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Optical Observations Concerning the Polymorphic Transition in the Potassium Halides

S. WIEDERHORN AND H. G. DRICKAMER

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At approximately 20 000 atm the potassium halides undergo a phase transition from the FCC (NaCl) structure to the SC (CsCl) structure. Using optical equipment developed in this laboratory various optical effects were observed including the rate of cutoff of the light and the wavelength dependence of the scattered light. The phase transition is apparently initiated by shear involving a large cutoff of light with little or no volume change. At the beginning and end of the transition the scattering is largely small particle scattering, with large particles dominating the middle region. Rb^+ impurity has little effect on the transition. Na^+ impurity apparently inhibits the nucleation strongly, and, to some extent, the growth.

From the absorption spectra of Pb^{++} ion impurity it is apparent the nuclei consist of hundreds of ions, rather than smaller units.

THE pressure induced, first order, phase transformation of the potassium halides has been studied by optical means. The potassium halides undergo a phase transformation at about 20 000 atm at room temperature,[1] and change from a sodium chloride to a cesium chloride type structure.[2,3] As these salts undergo transformation, they become opaque.[4] The opacity is due to light scattering, which is caused by the formation of some cesium chloride type phase within the sodium chloride phase. Information on the mechanism and kinetics of the transformation were obtained by making various optical measurements on the salt during the transformation.

Single crystals, obtained from the Harshaw Corporation, were used in all pure sample measurements. Impurity samples of NaCl and RbCl in KCl, and PbI_2 in KI were made in the laboratory from Fisher Certified ACS grade chemicals. The pressure equipment used has been described previously.[5] In order to obtain right-angle scattering measurements, a third window was added at right angles to the first two. All samples were one-eighth inch in thickness and except for the wavelength dependence readings, all light intensity measurements were made at 580 mμ. The wavelength dependence measurements were made at 50 mμ intervals from 450 to 650 mμ. The volume change of the sample as it proceeded through the transformation was obtained by measuring the displacement of the piston which, in turn, was obtained from the amount of oil used to displace it. The fraction of the sample transformed is calculated from these volume measurements.

The decrease in the intensity of the light being transmitted through a sample of potassium halide is due to light scattering, since the potassium halide does not absorb in the range studied, 450 to 650 mμ. The onset of darkening is an indication of the nucleation of the new phase. The intensity of the light coming through the bomb, at constant pressure, changes with time, as shown in Fig. 1. There is a continuous change in the shape of the curves as one passes from a low to a high pressure. In fact, if the individual curves are translated an appropriate distance along the time axis, they form part of a general curve. This leads one to believe that, except for the size of the time unit, the kinetics of the reaction are independent of the pressure. The transformation is therefore isokinetic, as defined by Avrami.[6–8]

The rate of darkening and the pressure at which darkening first occurs depends not only on the pressure used but also on the history of the sample. Table I shows how the pressure at which darkening first occurs varies with the number of times that the sample is transformed. For potassium chloride, the darkening occurs at the lowest pressure, 24 200 atm, the first time through the transition. The pressure at which darkening first occurs gradually approaches an upper limiting pressure, 25 900 atm, with succeeding times through

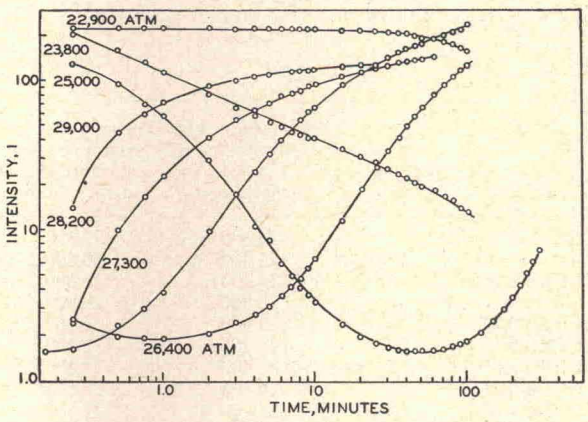

FIG. 1. Darkening curve KCl-single crystal-intensity vs time. Sample thickness 0.015 in.

[1] P. W. Bridgman, Z. Krist. **67**, 363 (1928).
[2] R. B. Jacobs, Phys. Rev. **54**, 468 (1938).
[3] J. C. Jamieson, J. Geol. **65**, 334 (1957).
[4] I. S. Jacobs, Phys. Rev. **93**, 993 (1954).
[5] R. A. Fitch, T. E. Slykhouse, and H. G. Drickamer, J. Opt. Soc. Am. **47**, 1015 (1957).
[6] M. Avrami, J. Chem. Phys. **7**, 1103 (1939).
[7] M. Avrami, J. Chem. Phys. **8**, 212 (1940).
[8] M. Avrami, J. Chem. Phys. **9**, 177 (1941).

TABLE I.

Sample	No. of times through the transformation	Pressure at which darkening first occurs—atmospheres
KCl	1	24 200
	2	25 500
	3	25 900
	4	25 900
	5	25 900
	10	25 900
KCl:Na 0.5%	1	25 100
	2	26 800
	4	27 700
	15	27 700
KCl:Rb 3.0%	1	23 800
	2	24 200
	3	25 100
	4	25 100
	5	25 500
	10	25 500

the transition. These results show that some sort of work hardening has occurred. It requires more energy to nucleate the new phase in a sample which has been transformed many times, than for one which has been transformed only once or twice. This energy increase is probably due to the breaking up of the sample from a single crystal into a polycrystalline mass, with large angle grain boundaries. X-ray diffraction patterns from samples which have been transformed more than ten times show that the samples are polycrystalline with very small crystals.

The transformation may proceed below the minimum darkening pressure. In order for this to happen, the pressure is first raised above the minimum darkening pressure and then quickly dropped to the pressure under consideration. The sample continues to darken and the transformation occurs at a pressure of only 100 atm above equilibrium. There is probably considerable reversibility once the nuclei have formed, and the continued darkening is probably due to growth rather than to new nucleation.

TABLE II.

Sample	No. of times through trans	Pressure at which volume first changes atmospheres	Pressure at which volume change is complete atmospheres
KCl	1	23 800	29 500
	10	26 400	30 800
KCl:Rb 3.0%	1	23 800	28 600
	10	26 800	29 900
KCl:Rb 0.1%	5	25 900	32 100
KCl:Rb 0.5%	5	27 200	32 100
KCl:Rb 3.0%	5	26 400	32 100
KCl:Na 0.1%	5	26 400	30 800
KCl:Na 1.0%	5	27 700	32 100
KCl:Na 3.7%	5	29 000	39 100
KCl:Na 10%	5	29 900	42 200
KCl:Na 0.5%	1	25 100	30 300
	2	26 800	33 800
	4	28 600	34 700
	15	28 200	33 000

The first time through the transition, the light intensity decreases quite suddenly, to a nearly constant final value, which depends on the pressure used. If the pressure is increased, the intensity again decreases quite suddenly. This is similar to the shattering that I. S. Jacobs[4] observed visually. The discrete decreases in intensity were observed visually. They appear to occur in times of the order of a second. The sample can also be heard to shatter as it proceeds through the transition the first time. No noise is heard in later transformations. The light intensity ceases to decrease in discrete jumps as the intensity approaches a minimum. After the first time through the transition, the light intensity changes in a continuous manner with pressure, as shown in Fig. 1.

Volume change measurements in Table II give results which are very similar to those obtained from intensity measurements. The first time through the transition, the pressure at which the transition starts

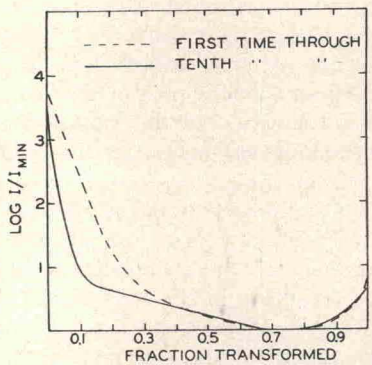

FIG. 2. Log I/I_{min} vs fraction transformed.

is 23 800 atm, 2600 atm lower than the tenth time through 26 400 atm. This is further proof that some sort of work hardening has occurred. The first time through the transformation, 15% of the sample is transformed at the pressure at which the volume initially starts to change discontinuously. If one attempts to increase the pressure, the volume merely decreases and the pressure stays constant. After the sample is about 15% transformed, it supports a higher pressure. In the original untransformed crystal, there are probably a great many points, of nearly equal activation energy, at which the transformation can start.

The intensity of light passing through the sample is calibrated with the fraction of the sample transformed into the new phase, by plotting the log I/I_{min} vs the fraction transformed, where I_{min} is the lowest intensity of light coming through the sample during the transformation. Figure 2 is a light intensity calibration curve for the first and tenth time through the transformation. The tenth time through the transformation, the light intensity changes by 4.3 orders of magnitude, and more

than 99.9% of the light has been cutoff before the sample is 10% transformed. The light intensity starts changing 400 atm before the initial change of volume. Thus many scattering centers are formed before any growth has occurred. If the nuclei of the new phase are equated with the scattering centers, this seems to indicate that the scattering centers are formed by some sort of shear mechanism.

The first time through the transformation, more growth occurs at the beginning of the transformation, than at the beginning of the transformation the tenth time through. The nuclei formed during the initial transformation grow to a larger size. The first time through the transformation, the light intensity changes 3.7 orders of magnitude and decreases to 99.9% of its initial value by the time the sample is 25% transformed.

The intensity of light coming through the sample, at any given fraction transformed, was found experimentally to have the following dependence on wavelength: $I/I_0=a/\lambda^\alpha$; λ=wavelength; I=intensity of light coming through the sample at a given fraction transformed; I_0=Intensity of light coming through the sample before any transformation has occurred; α=An experimentally determined constant, wavelength dependence; a=arbitrary constant.

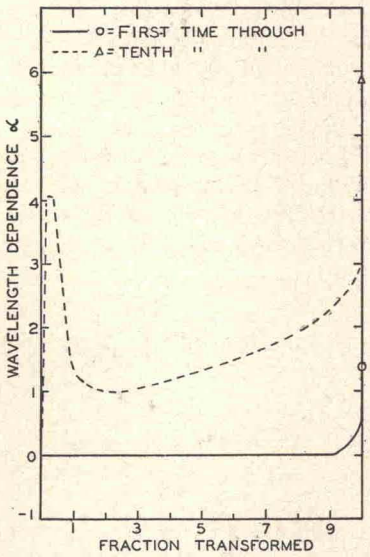

FIG. 3. Wavelength dependence α vs fraction transformed.

The approximate size of the regions being transformed were determined by measuring α for the light being transmitted at several different percentages transformed. Figure 3 is a plot of α vs the fraction transformed. The first time through the transformation, the value of α remains fairly constant throughout the transformation, rising to a value of 1.5 at the completion of the transformation. The results are quite different for a sample which has been transformed more than ten times. Then α rises to a value of 4 early in the transformation and then drops to a value of 1. It then increases to a value of about 6 at the end of the transformation. It is reasonable to assume that the large values of the wavelength dependence are caused by small particle scattering and the small values of α are caused by large particle scattering. The first time through the transformation, the scattering is probably caused by centers which are large in comparison to the wavelength of the light. The tenth time through the transformation, small particle scattering probably occurs at the beginning and at the end of the transformation. Scattering at the beginning of the transformation is caused by newly formed regions of the new phase. At the end of the transformation, the scattering is caused by residue of the old phase, which is still untransformed. It is possible that multiple scattering occurs in the middle of the transformation. The results of Chandrasekhar[9,10] show that forward scattering, from an atmosphere of Rayleigh-type particles, is negligible compared to the flux in the forward direction, up to an optical thickness of one. Therefore, the single particle scattering approximation should be valid up to an optical thickness of one and probably beyond. Between 80 and 90% of the wavelength dependence increase occurs when the optical density is less than 2.

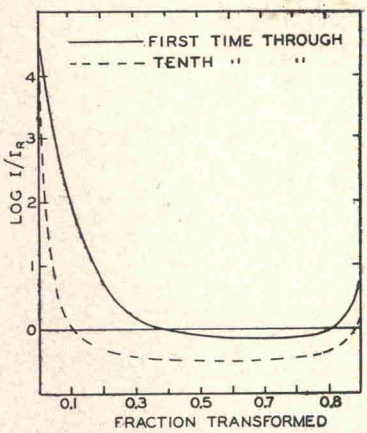

FIG. 4. Comparison of extinction with intensity of right angle scattering-KCl. Log I/I_R vs fraction transformed.

An indication that the particles are smaller the tenth time through the transition than they are the first comes from right angle scattering measurements. Figure 4 is a plot of log I/I_R vs the percent transformed, for the first and tenth time through the transformation. I is the intensity of the light coming directly through the bomb and I_R is the intensity of the light coming out of the bomb at right angles. Near the minimum intensity, a greater amount of light leaves the bomb at a right angle than at an angle of 180°. Since it is well known that small particles scatter more light at right

[9] S. Chandrasekhar and D. D. Elbert, Trans. Am. Phil. Soc. 44, 643 (1954).

[10] S. Chandrasekhar, *Radiative Transfer* (Clarendon Press, Oxford, England, 1950).

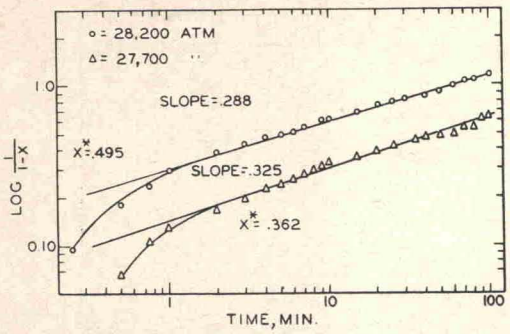

FIG. 5. Log$1/1-x$ vs time-KCl. Tenth time through the transition. x^*=fraction transformed at which curve becomes linear.

angles than do large particles, the particles are apparently smaller the tenth time through the transition.

The fraction x of the potassium halide transformed to the new phase is a function of time and may be described by the equation,[7,11]

$$x=1-\exp(-bt^n),$$

where b and n are empirically determined constants. The slope of a plot of the log-log $(1/1-x)$ vs log$t$ is equal to n. For a single crystal of potassium chloride the first time through the transformation, the value of n is close to zero and the percent transformed remains nearly constant with time. The potassium chloride is transformed to its final value, approximately 18%, in less than 15 sec, which is the minimum time necessary to bring the equipment to a constant pressure. We may deduce from this observation that after 18% of the sample has been transformed, both the nucleation and growth of the new phase have ceased. For if either growth or nucleation continued, the sample would become completely transformed.

Figure 5 shows some typical kinetics curves for potassium chloride after it has been transformed more than ten times. The graphs show a great deal of curvature early in the transformation and approach straight lines for large times. The initial slope of the curves at 0.25 min is 1.25. Because of the large curvature, the slope of the curves are probably greater than this for times less than 0.25 min. When 40-60% of the sample has been transformed, the curves approach a straight line with a slope of about 0.3. The curve belonging to the sample which is transformed at the higher pressure, approaches a straight line at a higher percent of transformation. Qualitatively similar curves are obtained for potassium iodide.

Johnson and Mehl,[11] making the assumption that a domain could not grow across a grain boundary and that nucleation occurred, at a constant rate, only at grain boundaries, showed that n approached 1 at large times t. Cahn,[12] assuming that the rate of growth was constant and that the nucleation rate, $J=At^c$, showed that n could not be less than 1 at large times. Therefore, in order to explain the above data, it must be assumed that both the rate of nucleation and the rate of growth are time dependent and decrease with time. A derivation, using these assumptions, is given below.

Assume that both the rate of growth u and the rate of nucleation J, are functions of time. It is not known what these functions are. However, simple functions, which give a reasonable physical picture of what is happening, will be used. It is assumed that a domain will grow at a constant rate until a maximum size is attained, after which the growth stops. Since we know that growth will stop after a short time, in a crystal which is being transformed for the first time, the assumption that growth ceases is consistent with the experimental data. A second assumption is that the nucleation occurs at arbitrary points within the lattice and that $J=it^{-m}$, for $t>t_0$ where $0<m<1$. This is similar to the assumption made by Cahn.[12] In order to avoid a singularity in the nucleation rate at $t=0$, it will be assumed that there is an initial nucleation rate J_0, which is constant until $t=t_0$ and that the number of nuclei formed before $t=t_0$ is small with respect to those formed after. Let t^* be the time it takes for a nucleus to complete its growth. t^* is of the order of several seconds. This is small compared to the length of time it took to complete a run, 100 min

$$\text{for} \quad t<t^* \quad X_{ex}=gu^3\int_0^t (t-\tau)^3 J d\tau \tag{1}$$

$$\text{for} \quad t>t^* \quad X_{ex}=gu^3\int_{t-t^*}^t (t-\tau)^3 J d\tau + g(ut^*)^3 \int_0^{t-t^*} J dt. \tag{2}$$

For $t\gg t^*$, the first term on the right of (2) becomes negligible

$$\begin{aligned} X_{ex} &= g(ut^*)^3\int_0^{t-t^*} J dt \\ &= g(ut^*)^3 J_0 t_0 + g(ut^*)^3 i\left[\frac{t^{-m+1}}{-m+1}\right]_{t_0}^{t-t^*} \\ &\simeq bt^{-m+1}. \end{aligned}$$

At large values of t,

$$n=1-m.$$

For $t\ll t^*$, Eq. (1) is used and the analysis by Cahn shows that the slope, $n=4-m$.

The experimental results obtained for potassium chloride fit the theory if $m=0.7$. The initial slope should be 3.3, however, it was not possible to measure

[11] W. A. Johnson and R. F. Mehl, Trans. Am. Inst. Mining and Met. Engrs. **135**, 416 (1939).

[12] J. W. Cahn, Acta Met. **4**, 449 (1956).

this slope with the equipment used. A similar analysis could be made for surface and edge nucleation.

The same type of experiments which were made on the pure potassium chloride, were made on impurity samples of rubidium chloride and sodium chloride in potassium chloride. Since rubidium chloride exists in the cesium chloride structure at 20 000 atm, it was thought that it would form nucleation centers for the phase transformation. This did not prove to be the case. In fact, rubidium chloride seemed to have little or no effect on the transformation. It was expected that sodium chloride would hinder the transformation. This was in fact observed.

The pressure at which darkening first occurs, vs the number of times through the transformation is given in Table I for KCl, KCl:Na 0.5%, and KCl:Rb 3%. It should be noticed that the first time through the transformation, the potassium chloride and the rubidium impurity samples start to darken at nearly the same pressure. The sodium impurity sample darkens at a slightly higher pressure. The pressure at which darken-

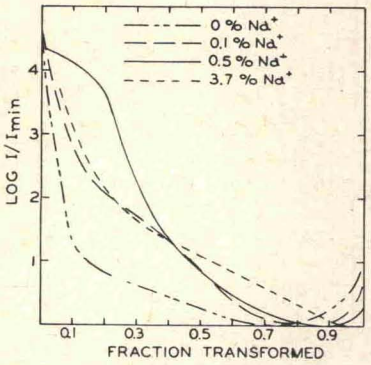

FIG. 6. Log I/I_{min} vs fraction transformed. Na^+ impurity in KCl. Tenth time through the transition.

ing first occurs increases with the number of times through the transition. An upper limiting pressure is finally reached. This final pressure is higher for samples with sodium impurity in them. The higher pressures obtained for sodium impurities are an indication that sodium impurities hinder the transition.

Table II is a summary of the pressure-volume data obtained for sodium and rubidium impurity samples. The similarity between the pure sample and the sample with rubidium impurities should be noted. The effect of the sodium impurity is noticeable in samples of high concentration.

Figures 6 and 7 are light intensity calibration curves for sodium and rubidium impurity samples. The curves, for the sodium impurities, show large deviations from the pure potassium chloride curve. Although the shapes of the sodium impurity curves are different, the samples are all about 40% transformed when 99.9% of the light has been cut off. This may be compared to the pure sample where 99.9% of the light is cut off before it is

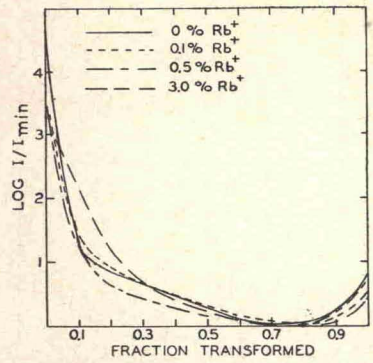

FIG. 7. Log I/I_{min} vs fraction transformed Rb^+ impurity in KCl. Tenth time through the transition.

7% transformed. At the beginning of the transformation, the 0.5% sodium impurity sample shows an especially large fraction transformed with little light intensity change. If the decrease in light intensity coming through the sample is associated with nuclei formation, the sodium impurity diagrams show that the nucleation rate is more strongly affected by the sodium impurity than is the rate of growth. In the pure sample, a great deal of nucleation occurs at the beginning of the transformation, without an accompanying volume change. This accounts for the large decrease in the light intensity with only a small amount of transformation. Less nucleation and more growth occurs at the beginning of the transformation in the sodium impurity samples. This accounts for the large amount of transformation accompanied by a relatively small change in the light intensity. The exact shape of each curve depends on the relative amounts of nucleation and growth occurring during the transformation. In general, a large slope of the light intensity calibration curve indicates that a great deal of nucleation is occurring.

The effects of rubidium on the transformation are quite small. In Fig. 7 the largest deviation from the

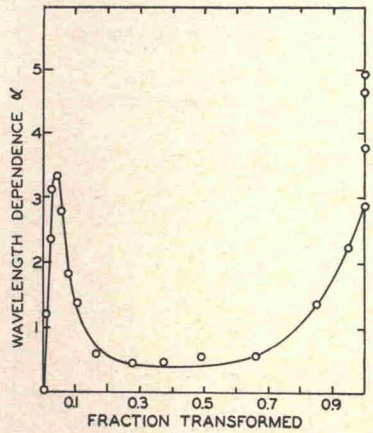

FIG. 8. Wavelength dependence curve KCl with 0.5% Rb. Fifth time through the transition.

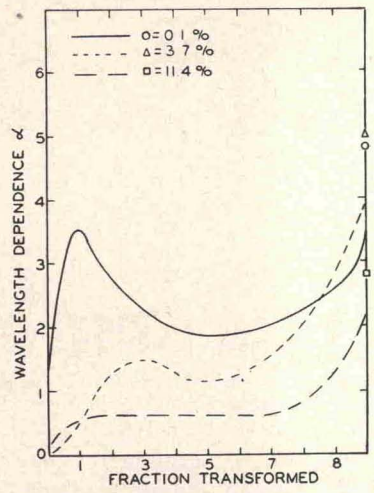

FIG. 9. Wavelength dependence curve. KCl:Na 0.1%; KCl:Na-3.7%; KCl:Na 11.4%; fifth time through the transition.

pure potassium chloride is for the 3.0% rubidium sample, for which the sample is about 23% transformed when 99.9% of the light intensity has been cut off. The 0.1 and 0.5% rubidium samples are 10 and 12% transformed when 99.9% of the light intensity has been cut off. The deviations are slight, showing that rubidium impurities have little effect on the phase transformation.

The wavelength dependence of the scattering was determined for the rubidium and sodium impurity samples. The results obtained for the rubidium are quite similar to those of the pure sample. Figure 8 is a plot of the wavelength dependence of a 0.5% rubidium impurity sample. The scattering results obtained for sodium impurity samples, Figs. 9 and 10, differ widely from the pure sample. As the sodium concentration increases, Fig. 9 the first scattering peak decreases in size and moves to a higher fraction transformed. The first peak always occurs at a percentage of transformation where the slope of the light intensity calibration curve is the greatest. This means that domains which

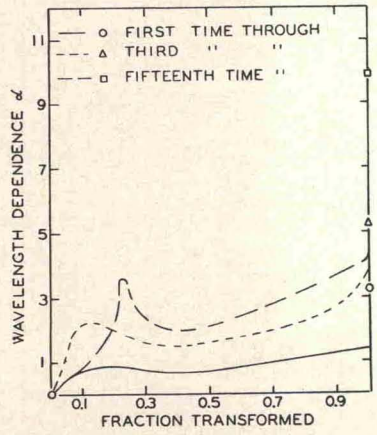

FIG. 10. Wavelength dependence curve; KCl:Na 0.5%; first, third, and fifteenth times through the transition.

are small when compared to a wavelength of visible light, occur at a point where the nucleation is the greatest. Small particle scattering occurs at the end of the transformation. Figure 10 shows how the wavelength dependence curves develop, for a 0.5% sodium impurity sample, as the sample is put through the transformation many times. The first time through, there is no peak at the beginning of the transformation and the scattering is caused mainly by large particles. As the sample is repeatedly put through the transformation, a peak, which is due to small particle scattering, appears at the beginning of the transformation. This is again proof that the sample breaks up into a polycrystalline mass after passing through a transformation many times. It is interesting that, after many times through the transformation, the 0.5% sodium impurity sample shows an extremely large wavelength dependence at the end of the transforma-

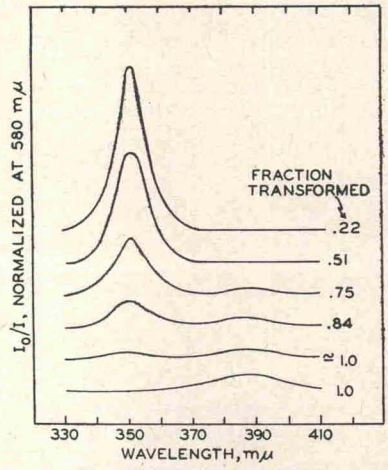

FIG. 11. Absorption spectra KI:Pb 0.5%; tenth time through the transition.

tion. Some other effect besides small particle scattering must also be involved.

The kinetics curves obtained for the impurity samples are similar in shape to those of pure potassium chloride, Fig. 5. The slope n of the rubidium impurity samples was about the same as the pure potassium chloride. The slope of the 0.5% sodium impurity sample is approximately equal to 0.08, which is about one-fourth of the value obtained for the pure sample. The low value of n is an indication that the nucleation rate of the sodium impurity sample is more strongly time dependent than that of the pure sample. From the theory described in the foregoing

$$J = i_0 t^{-0.92},$$

for the 0.5% sodium impurity sample. The curves of the impurity samples approach straight lines at between 30 and 60% transformed. The greater the pressure used for the transformation, the higher the

percent transformed at which the kinetics curves approach a straight line.

The absorption spectra of lead, thallium, and indium ions in a potassium iodide lattice were obtained as the potassium iodide proceeded through the transformation. The maximum absorption of the impurity peaks occurs at different wavelengths in the sodium chloride and the cesium chloride phases. The manner in which the peak shifts position as the potassium halide proceeds through the transformation gives some information on the size of the domains during the transformation. If the maximum size of the domains is small, 20–50 ions, then an impurity atom in a domain would feel the effect of neighboring domains and would not exist only in the field of its domain. The perturbation, of the neighboring domains, would be expected to effect the absorption spectra of the impurity ion and as the potassium halide proceeded through the transition, it might be expected that the absorption peak would gradually shift from a position characteristic of the sodium chloride phase, to one characteristic of the cesium chloride phase. On the other hand, if the maximum size of the domains is large, several hundred ions, then the perturbation of neighboring domains is negligible and two distinct peaks should exist during the transformation, one for those ions existing in the sodium chloride phase and one for those in the cesium chloride phase. Because of the large separation of the absorption peak in the different phases, the clearest results were obtained for lead impurities in potassium iodide lattice. Figure 11 shows the peak at various percentages transformed. The second peak appears at about 75% transformed. At nearly 100% transformed, the two peaks are of equal size. At 100% transformed, only one peak exists. The absorption peaks do not shift. One grows with respect to the other. The absorption peak of the sodium chloride phase is more intense than that of the cesium chloride phase, and probably hides the cesium chloride peak through most of the transformation. (The peak in the CsCl phase is very broad even at very high pressure.) It may be concluded that the domains contain at least several hundred ions during the transformation.

ACKNOWLEDGMENT

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