

FIG. 1. Specific heat as a function of temperature.

heated in a glass vessel, 2g in weight, at a rate of about 2°C/min. The heat capacity of the empty calorimeter was calibrated with KCl as a standard substance. The specific heat vs temperature curve is shown in Fig. 1.

As is seen in Fig. 1, there is a rather large anomaly of the specific heat in the transition region. The specific heat curve shows a sharp peak at 490°C, corresponding to the anomalies of permittivity and lattice spacing. Attention must be paid to the fact that the specific heat shows an anomaly over a wide temperature range. Though it is difficult to estimate the transition energy accurately from such a curve, we have tentatively assumed that the normal specific heat corresponds to the broken line shown in the figure. We thus obtain the transition energy as 1150 cal/M in the range 340 to 540°C. The accompanying entropy change is about 0.80R. This large anomaly is to be compared with the small transition energy in BaTiO₃,⁴ which is about 20 to 40 cal/M.

According to the theory of barium titanate proposed by Devonshire,⁵ the anomalous internal energy associated with the spontaneous polarization can be written as

$$E = A \cdot T_c \cdot P^2 + \dots = B \cdot T_c \cdot (c/a - 1) + \dots, \quad (1)$$

where T_c represents the Curie temperature and B depends on the piezoelectric and elastic constants. This relation between polarization and crystal strain has been confirmed experimentally by Merz⁶ in the case of barium titanate. Though the value of the spontaneous polarization of lead titanate has not been estimated, we have found that c/a , which is 1.063 at 30°C, begins to decrease considerably from a temperature far below the Curie point. Taking account of this fact, it seems to be reasonable to assume that the specific heat also has an anomaly in the same temperature range. Utilizing the normal specific heat shown in Fig. 1, we have calculated the anomalous internal energy E , as is shown in Fig. 2.

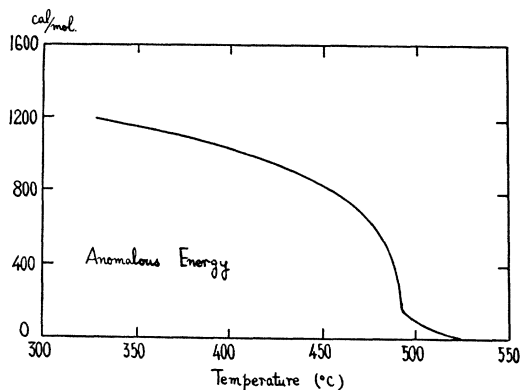


FIG. 2. Anomalous internal energy estimated from the specific heat curve.

This curve is quite similar to the temperature dependence of the axial ratio c/a , shown in the previous letter.¹ It is found that Eq. (1) holds approximately in this temperature range with $B=40$ cal/M. On the other hand, we have estimated that B is about 15 cal/M in the case of BaTiO₃.

It is difficult at present to determine whether there is a latent heat at the transition point.

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A Note on the Distribution of Impurities in Alkali Halides

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THE manner in which impurities are distributed in a crystal is not readily determined by direct measurement. In the absence of specific information it is frequently assumed, particularly for small concentrations, that the impurities are distributed at random. Large deviations from a random distribution may result, however, from the formation of stable aggregates of two or more impurity atoms as in the aggregation of trapped electrons and trapped holes in the alkali halides.¹ The purpose of this note is to present evidence from optical data for the formation of impurity aggregates in NaCl crystals containing Pb⁺⁺ and to discuss the conditions under which such deviations from random distribution may, in general, be expected.

Although NaCl, KCl, and RbCl crystals containing Pb all exhibit absorption bands at approximately 2730 and 1960Å, variations in the character of these bands have been noted by earlier investigators.² The present study has revealed additional bands in NaCl:Pb which vary with the growth and thermal history of the specimen.³ Similar variations with growth history have been observed in the absorption bands of other impurities in alkali halides, particularly in NaCl:Cu and KCl:Cu.⁴

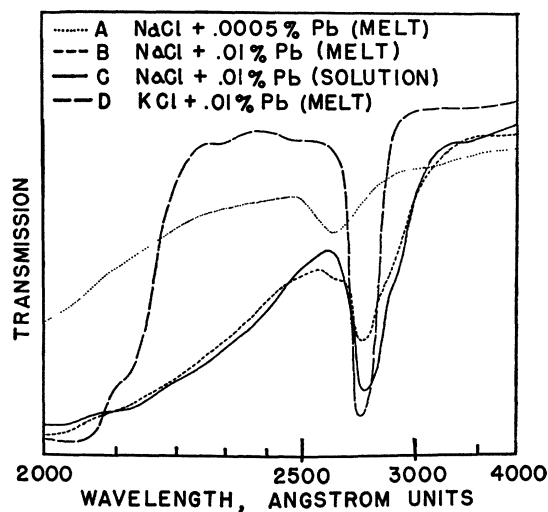


FIG. 3. Transmission curves of NaCl:Pb crystals, grown from the melt and from solution, contrasted with a curve for a melt-grown KCl:Pb crystal. The concentrations of Pb shown are those in the melt and solution. The corresponding concentrations in the crystals are lower.

Transmission curves for several NaCl:Pb crystals grown from the melt and from solution are shown in Fig. 1, together with a curve for a melt-grown KCl:Pb crystal.⁵ The NaCl:Pb curves are markedly different from the KCl:Pb curve in every case. Absorption bands appear at 2900 and 2600Å in NaCl:Pb which are absent in KCl:Pb, while bands appear at 2050, 2100, 2300, and 2450Å in KCl:Pb which are absent in NaCl:Pb. In one curve, which is typical of a number of NaCl:Pb crystals with low Pb content, only the 2600Å band appears. The curves for NaCl:Pb crystals with high Pb content (not shown), on the other hand, resemble those for PbCl₂ films.

The effect of various heat treatments (always followed by rapid quenching to room temperature) on the absorption bands of two of the melt-grown NaCl:Pb crystals is shown in Fig. 2. In each

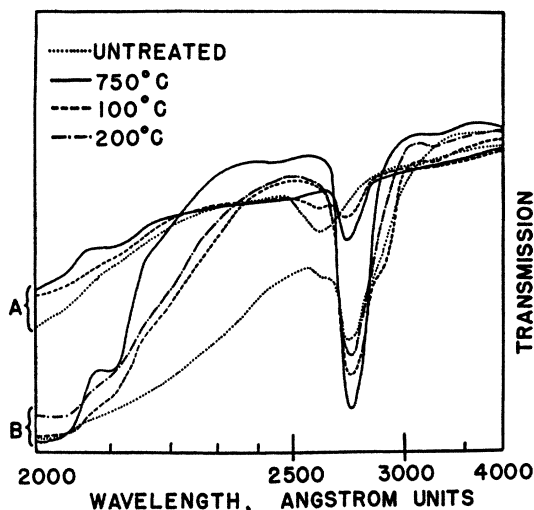


FIG. 2. The influence of various heat-treatments followed by rapid quenching to room temperature on the Pb absorption spectrum of two melt-grown NaCl:Pb crystals, specimens A and B of Fig. 1.

case heating at 750° yields curves which are similar to the KCl:Pb curve of Fig. 1. After several days at room temperature, the 2730Å band in the crystal with high Pb content weakens and a new band appears at 2900Å. The same result is obtained by heating the crystal for only a few minutes at approximately 100°C. Heating at 200°C removes most of the 2900Å band, while heating at 400°C yields a curve similar to that obtained at 750°C. In the crystal with a low Pb content, subsequent heating at 100° partly reconverts the 2730Å band into the 2600Å band. Applying similar heat treatments to KCl:Pb crystals does not alter the absorption spectrum appreciably and bands analogous to the 2900 and 2600Å bands in NaCl:Pb crystals do not appear.

The influence of the growth and thermal history of NaCl:Pb crystals on the aggregation of Pb can be explained qualitatively as follows. Pb is only slightly soluble in NaCl at room temperature but is appreciably more soluble at high temperatures. Above approximately 400° it is probably present in the various NaCl:Pb crystals as randomly distributed mobile single Pb centers. When the crystals are quenched rapidly from high temperatures to room temperature, the Pb ions become less mobile and are practically frozen in their random positions. Positive ion vacancies, which are still mobile at room temperature, associate with the Pb ions to form mobile Pb-vacancy centers.⁶ In crystals with moderate or high Pb content, the Pb-vacancy centers migrate and combine with one another and with unassociated Pb ions to form stable Pb-Pb pairs (associated with one or two positive ion vacancies) and larger aggregates which ultimately, at high Pb concentrations, precipitate out as a PbCl₂ phase. The rate at which these processes occur depends on the Pb concentration, the mobility of the Pb-vacancy centers, and the stability of the various clusters. The mechanism for the aggregation of Pb in NaCl is thus very similar

to that suggested recently for the aggregation of trapped holes in the alkali halides.¹ In crystals with low Pb content the tendency to form Pb-Pb pairs and larger aggregates is quite small since it depends on the second or higher power of the Pb concentration. On the other hand, Pb may combine with vacancy clusters or with other impurities (possibly O⁻ which may be present) to form centers which depend on the first power of the Pb concentration.

On the basis of these considerations it is suggested tentatively that the 2900Å band is due to Pb-Pb pairs, the 2600Å band is due to Pb-impurity or Pb-vacancy cluster centers, and the 2730Å band is due to a combination of single Pb centers, Pb-vacancy centers, and PbCl₂.

In general, a stable aggregation of two or more impurity atoms may be expected whenever the binding force between impurities is greater than that between impurity atoms and atoms of the host crystal. Aggregation will also be favored whenever the strain energy associated with the distortion of the lattice in the vicinity of the impurity cluster is smaller than that caused by the single impurity atoms. Lattice defects in the form of vacancies and dislocations also play an important role in impurity aggregation.⁷ The lattice distortion is probably a dominant factor in the aggregation of Pb in NaCl. Thus, cluster formation occurs readily in NaCl where Pb²⁺ ($r=1.32\text{Å}$) is larger than Na⁺ ($r=0.98\text{Å}$), but not in KCl, where Pb²⁺ is the same size as K⁺ ($r=1.33\text{Å}$). The same factor is probably also dominant in the aggregation of Cu in NaCl and in KCl.

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Quantum Efficiency of Bismuth Counters for Electromagnetic Radiation of 0.07-Mev to 2.8-Mev Energy*

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THE absolute quantum efficiency of Geiger-Müller counters has been measured by several authors using the coincidence method.¹ This method presupposes a knowledge of the decay schemes of the radioactive isotopes used and of the angular correlation of successively emitted radiations. It has only been in the last few years, however, that an appreciable number of decays has become completely known and only recently have angular correlation measurements been performed with success. For these reasons it seemed worthwhile to redetermine the quantum efficiency of G.-M. counters as a function of the energy of the incident radiation. At the same time the variation of the local efficiency at different points of the counters was investigated.

The counter tubes used were of the cylindrical type having bismuth cathodes of 0.77-g/cm² thickness for the detection of high energy gamma-radiation (0.4-3.0 Mev) and 0.080-g/cm² thickness for the low energy region (0.07-0.4 Mev). The counters were filled with argon (9 cm Hg) and ethyl alcohol (1 cm Hg).

The local efficiency of the counters was measured with a well collimated gamma-ray beam using energies of 0.511, 0.73, 1.25, and 2.62 Mev. The intensity of the beam was calibrated with an anthracene scintillation counter. The quanta absorbed in the anthracene crystal were known to be detected with an efficiency of (96±6) percent. A considerable variation of the local efficiency across the G-M counter was observed (points in Fig. 1). It was found, however, that this variation can be well described by assuming that all secondary electrons counted are produced in an