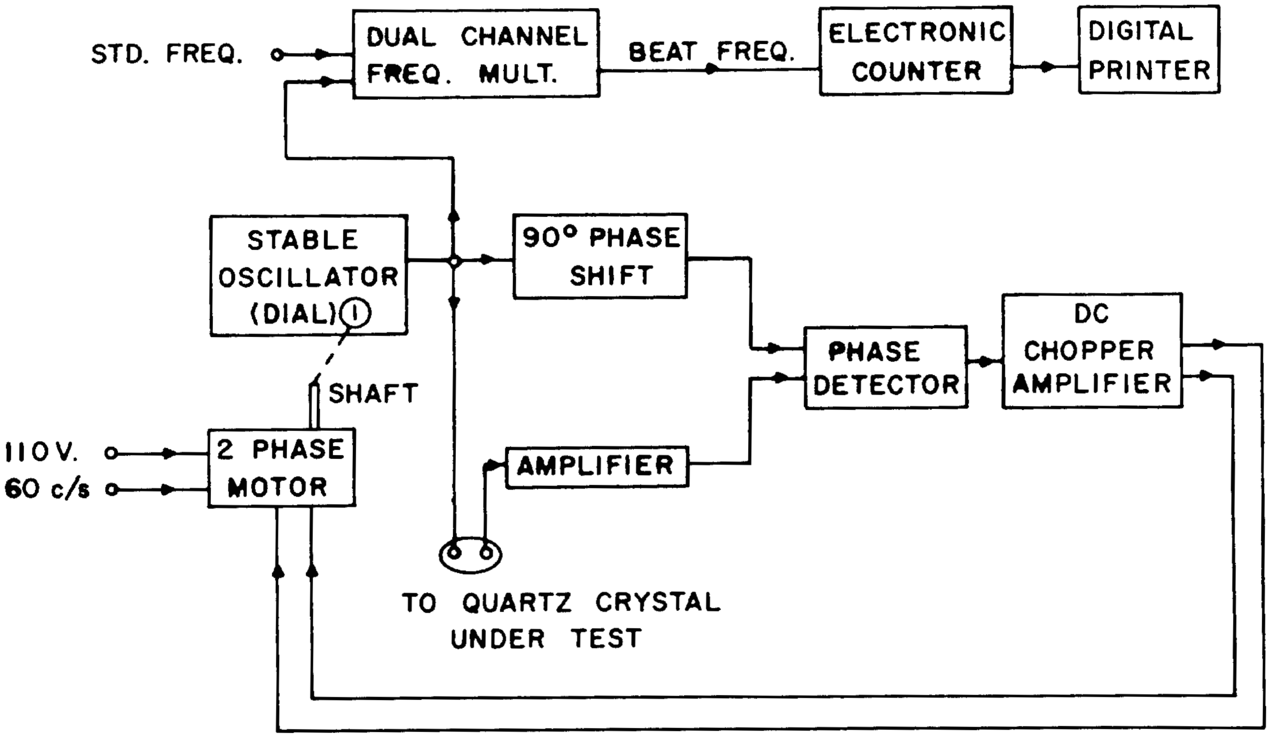


(A) EXTENSION OF PRECISION OSCILLATORS TO 2.5, 5 AND 10 Mc.



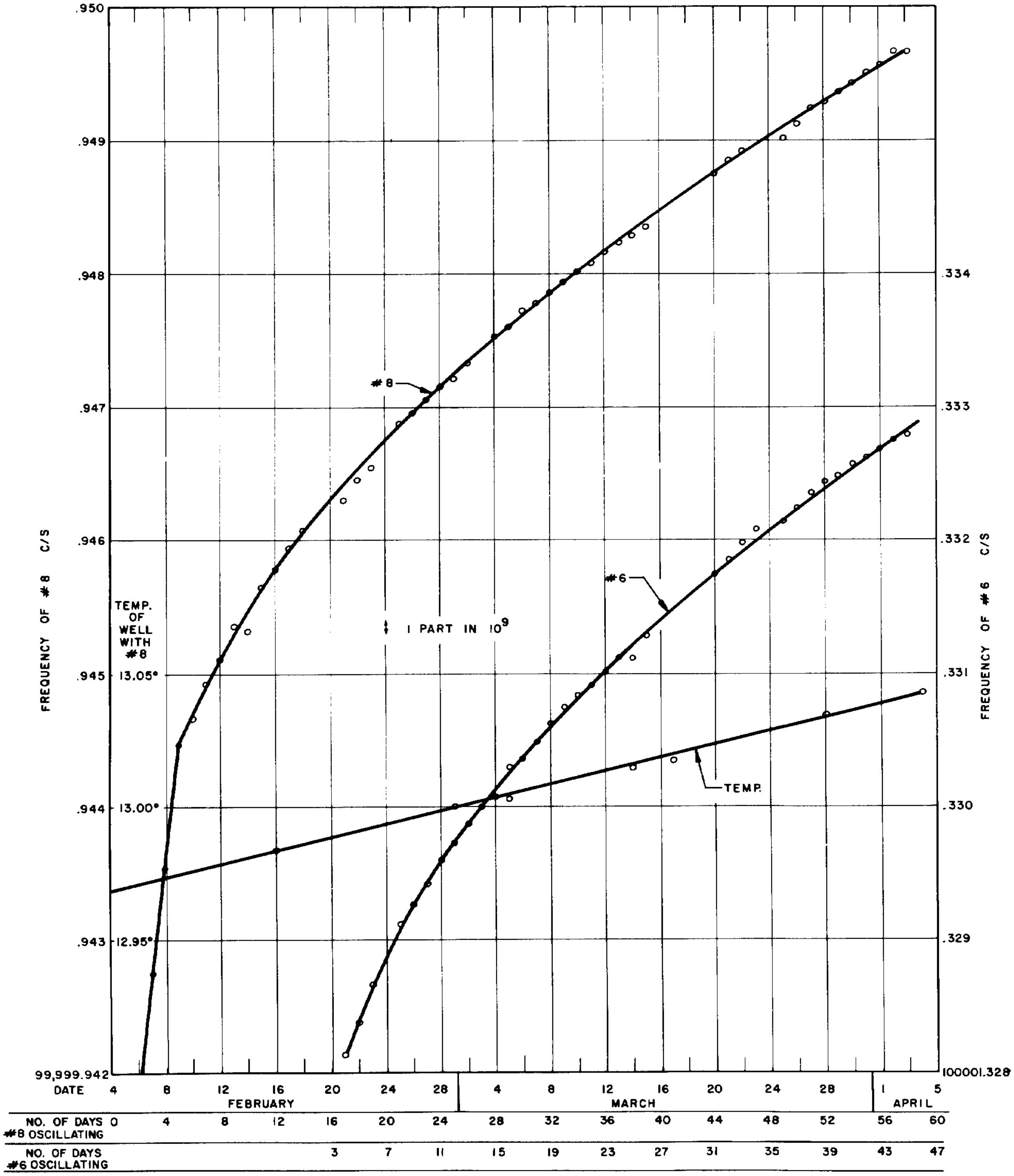
(B) 5Mc OSCILLATOR AND TUNEABLE FREQ. MULT.

Slide 1



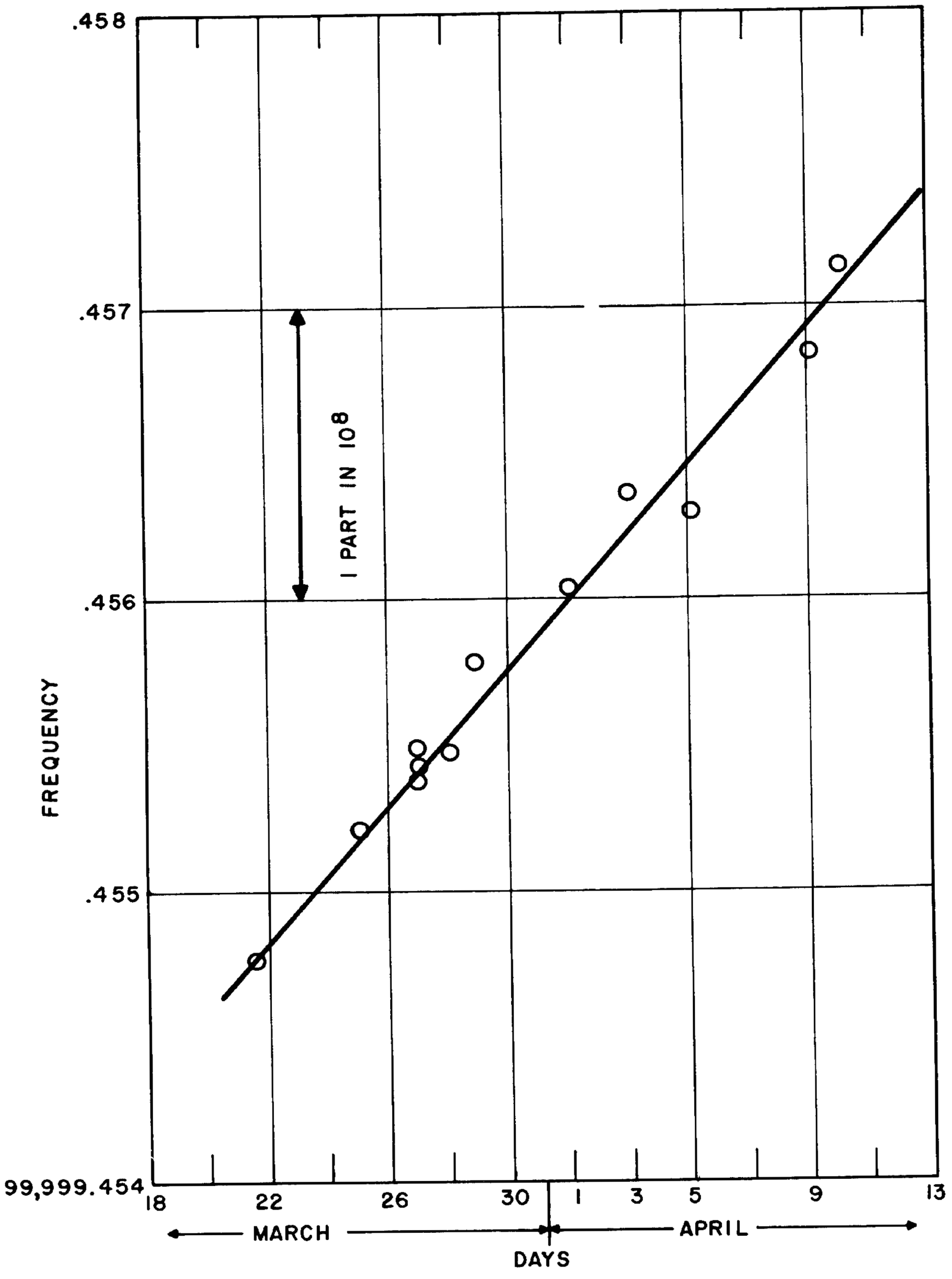
CRYSTAL - AGING MEASURING SYSTEM

Slide 2



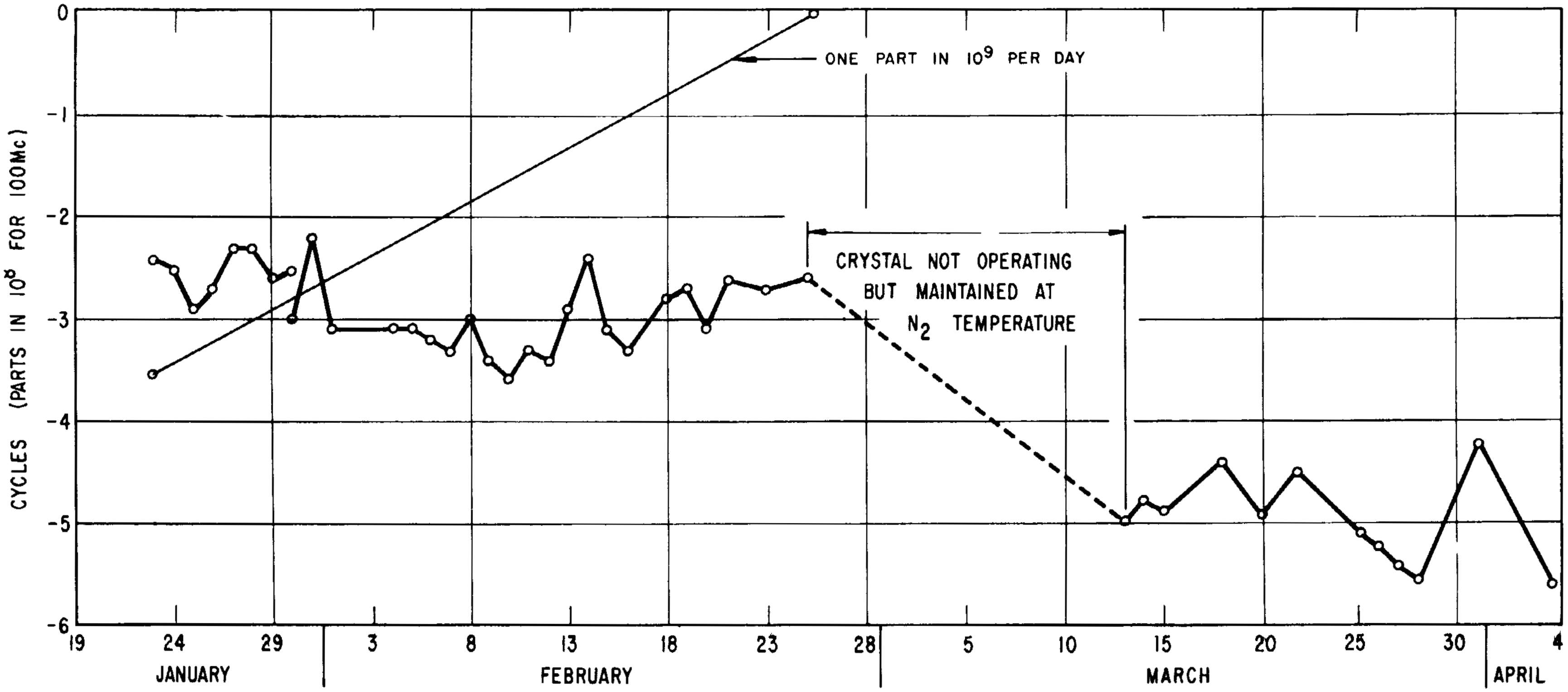
FREQUENCY OF CRYSTAL UNITS 6 AND 8 — TEMPERATURE 13°C.

Slide 3



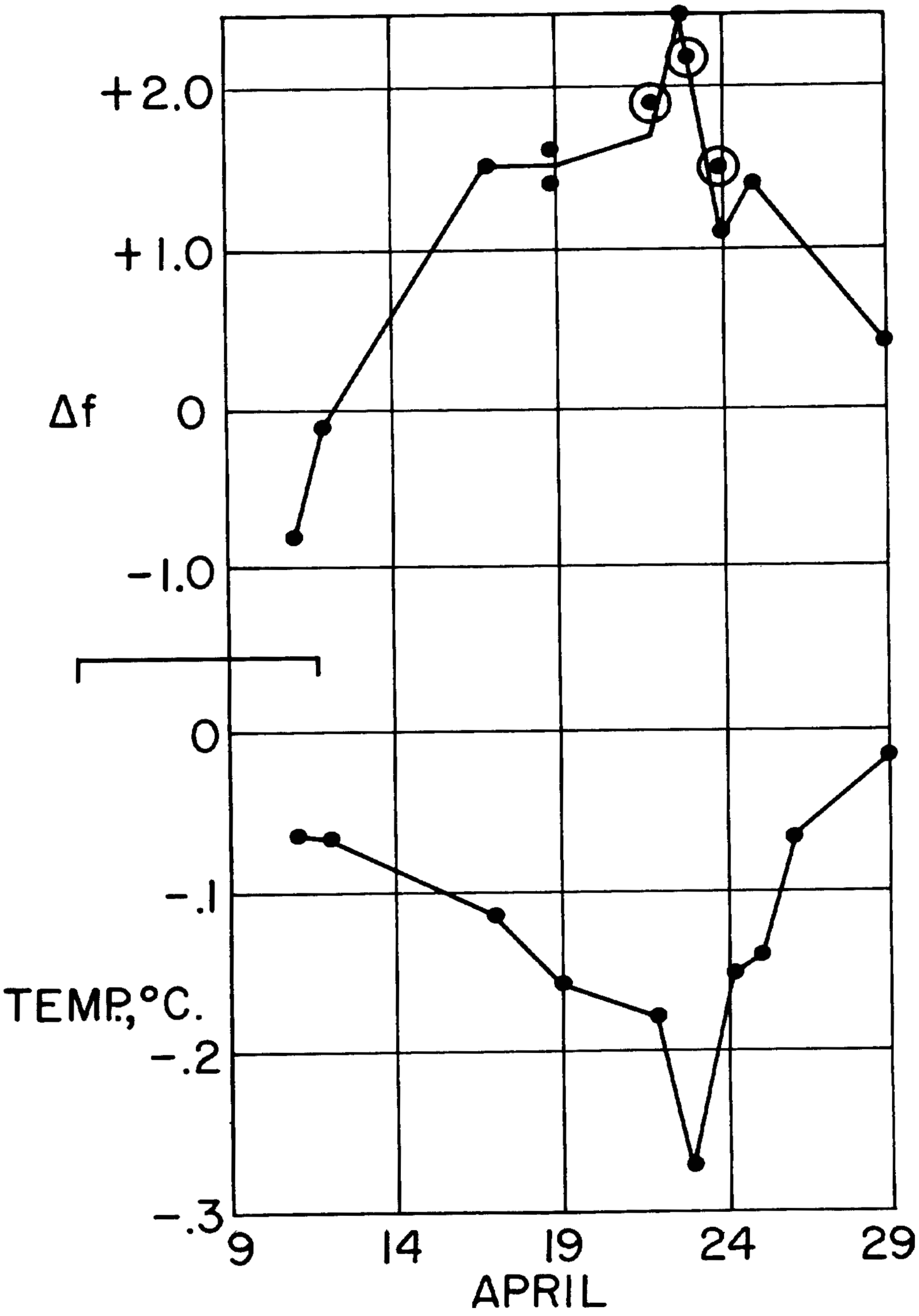
AGING OF CRYSTAL # 1-P

Slide 4



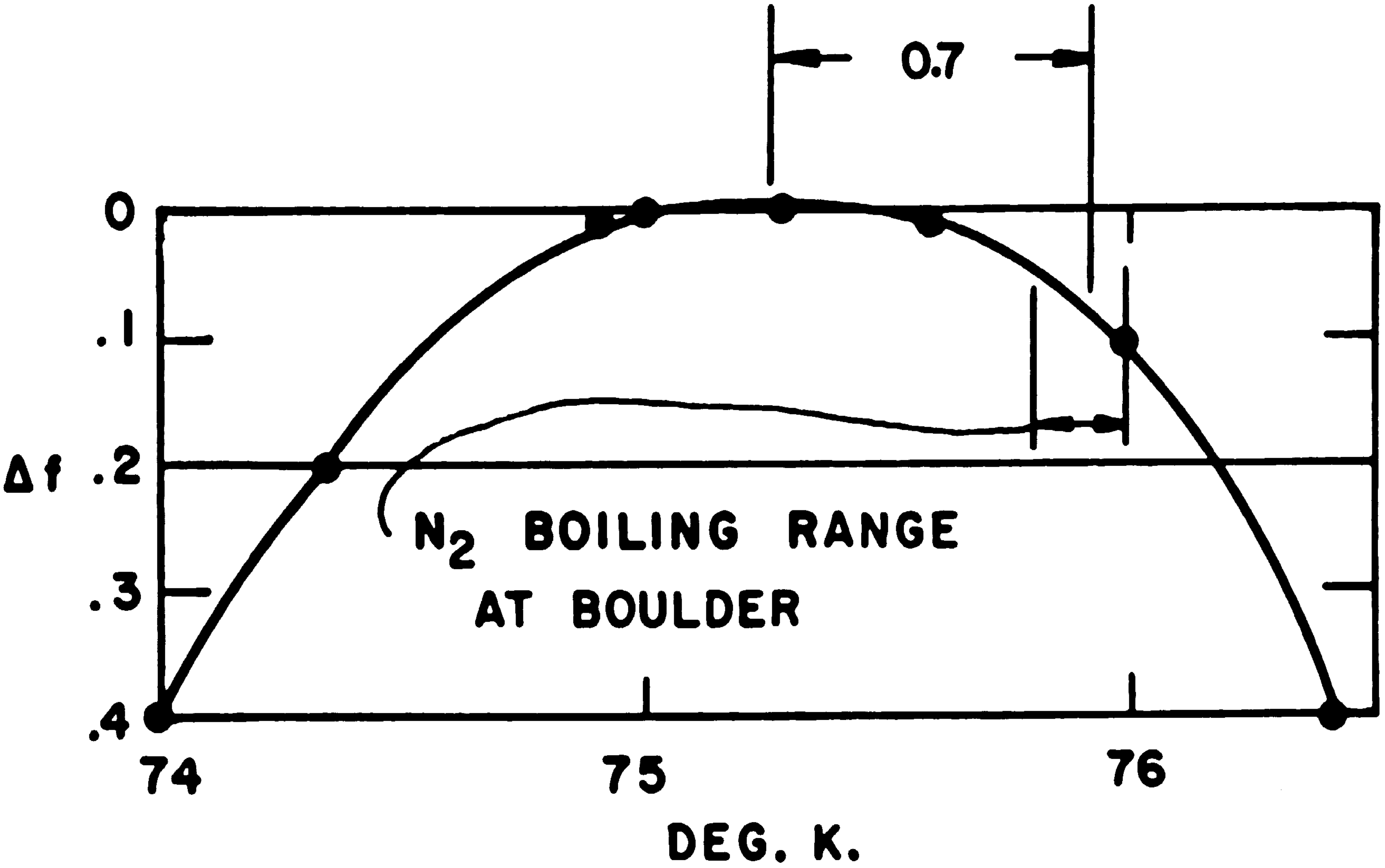
CRYSTAL UNIT NBS I-21 IN N_2 OPEN TO AIR

Slide 5



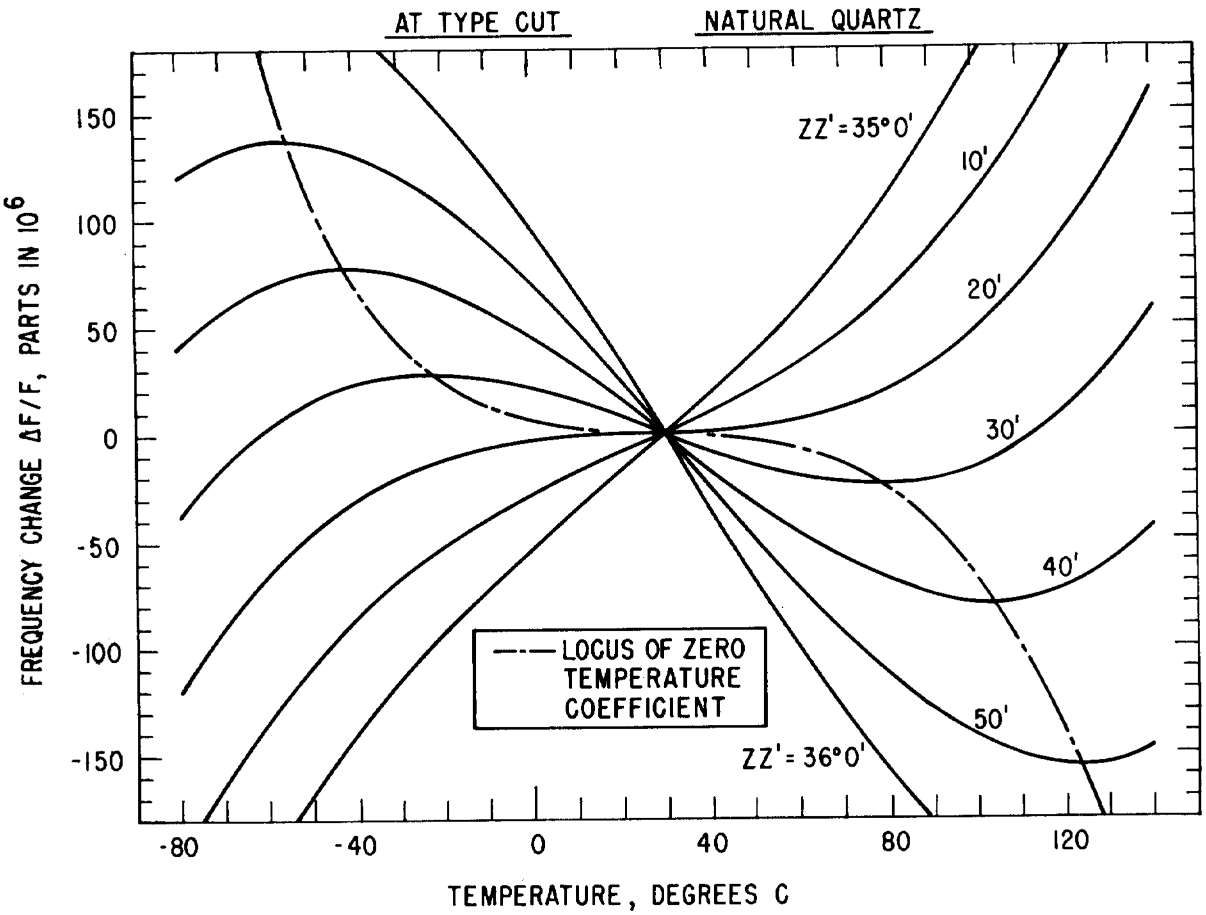
CRYSTAL #1-21

Slide 6

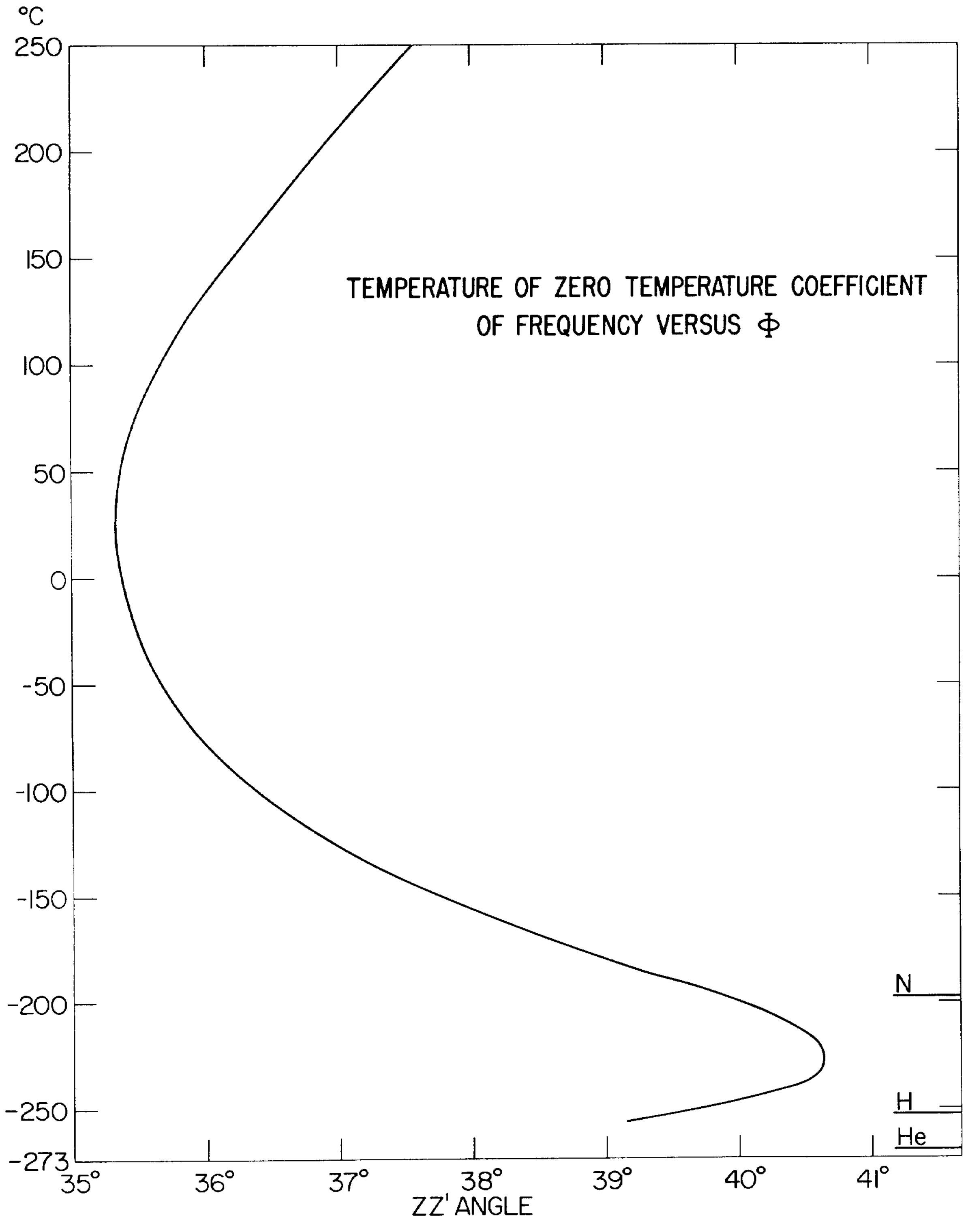


CRYSTAL # 1-21

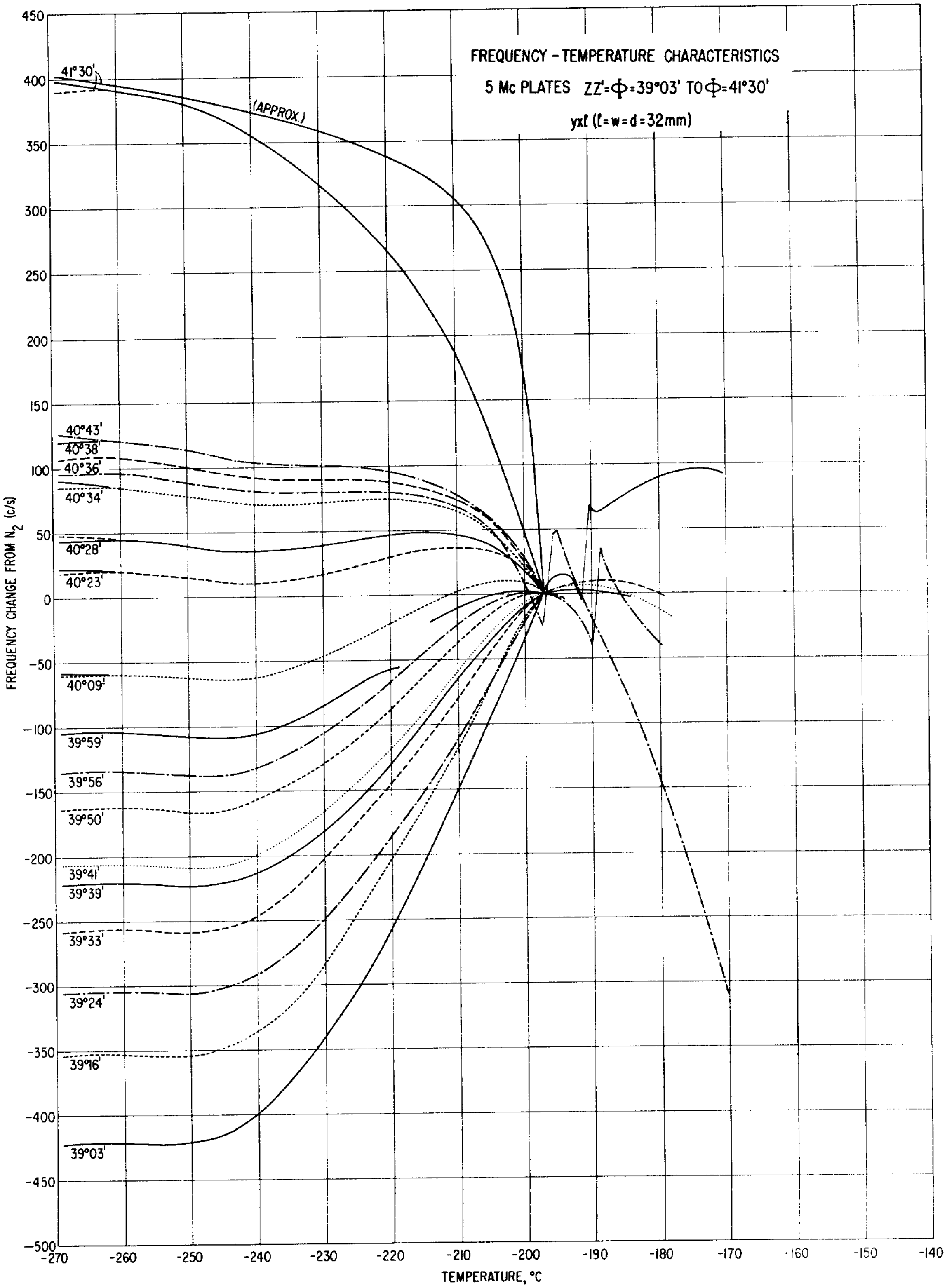
Slide 7


AT TYPE CUT
NATURAL QUARTZ
ZZ'=35°0'
10'
20'
30'
40'
50'
ZZ'=36°0'
LOCUS OF ZERO TEMPERATURE COEFFICIENT
FREQUENCY CHANGE ΔF/F, PARTS IN 10^6
150
100
50
0
-50
-100
-150
-80
-40
0
40
80
120
TEMPERATURE, DEGREES C

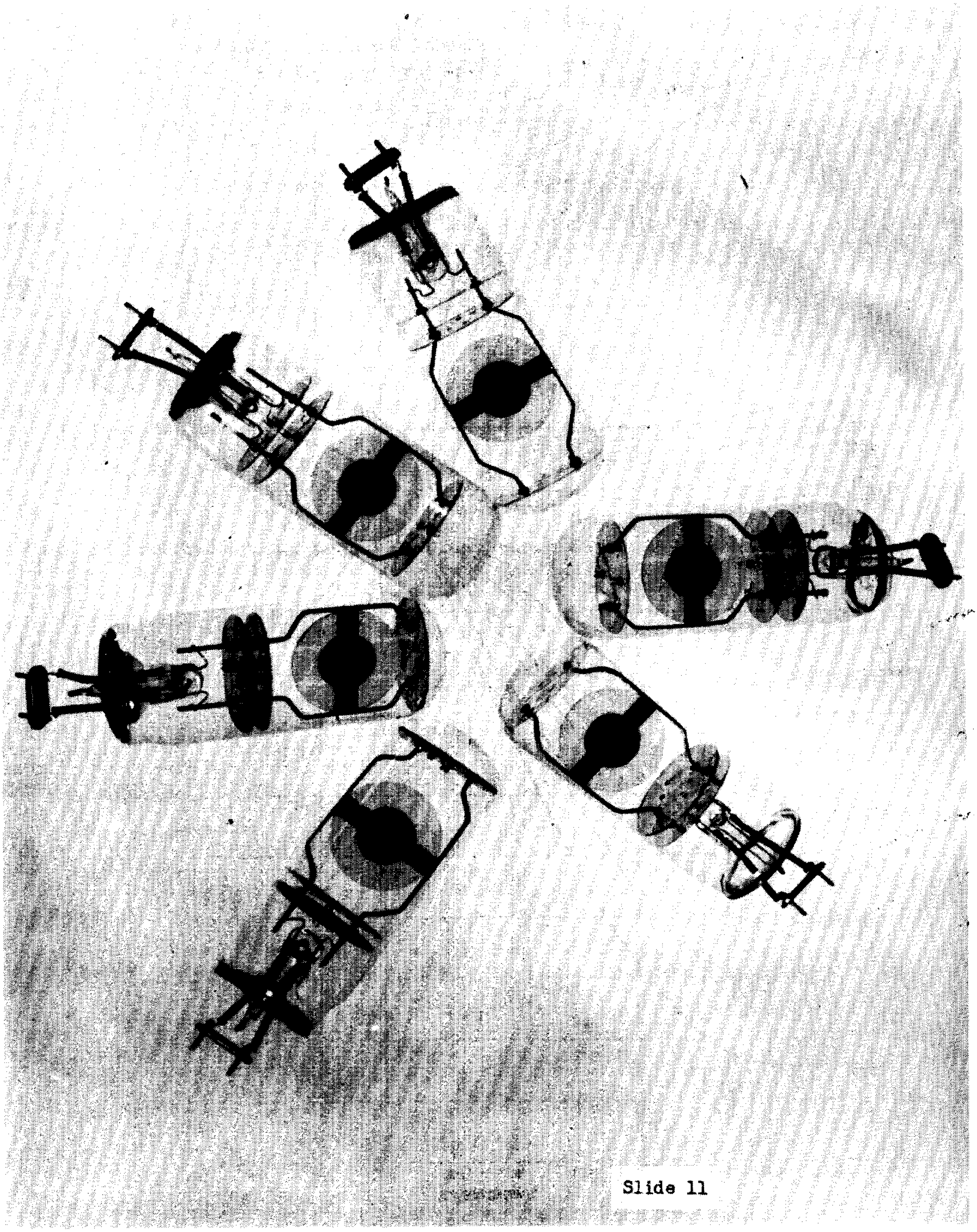
Slide 8


°C
250
200
150
100
50
0
-50
-100
-150
-200
-250
-273
TEMPERATURE OF ZERO TEMPERATURE COEFFICIENT OF FREQUENCY VERSUS Φ
N
H
He
35°
36°
37°
38°
39°
40°
41°
ZZ' ANGLE

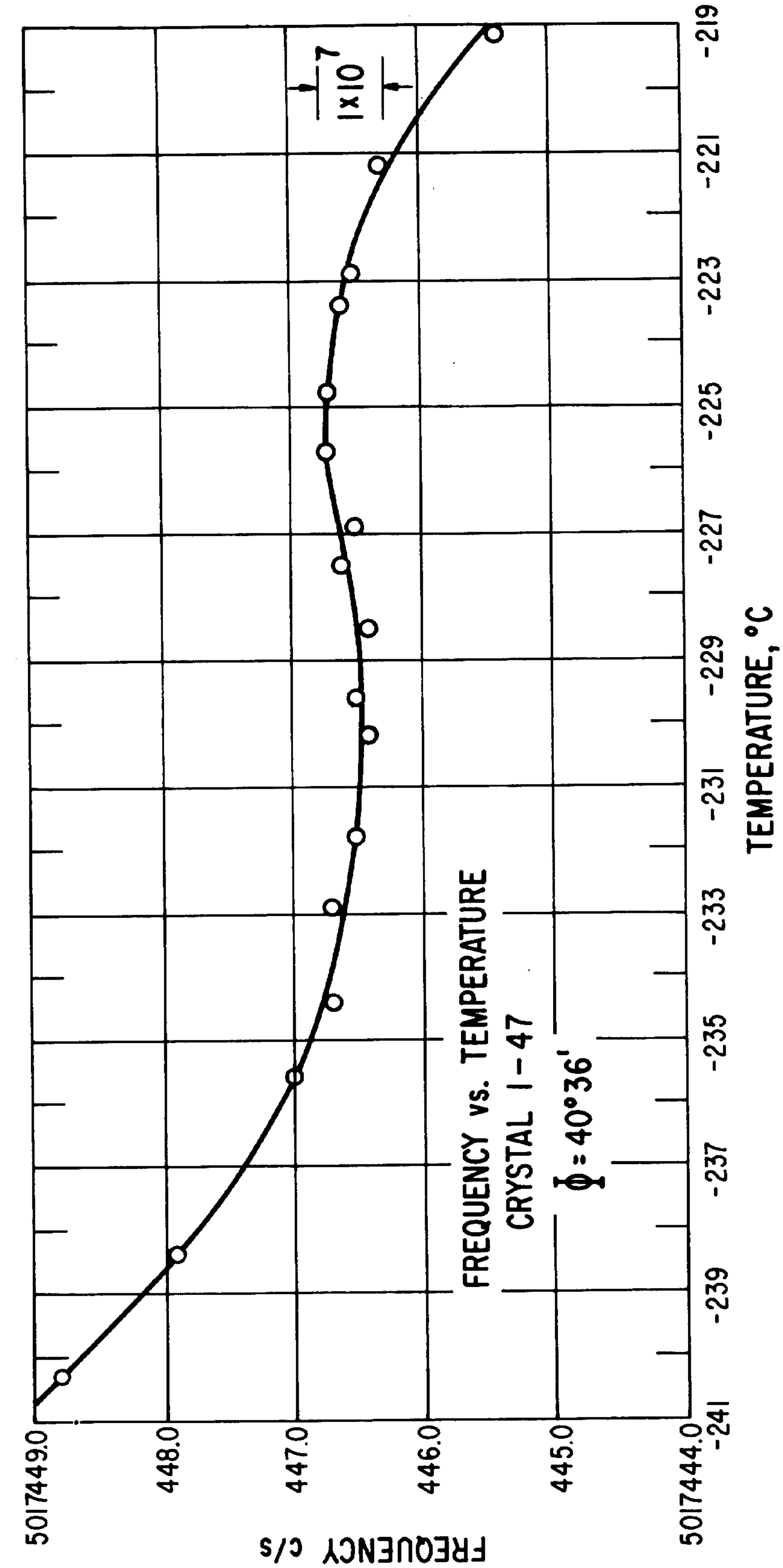
Slide 9


FREQUENCY - TEMPERATURE CHARACTERISTICS
5 Mc PLATES ZZ'=Φ=39°03' TO Φ=41°30'
yxl (l=w=d=32mm)
41°30'
(APPROX.)
40°43'
40°38'
40°36'
40°34'
40°28'
40°23'
40°09'
39°59'
39°56'
39°50'
39°41'
39°39'
39°33'
39°24'
39°16'
39°03'
FREQUENCY CHANGE FROM N_2 (c/s)
450
400
350
300
250
200
150
100
50
0
-50
-100
-150
-200
-250
-300
-350
-400
-450
-500
-270
-260
-250
-240
-230
-220
-210
-200
-190
-180
-170
-160
-150
-140
TEMPERATURE, °C

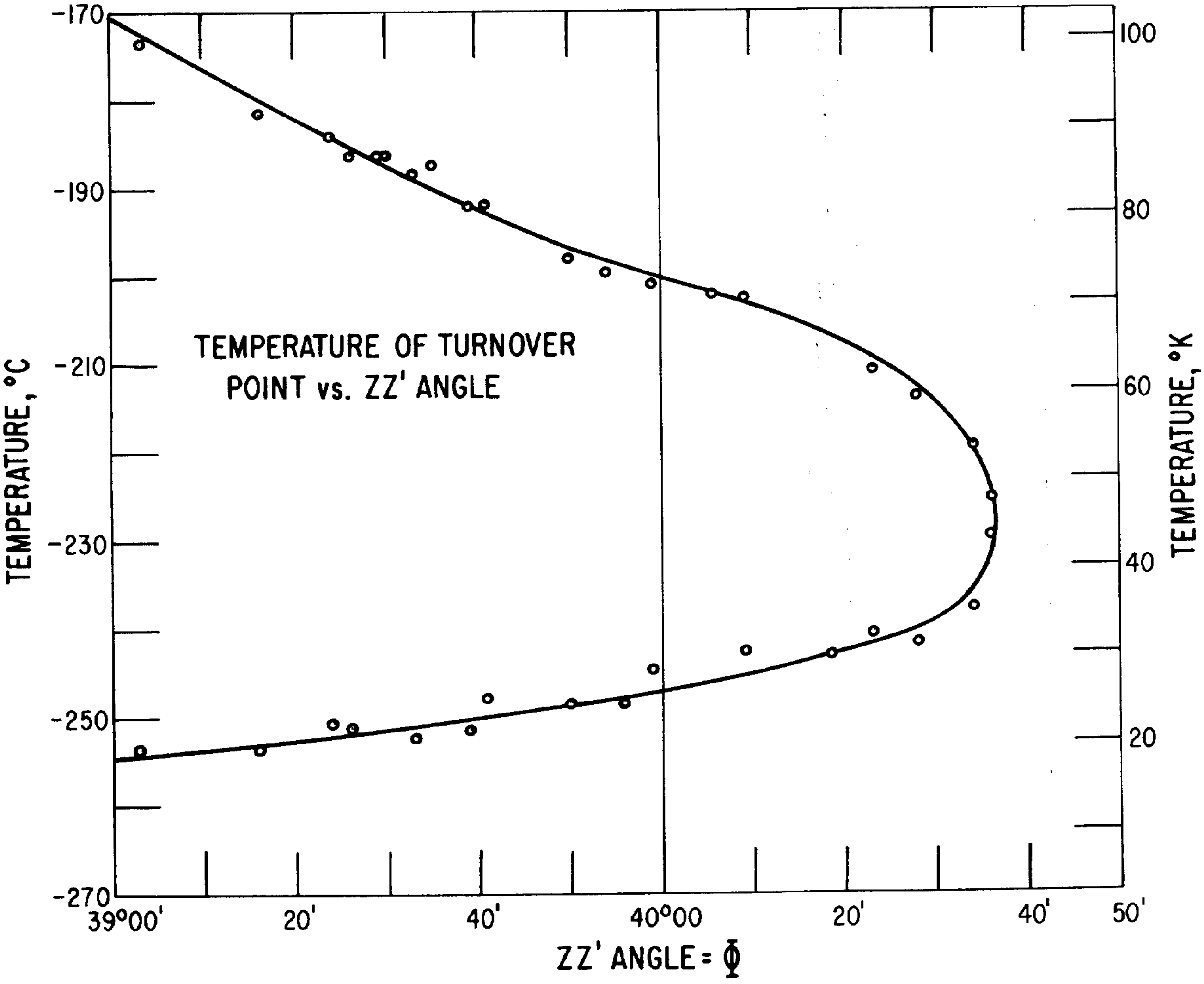
Slide 10



Slide 11


FREQUENCY vs. TEMPERATURE
CRYSTAL I-47
Φ = 40°36'
1×10⁻⁷
TEMPERATURE, °C
FREQUENCY c/s
5017449.0
448.0
447.0
446.0
445.0
5017444.0
-241
-239
-237
-235
-233
-231
-229
-227
-225
-223
-221
-219

Slide 12


TEMPERATURE OF TURNOVER POINT vs. ZZ' ANGLE
TEMPERATURE, °C
-170
-190
-210
-230
-250
-270
TEMPERATURE, °K
100
80
60
40
20
39°00'
20'
40'
40°00
20'
40'
50'
ZZ' ANGLE = Φ

Slide 13