

Temperature Dependence of the Angular-Correlation Curves of Positrons Annihilating in Metals

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(Received 19 January 1970)

In order to understand the temperature effect on the two- γ positron annihilation in crystals, we have performed new measurements in Al, Zn, Cd, Co, Pb, and Bi single crystals and Al, Zn, Pb, and Bi polycrystals. Our measurements show that, by lowering the temperature from 300 to 77 °K, the area under the two- γ angular-distribution curve decreases in single crystals but not in polycrystals. According to our measurements, the observed temperature effect is Z dependent. We discuss the significance of our results in relation to the possible ideas which could explain the effect. In conclusion, we suggest a model, based on the channeling of the positrons, consistent with all the experimental data.

I. INTRODUCTION

In some previous papers,^{1,2} for positrons annihilating in bismuth, a new interesting effect has been reported which may give very important information on the interactions e^+ lattice and e^+e^- in a crystalline structure.

The effect consists in the decrease of the area under the angular-distribution curve when the temperature goes down from room temperature to liquid N_2 and He temperature.

Because the explanation of the effect was still unclear we have extended our previous measurements: (i) We have observed the annihilation rate up to angles of 30 mrad, which correspond to a center-of-mass energy of the annihilating pair of the order of 200 eV, and (ii) we have made systematic measurements on a set of single crystals and polycrystals, covering a wide range in Z , with different characteristics.

II. EXPERIMENTAL APPARATUS

Measurements of the angular distribution of the two- γ positron annihilation have been performed with the experimental apparatus shown in Fig. 1.

The γ -ray detectors consist of two RCA 6342A photomultipliers optically coupled with 2×2 -in. NaI(Tl) crystals. The two detectors are symmetrically placed with respect to the source at a distance of 750 mm. One of the detectors can be moved over a circular trajectory centered at the source position. Lead slits through which γ rays reach the photomultipliers subtend an angle of 0.8 mrad. The length of the slits makes an integration over the $K\hat{x}$ - $K\hat{y}$ plane which extends to a value of $\sim 3K_F$.

Pulses coming from detectors, selected by means of window discriminators centered at 511-

keV γ energy, are fed to a fast-slow coincidence circuit having a measured resolving time of 50 nsec.

All the samples used have the shape of a hollow cylinder, 1 mm thick, into which 3 mCi of conventional Na^{22} source was sealed.

The samples, supplied by Metals Research, have a purity of 99.999%. For the single crystals the axis of the cylinder is parallel to the growth one.

The cooling of the sample is made according to the cold-finger technique, which avoids the correction due to the absorption in the cryogenic liquid.

III. EXPERIMENTAL RESULTS

Measurements have been performed at the temperatures 300 and 77 °K on the following samples: Al, Co, Zn, Cd, Pb, and Bi single crystals, and Al, Zn, Pb, and Bi polycrystals.³

In Figs. 2 and 3 are reported all the angular-distribution measurements. The curves are normalized to equal counting times⁴ and best fitted by a polynomial curve fitting program.

The break at the angle corresponding to the Fermi momentum in the angular-distribution curves is greatly reduced by the smoothing effect of the fit used and by the fact that the experimental points were performed in steps of 1 or 2 mrad. On the other hand, we were not interested in observing details of the Fermi surface.

The temperature effect has been calculated according to the formula

$$E(T_1, T_2) = 2 \frac{N(T_2) - N(T_1)}{N(T_2) + N(T_1)},$$

$$N(T) = \int_0^{15 \text{ mrad}} n(\theta, T) d\theta,$$

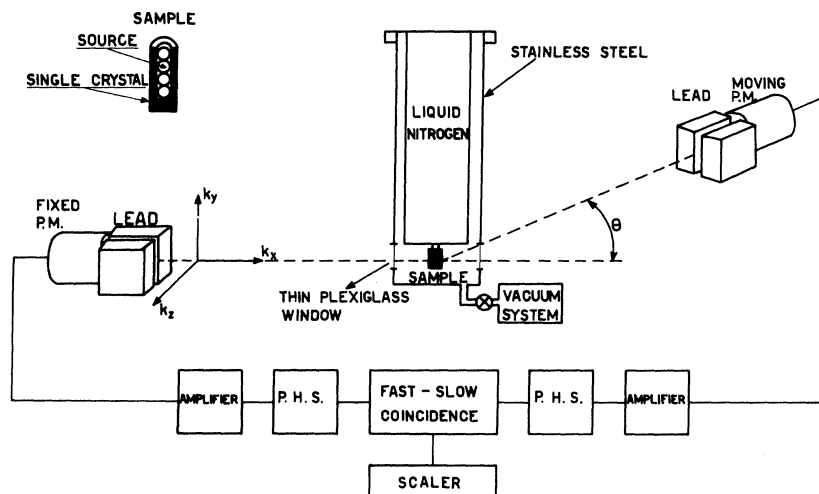


FIG. 1. Sketch of the experimental apparatus.

and $n(\theta, T)$ is the coincidence counting rate at an angle θ and temperature T , with the background counting rate subtracted.

In Table I are reported the values of the observed temperature effect E , for the single crystals investigated.

In the case of the Pb single crystal we have extended angular-distribution measurements up to 30 mrad; as is possible to see from Fig. 3, the tails of the two angular distributions overlap in a surprisingly good way. We have also performed lifetime measurements using a time-to-amplitude converter described elsewhere⁵; the lifetime measurements do not show any variation due to the change of the temperature.

IV. DISCUSSION

Now we want to discuss step by step the significance of our experimental results related to different ideas which could, perhaps, explain the observed temperature effect.

We suggested, in our previous paper,² that this effect could be explained if we think that the annihilation process at low temperature takes place with three bodies in the initial state, i. e., the electron, the positron, and an unidentified excitation contributing a momentum \bar{K}_c to the total momentum.

This kind of process seemed to be justified because (i) the effect is present only in single crystals, (ii) the lifetime remains unchanged by tem-

perature, and (iii) the single-channel counting rates also are temperature insensitive. On our hypothesis, in the simplified form of an excitation having a δ -function momentum spectrum, the tails of the curves have to increase at the expense of the central parts, in such a way to keep the total area constant. Taking into account the energy-momentum conservation and the possible maximum value \bar{K}_c of the known excitation collective modes (phonons, plasmons, excitons, ...) the variation of the tails must appear within 20 mrad. Pb measurements (Fig. 3) extended up to 30 mrad do not show any variation of the tails versus temperature.

Another suggestion⁶ is related to the fact that a fraction of the positrons, in single crystals, suffers a diffraction reflection from crystal planes. In this case, the number of annihilating positrons, N_a should depend on the temperature according to the formula $N_a = N_0[1 - A \exp(-2W)]$, where A is a constant independent of temperature and $\exp(-2W)$ the Debye-Waller factor. A comparison between the observed effect and the calculated one gives the figures of Table II. Both numerical values and the trend of the calculated effect do not agree with the measured ones.

Brandt *et al.*⁷ have treated theoretically the temperature effect expected from the momentum distribution of the positrons and from the lattice vibrations. Their analysis leads to the result of a smearing of the angular distribution near K_F ,

TABLE I. Measured temperature effect E in the single-crystal samples.

Sample	Al	Co	Zn	Cd	Pb	Bi
E (300 °K; 77 °K) (%)	7.9 ± 2.5	7.8 ± 2.5	9.5 ± 1.0	12.3 ± 0.6	18.0 ± 0.5	21.4 ± 0.3

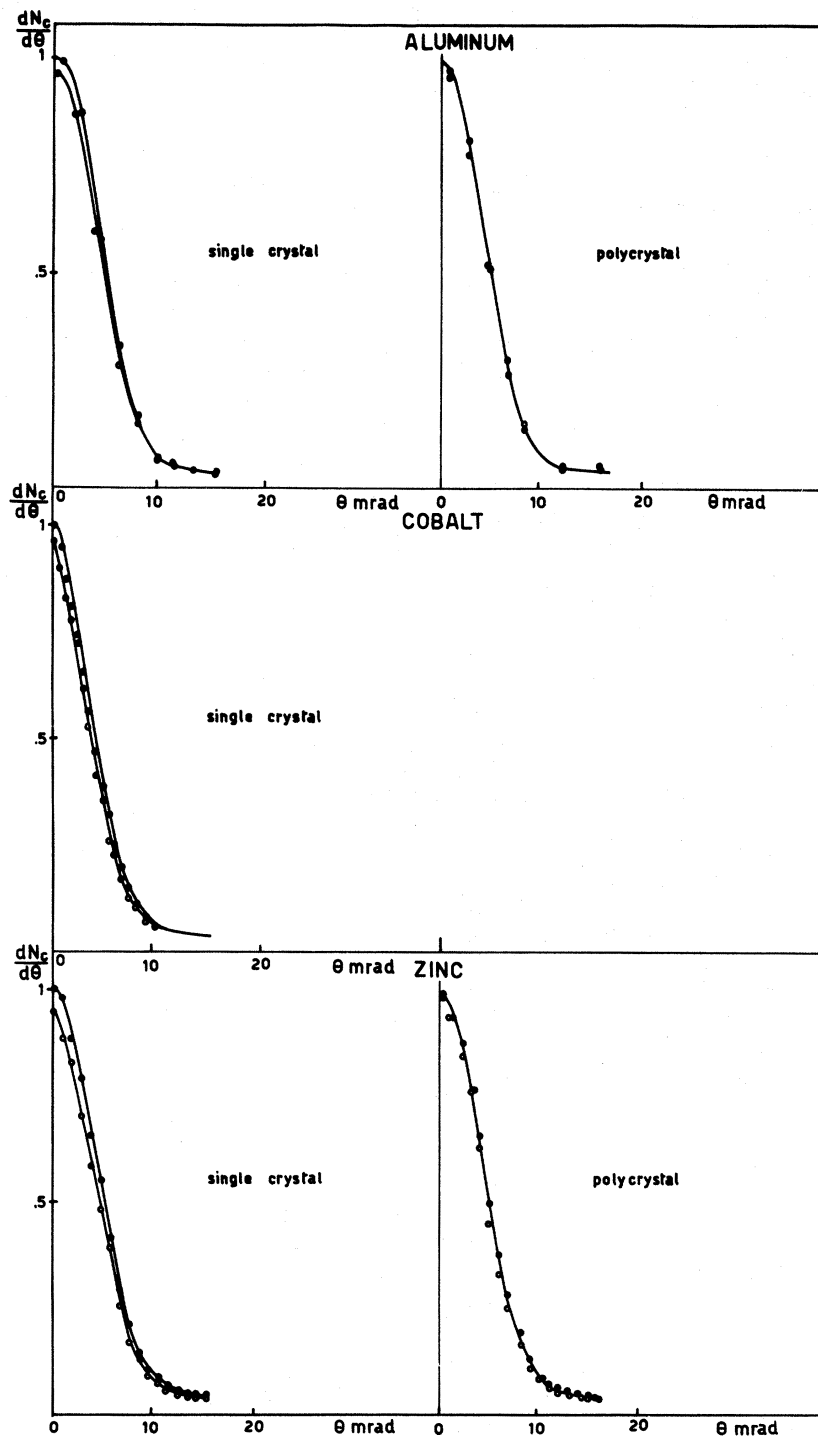


FIG. 2. Measured angular distributions for Al, Co, and Zn. Solid dots: $T = 300^\circ\text{K}$, open dots: $T = 77^\circ\text{K}$.

while from our experimental results all electrons with $|K| < |K_F|$ seem to be involved. Brandt's analysis does not explain the temperature effect observed by us and the dependence on the Z of the sample.

More recently,^{8,9} it has been shown that changes

in angular correlation and lifetime¹⁰ are produced by plastic deformation of the sample due to a variation of the vacancy concentration. These changes, similar to those which result from varying the temperature of the sample, cannot explain our effect for the following reasons: (i) No change is

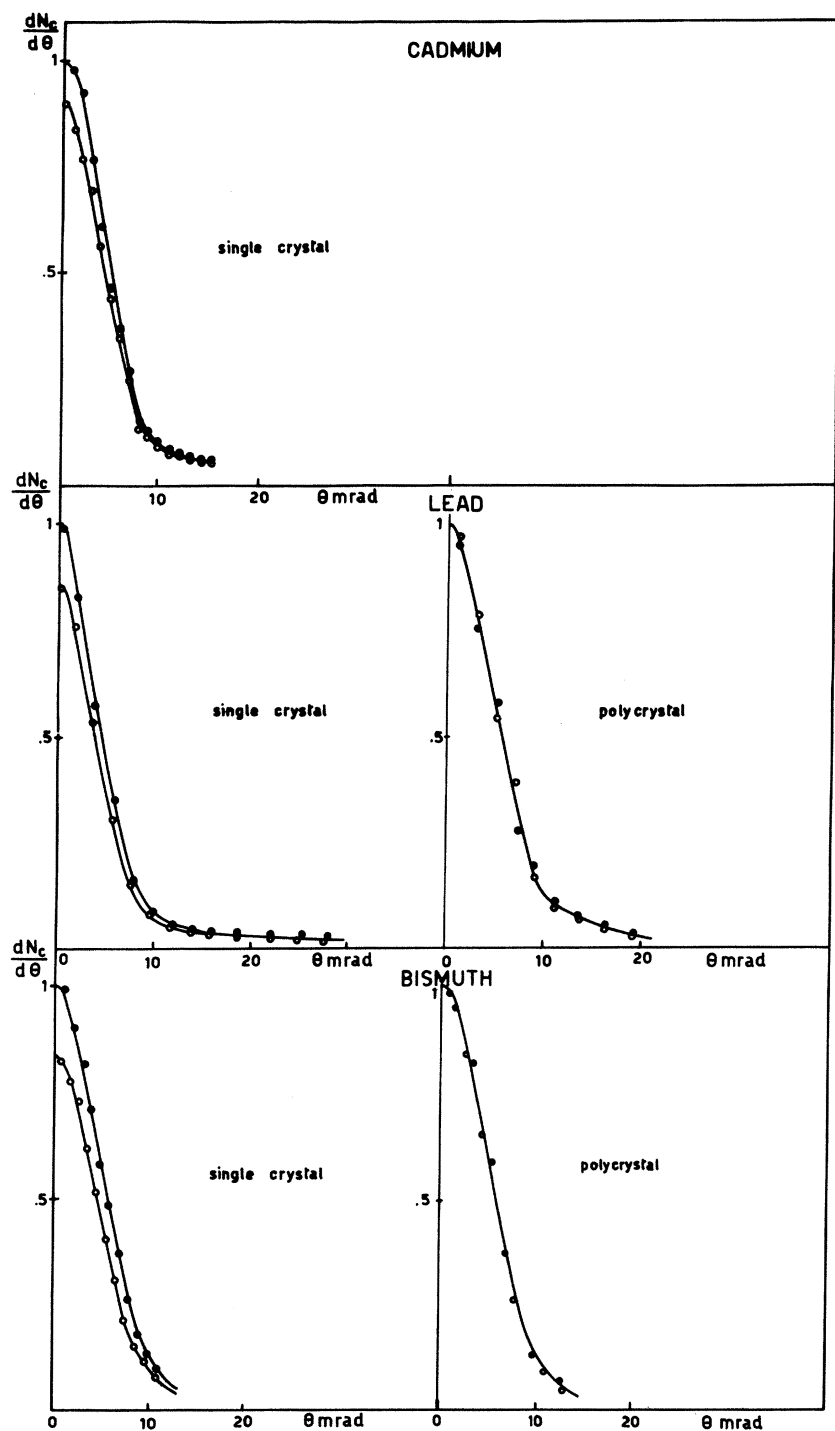


FIG. 3. Measured angular distributions for Cd, Pb, and Bi. Solid dots: $T=300^\circ\text{K}$, open dots: $T=77^\circ\text{K}$.

observed in the lifetime, (ii) no change is observed in the shape of the angular correlation curve, and (iii) no effect is observed in polycrystals.¹¹

Having in mind the difference between polycrystals and the fact that positrons do not escape from the crystal¹² we think that the long-range order

must be taken into account for explaining the observed effect. In fact, the motion of a positron in a lattice depends on the angle of incidence which the direction of motion forms with the crystallographic planes.¹³ The positron can be channeled by the Coulombian forces in the interplanar re-

TABLE II. Comparison between the observed temperature effect E and the one E' calculated according to the suggestion of Ref. 5. In the table are also summarized some properties of the single crystals used.

Sample	Z	Structure	Debye temperature	E (300 °K; 77 °K) (%)	E' (300 °K; 77 °K) (%)
Al	13	fcc	375°	7.9 ± 2.5	2.24
Co	27	hcp	385°	7.8 ± 2.5	2.55
Zn	30	hcp	235°	9.5 ± 1	4.42
Cd	48	hcp	165°	12.3 ± 0.6	3.80
Pb	82	fcc	96°	18.0 ± 0.5	2.07
Bi	83	Rhombohedral	117°	21.4 ± 0.3	1.51

gions and this effect produces a nearly free motion of the positron with a consequent reduction of probability of the inelastic scattering, which the thermalization time depends on.¹⁴ The over-all result is that in a single crystal the positron at annihilation has a quite high probability of not being thermalized, in contrast to what happens in a polycrystal. Accordingly, the model we propose is the following, as we suggested for the first time in the Ref. 3: At high temperature the thermalization time of positrons is shorter than the annihilation time both in polycrystal and in single-crystal specimens. This is due to the fact that in the single crystal the lattice vibrations at high temperature reduce strongly the positron channeling, increasing the inelastic scattering probability which becomes of the same order as the one for the random structure of the polycrystal. The angular-distribution measurements in Fig. 4 seem to confirm this statement, showing the overlapping of the curves at high temperature in Zn polycrystal and single crystal. At low temperature the lattice vibrations are damped¹⁵ and consequently, due to the channeling effect, the positron can annihilate saving a fraction of its initial momentum. From an experimental point of view the result appears as a reduction in the central part of the angular-correlation curve.

The hypothesis of incomplete thermalization before annihilation has been suggested and verified, respectively, by Carbotte¹⁴ and Kim *et al.*¹⁶ in alkali-metal polycrystals, with a mechanism which is different from the one proposed by us. In fact, the Carbotte interpretation cannot explain the kind of effect we observed.

Following our idea³ we can calculate the expected Z dependence of the observed temperature effect from the characteristics of the sample in which the annihilation process takes place.

Both the classical¹³ and the quantum-mechanical theories¹⁷ regarding the motion of a positron in a lattice give the same value Ψ_c for the critical angle between the direction of motion of the positron

and a direction of a lattice plane. As is well known Ψ_c separates the channeled component ($\Psi < \Psi_c$) from the random one ($\Psi > \Psi_c$) in the positron beam.

If the effect E measured by us depends on the

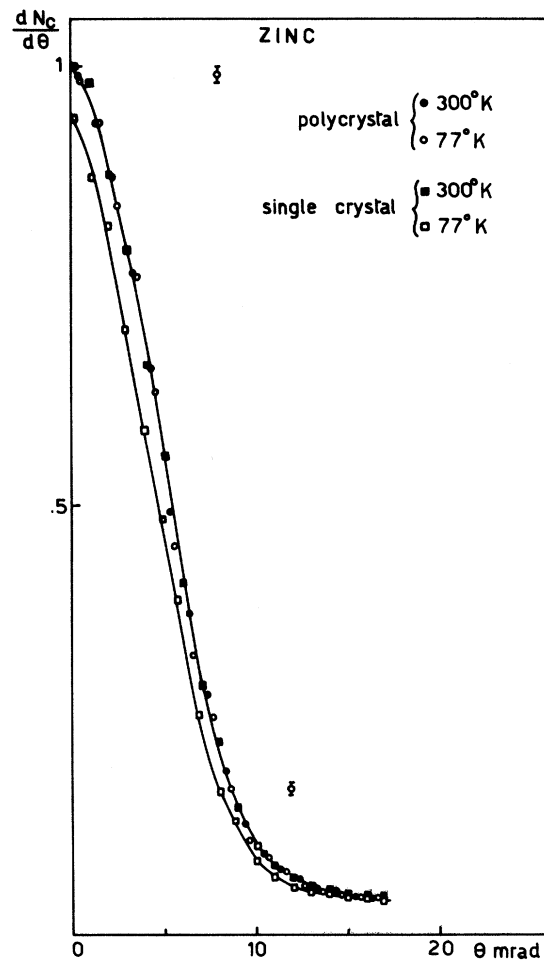


FIG. 4. Typical result for the angular-distribution measurements as a function of temperature in Zn polycrystal and single crystal. The errors are the statistical ones.

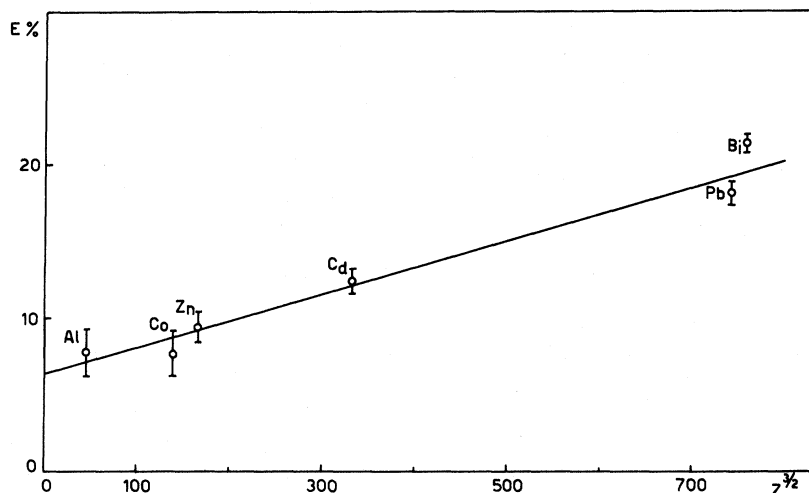


FIG. 5. Measured temperature effect versus $Z^{3/2}$ for all the samples. The straight line represents the best fit.

channeled component only, taking into account the total solid angle between crystallographic planes, E must depend on Ψ_c , on the number n of low-index planes available, and on the electronic density ρ_e , i. e., $E \propto n\Psi_c\rho_e$. As is well known,¹⁸ Ψ_c is proportional to $Z^{1/2}$, so that assuming both Ψ_c and n to be roughly constant, and ρ_e proportional to Z , we get $E \propto Z^{3/2}$ in good agreement with our experimental results (Fig. 5).

In order to give a quantitative evaluation we need to know the Ψ_c value for positrons, but unfortunately the experimental literature in this field is quite limited.^{19,20} Nevertheless, from the work of Tomlinson and Howie²⁰ we have a $\Psi_c = 2^\circ$ for Pb, and considering a planar channeling with equal probability only for the lowest-index planes (0, 1, 2) we

get a total fractional solid angle available for channeling of about 50%.

It is clear that though the model proposed by us seems satisfactory to explain qualitatively the set of experimental results, and in particular the observed Z dependence for a quantitative evaluation, some doubt remains which mainly arises from the lack of experimental information about positron channeling. In any case this seems to us, till now, the only explanation which is in agreement with all the experimental results obtained.

We are planning at present an experiment with a collimated and monoenergetic positron beam which will allow us to measure the annihilation coincidence rate as a function of temperature in channeled and unchanneled conditions.

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⁴We believe that the only normalization having a physical meaning is obtained by keeping constant the total number of annihilations observed. In a previous paper (Ref. 2) we showed experimentally that, with our high counting rate, time normalization gives the same results as the constant number of annihilations normalization.

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PHYSICAL REVIEW B

VOLUME 2, NUMBER 7

1 OCTOBER 1970

Optical Properties of Divalent Manganese in Calcium Fluorophosphate

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(Received 30 April 1970)

We have studied the optical absorption, fluorescence excitation, and fluorescence emission spectra of single crystals of calcium fluorophosphate containing divalent manganese. A comparison of these measurements with electron-spin-resonance measurements made on the same crystals has enabled us to identify the optical excitation and emission spectra of divalent-manganese ions located on each of three inequivalent sites in the lattice. The sites observed are the Ca(I)-type site, the Ca(II)-type site, and a site similar to the Ca(II) site except with a "modified" environment. A fourth site, a "modified" Ca(I)-type, has been detected by electron spin resonance, but its optical properties could not be obtained. The excitation and emission spectra of manganese on the Ca(I), Ca(II), and Ca(II) "modified" sites are presented, as well as a discussion of the effects of temperature, manganese concentration, and crystal-growth conditions on the optical properties of the crystals.

I. INTRODUCTION

The calcium fluorophosphate or fluorapatite system (FAP) doped with manganese has been the object of considerable interest over the last two decades, primarily because of the commercial value of fluorescent-lamp phosphors using the halophosphate system. Fluorapatite has the hexagonal space group $P6_3/m$ (C_{6h}^2) with two molecules of $Ca_5(PO_4)_3F$ per unit cell. There are two inequivalent sites for the Ca^{+2} ions in this structure, 40% of the Ca^{+2} ions being on the so-called Ca(I) sites with the remainder on the Ca(II) sites. The Ca(I) site has C_3 point-group symmetry with each calcium ion having six oxygen nearest neighbors which form a slightly twisted triangular prism about it. The Ca(II) site has C_{1h} point-group symmetry with the Ca^{+2} ions sitting at the corners of equilateral triangles with an F^- ion in the center. Mn^{+2} ions are expected to enter FAP crystals by simple substitution for Ca^{+2} ions on either the Ca(I) or the Ca(II) sites. However, if one includes the possibility of interstitial sites, interactions with other crystalline imperfections, and manganese valence states higher than +2, the number of ways in which manganese could be incorporated into a FAP crystal becomes quite large. Although optical and ESR measurements have been made on halophosphate powders by others,¹⁻³ the complexity of the apatite crystal structure is such that limited progress was made in deciding between these alternatives until single crystals of FAP become available. Johnson² was the first to suc-

cessfully grow crystals of FAP using the Czochralski method. He doped some of his crystals with manganese and measured their optical properties and attempted to deduce the site(s) of the manganese ions.^{2,4,5} We find that the optical emission that Johnson observed and ascribed to Mn^{+2} is very strong in most crystals but is due not to Mn, but instead to a defect center associated with the deviation of the crystals from stoichiometry. We have studied the optical properties of this defect center (termed here the "X" center) and how its concentration can be altered both by variations in the stoichiometry of the melt and by the addition of manganese to it. We have been able to study the true optical properties of manganese in FAP only after separating out the optical properties of this defect center. When the optical properties of manganese are correlated with ESR measurements, we are able to divide the excitation and emission spectra of manganese into three or more parts due to manganese in three or more sites. A discussion of the description of these sites and the optical properties of manganese at each site is the purpose of this paper.

II. CRYSTALS

The fluorapatite crystals were grown by the Czochralski technique using induction heating. The equipment and techniques used have been described previously.⁶ An iridium crucible served as both container and susceptor and is the most satisfactory container material found since it is neither wet nor