A Slow Component in the Decay of the Scintillation Phosphors

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WE have measured the fraction of the light emitted by some of the common phosphors, which has a decay constant longer than about 0.5 μsec.[1] The following apparatus was used: The phosphor was held in a beaker lined with aluminum foil, excited by a beam of x-rays, and viewed by an end-window photomultiplier. The x-ray tube may be gated off by applying a negative pulse to its grid. The photomultiplier is normally turned off by making its first dynode 8 v negative with respect to the cathode; it may be gated on by applying a positive square wave to dynode 1. The sequence of events is the following: First the photomultiplier is gated on, then the x-ray tube is gated off, and then the photomultiplier is gated off. The x-ray beam turns back on after 40 μsec. Two photographs were taken of each phosphor, one showing the whole trace, the other with 10 times the gain to show the details in the region just after the x-ray beam is turned off.

The results are given in Table I. The residual signal in the case of the liquid phosphor may have been due to a number of effects, such as after-pulses in the photomultiplier and imperfect cutoff of the x-ray beam, as well as a slow component in the light emission. This measurement gives an upper limit of 0.1 percent for all these effects, and we have therefore neglected them in the analysis of the data for the crystals.

TABLE I. Fraction of the light emitted in the slow component, and its decay time.

	Decay time (μsec)	Percentage of light
Terphenyl in toluene 5 g/l	···	<0.1
Terphenyl crystal	47±6	2.5±0.2
Trans-stilbene	80±10	4.3±0.2
Anthracene	47±6	5.6±0.4
Sodium iodide	220±40	5.0±0.2

The absence of a slow component in the terphenyl solution, as contrasted with crystalline terphenyl, is probably due to a deformation of potential energy surfaces during collisions in the liquid, which allow a conversion of the excitation energy of the metastable state into thermal energy.[2] The shorter mean life of fluorescence in the liquid is presumed to be due to the same type of process.

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Spectral Location of the Absorption Due to Color Centers in Alkaline Earth Halide Crystals

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RECENTLY Smakula[1] has measured the spectral location of the absorption bands induced by x-rays in crystals of CaF_2 (3350A, 4000A, and 5800A) and BaF_2 (3800A, 4800A, and 6700A). His results for CaF_2 are in good agreement with those obtained earlier by Herman and Silverman[2] and later by Barile.[3] Smakula has obtained evidence for a fourth band in both CaF_2 and BaF_2 near 2200A. This additional band was determined by Barile as lying at 2280A in CaF_2, but the exact location in the case of BaF_2 is still not known. Measurements have apparently not been reported for other alkaline earth halides.

Smakula[1] has pointed out that his data do not fit the relationship, $\nu d^2=\text{constant}$ or $\lambda=ad^2$ (ν=frequency of maximum absorption, λ=the corresponding wavelength, d=lattice constant, and a=constant), obtained by Mollwo[4] experimentally for the case of the F-band in the alkali halides. The same expression has also been obtained theoretically by Fröhlich[5] on the basis of a model for the F-center which is not now generally accepted. The writer[6] has shown, however, that the location of the F, R_1, R_2, M, and V bands in the alkali halides having the NaCl structure can be satisfactorily related to the lattice constant[7] by equations of the general form $\lambda=ad^n$, where a and n are constants for a given band, but n is not necessarily equal to two ($n=1.84$ for the F, R_1, and R_2 band, 1.56 for the M band, and 1.10 for the U band). Inui and Uemura[8] have also recently considered the dependence of the F-absorption peak in the alkali halides upon the lattice constant from a theoretical viewpoint.

The two constants in the expression $\lambda=ad^n$ can, of course, be determined from Smakula's data for the three bands in CaF_2 and BaF_2. The results of these calculations are

$$\text{I:}\quad \lambda=614d,$$
$$\text{II:}\quad \lambda=346d^{1.444},$$
$$\text{III:}\quad \lambda=833d^{1.144},$$

where λ and d are both in Angstrom units. (For convenience the three bands, starting with that corresponding to shortest wavelengths, and going in the direction of increasing wavelength, have been indicated as I, II, and III.) It would be very desirable if data were available on a third alkaline earth halide to serve as a check on the reliability of the determination of the constants in the above relations, but this is unfortunately not the case.

TABLE I. Location of absorption bands in alkaline earth halides. (Values in parentheses are predicted.)

Compound	Lattice constant (angstroms)	Absorption peak (angstroms) I	II	III
CaF_2	5.451	3350	4000	5800
SrF_2	5.86	(3610)	(4450)	(6310)
BaF_2	6.184	3800	4800	6700
$SrCl_2$	7.00	(4300)	(5740)	(7730)
$BaCl_2$	7.34	(4520)	(6170)	(8170)

Because of the experience with the alkali halides, however, it is believed that the above equations are probably satisfactory for the purpose of predicting the spectral location of the absorption bands in alkaline earth halides of the same fluorite crystal structure as CaF_2 and BaF_2 (cubic, space group O_h^5) which are as yet unmeasured. Of the remaining alkaline earth halides, only SrF_2 and $SrCl_2$ normally possess this crystal structure. Vainshtein[9] has recently reported, however, the existence of the fluorite structure in very thin films of $BaCl_2$. The results of such calculations are shown in the Table I.

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[7] In the equations given in reference 6 for the alkali halides, d actually indicates the interionic distance and not the lattice constant. For the NaCl structure these quantities differ, of course, only by a factor of two.
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Purification and Prevention of Segregation in Single Crystals of Germanium

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GERMANIUM ingots of such high purity that they have intrinsic electrical resistivity at room temperature and germanium single crystals having an extrinsic resistivity which is essentially constant in over 80 percent of their volume have been prepared by new techniques. These new experimental results

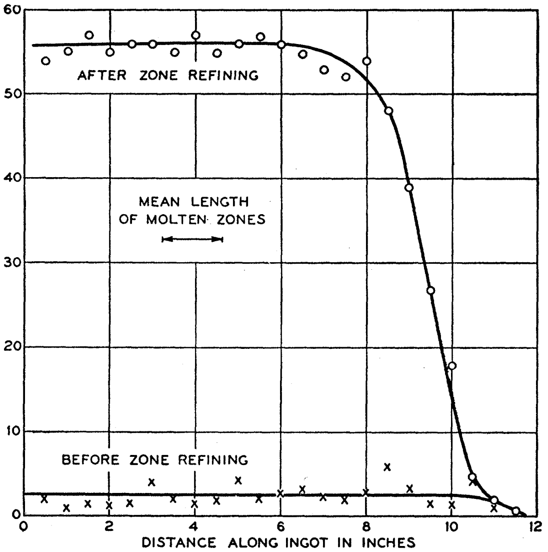

FIG. 1. Electrical resistivity *versus* location in germanium ingot before and after zone refining.

confirm an earlier analysis[1] of the distribution of solutes in an ingot by traveling molten zones.

The purification technique, known as *zone refining*, consists of slowly passing a number of short molten zones through a relatively long solid ingot of the impure substance. Each molten zone which passes through the ingot constitutes a stage of purification. The effect of passing 6 molten zones through an ingot of germanium containing a donor impurity believed to be arsenic is shown by the electrical resistivity curves of Fig. 1. The resistivity after zone refining is very close to intrinsic in about half the ingot. Resistivity measurements made at low temperatures by G. C. Dacey indicate that excess donor concentrations of less than 5×10^{12} atoms-cm^{-3} (one donor atom per 10^{10} germanium atoms) have been obtained in such ingots.

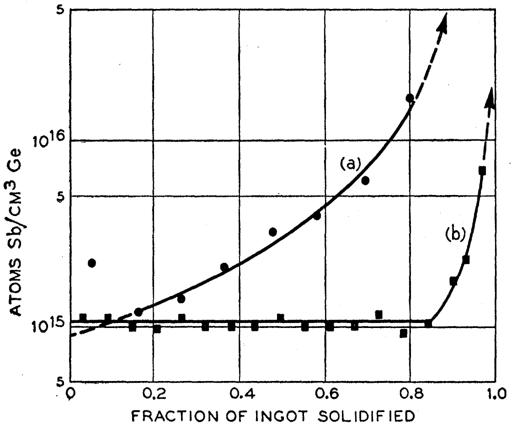

FIG. 2. Concentration of antimony *versus* location in germanium ingots: (a) normally frozen ingot, (b) zone-leveled single crystal ingot.

By comparing concentrations before and after zone refining an effective distribution coefficient k can be estimated,[1] which for the process of Fig. 1 is roughly 0.2, a value somewhat larger than the equilibrium k of 0.06 reported for arsenic in germanium.[2] The difference in k's may be attributed to nonequilibrium freezing and possibly to contamination during zone refining.

The technique for preventing solute segregation along the freezing direction is one of a number of methods known as *zone leveling*. Solute, in amount to be indicated, is placed at the beginning of a relatively long solid ingot of pure solvent, which in this case is germanium. Heating means are provided for producing a short molten zone at the beginning of the ingot and causing it to travel slowly through the ingot at constant length, l. The solute concentration C in the solid ingot can be shown to decay exponentially according to $C=kC_i\exp[-kx/l]$, where C_i is the initial solute concentration in the molten zone and x is the distance from the beginning of the ingot. This equation is valid in all but the last zone length and shows, for a solute having a very small k, that the concentration decreases very slowly as x/l increases. Thus, for antimony in germanium, for which $k=0.007$, C decreases by about 6 percent in 9 zone lengths, which is in marked contrast to normal segregation, where C *increases* by a factor of about 10 in the first 0.9 of the ingot.

The improvement in uniformity obtainable by zone leveling is illustrated in Fig. 2. Curve (a) is for a polycrystalline ingot of antimony-doped germanium[3] which was entirely melted and then frozen slowly from one end, producing a normal segregation of antimony. Curve (b) is for a single crystal of antimony-doped germanium which was prepared by zone leveling. The crystal was about 7 zone lengths long and it is seen that the concentration is essentially constant in all but the last zone length. To produce a single crystal a short section of a seed crystal abutting the beginning of the starting ingot was melted into the zone at the start.

Techniques of zone melting are not confined to germanium but can be used on metals, salts, and other organic or inorganic substances.

The writers are indebted to Mr. D. Dorsi for preparing the single crystal.

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The Probable Existence of an $E3+M4$ Mixture in an Isomeric Transition*

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THE existence of a 14±2 hour 74.2-kev isomeric transition in Os^{191m} has recently been established.[1] The energy of this transition is 0.33 kev above the threshold for K conversion. Lifetime-energy considerations would indicate an isomeric transition (I.T.) involving a spin change of three. The observed[1] $L_{\text{I}}:L_{\text{II}}:L_{\text{III}}$ ratio (42:25:100) was interpreted on the basis of general L-subshell ratios[2] to mean that the multipolarity was $M3$. Accepting the 7/2+ nature[1] of the Os^{191} ground state then leads to the designation of the isomeric state as $i_{13/2}$.

In following up these conclusions, however, certain discrepancies have arisen. (1) The relative thermal neutron activation cross section for the two levels was obtained by irradiating a sample of Os metal in the Brookhaven reactor for a given time at a known flux and comparing the number of transitions from the isomeric and ground levels by use of β-spectrographs. If one assumes the I.T. to be $M3$ with $K/L=1$, the ratio of formation of isomeric and ground levels (σ_m/σ_g) is found to be $\sim$100. General observations[3] on isomeric ratios show that, usually, a compound nucleus formed by neutron capture (in this case one of spin $\frac{1}{2}$) will decay more readily to a level nearer to it in spin. This is in direct contradiction to the isomeric ratio which we obtain on the assumption of an $M3$ transition. On the other hand, if we designate the I.T. as $E3$ ($K/L=0.1$), the ratio σ_m/σ_g computed from experiment is 5.8, consistent with a $p_{\frac{1}{2}}$ isomeric level. The activation experiments therefore favor an $E3$ isomeric transition assignment. (2) We have measured the ratio R of K x-rays due to internal conversion of the