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Gamma-Ray-Induced Expansion of Lithium Fluoride*

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Specimens were irradiated at several different temperatures, and the expansion, F- and 450-absorption bands were measured at room temperature. The ratio of F to 450 absorption varied greatly both with temperature and with length of irradiation. It was thus possible to resolve the expansion among these two centers. The result was a volume of LiF for each F center and 2 such volumes for each 450 center if the respective oscillator strengths are taken as 0.8 and $\frac{1}{4}$. Variability in the rate of formation of color centers was found among different specimens. It is suspected that some expansion (perhaps, in some specimens, as much as half that associated with the 450 center) may be associated with other centers formed in the lithium fluoride.

INTRODUCTION

About 10 years ago, Yuster suggested using the easily measured radiation-induced 450-mμ color band of lithium fluoride to determine the range of deuterons produced by the Argonne National Laboratory 60-in. cyclotron. When the method[1] was used, the bombarded lithium fluoride was found to be birefringent. Birefringence of this magnitude developed when lithium fluoride was placed on a hot plate for a few seconds, hence, it was at first concluded that the radiation-induced birefringence was associated with thermally induced strain patterns resulting from heating by the deuteron beam. Primak later examined these specimens, measured the birefringence quantitatively, and calculated the strains; and with Delbecq and Yuster demonstrated that a radiation-induced expansion of lithium fluoride was the major effect.[2] The expansion along the range calculated from the birefringence was approximately proportional to the 450-mμ absorption. They calculated the number of vacancies associated with the F center and the 450-mμ absorption (equal numbers of positive ion vacancies were assumed to meet the requirement of charge neutralization) (F-center absorption assumed proportional to 450-mμ absorption) with the aid of Smakula's dispersion formula. The expansion closely equaled the volume of this number of normally filled lattice sites. This result supported the hypothesis that the vacancies were generated during the irradiation.

The expansion along the range calculated from the birefringence was only approximately proportional to the concentration of 450 centers along the range, and Primak became concerned over whether the photoelastic method used gave the radiation-induced expansion reliably. To be considered were thermal effects which could increase or decrease the major effect caused by radiation, some kind of stress relaxation caused by radiation or plastic flow, and problems of optical measurement. He proved the existence of the expansion by measuring it directly interferometrically.[3] He also studied specimens irradiated with electrons, gamma rays, and x rays. The effects were so similar that any major effect from heating by the high-energy deuterons was ruled out. The flaw in the first investigation proved to be the assumption that the F-center absorption was proportional to the 450-mμ absorption; the ratio varied widely among different specimens. When measured F-center absorptions were used, the results were quite consistent with the explanations summarized above.

Primak did not investigate the causes of the large variation in the ratio of the 450 mμ/F-center absorptions, but suggested a temperature effect might be involved. The purpose of this investigation was to find the effect of temperature on the ratio and to attempt to separate the expansions associated with these two absorptions.

For general references on the subject material of these papers the reader is referred to the earlier papers.

EXPERIMENTAL

The lithium fluoride was cleaved from pieces obtained from the Harshaw Chemical Corporation. Some of the material was used as fabricated in the manner described below. Other material was, in addition, annealed to remove strains from fabrication. The annealing was conducted in air, the specimens resting upon a piece of silica tape. The temperature was raised over a period of several hours to about 100°C below the melting point (at which temperature the strains were observed to anneal very rapidly) and then allowed to cool gradually over a period of many hours. The introduction of strain during the cooling process was related to thermal gradients associated with furnace temperature control. The elastic limit seems to decrease with increasing temperature and hence smaller thermal gradients at the higher temperatures are effective in leaving residual strain. To speed the process, the cooling rate was increased as the temperature decreased.

Specimens were uniformly irradiated with gamma

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

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[1] C. J. Delbecq, W. J. Ramler, S. R. Rocklin, and P. H. Yuster, Rev. Sci. Instr. 26, 543 (1955).

[2] W. Primak, C. J. Delbecq, and P. H. Yuster, Phys. Rev. 98, 1708 (1955).

[3] W. Primak, Phys. Rev. 112, 1075 (1958).

rays. According to which was available at the time, a cobalt source or a spent-fuel element source was used. The dose rate was determined with ferrous sulfate dosimetry with the spent-fuel element source, and the two sources were compared by the rate at which the *F* band was formed in specimens of lithium fluoride. The specimens were immersed in petroleum ether during irradiations at room temperature or below; in xylene at higher temperatures. The glass tube containing the petroleum ether was placed in a Dewar containing a suitable material to maintain the temperature: e.g., salt-ice for -18°C, ice for 0°C, sodium thiosulfate–water mixture for the intermediate temperature, and water for high temperature. The high temperature was nearly maintained by the absorption of gamma rays.

Although the specimens were irradiated at different temperatures, the measurements were all made at room temperature. In some cases, several irradiations were made during a single day. In other cases, measurement was made during the day and then the measurement was repeated the following morning (about 20 h later) to note any effect from the conversion of the 620 band.[4] Very little, if any, change was noted over the 20-h period except for the specimens irradiated at ice temperature, the lowest temperature for which expansions were measured. For these last specimens, the 450 band increased about 5% overnight.

Expansion was measured by comparing the length of an irradiated end standard[5] with an unirradiated one in a double Twyman-Green interferometer[6] using the white light achromatic fringe to identify the zero order mercury green light fringe. The end standards were parallelepipeds with faces about $\frac{1}{4}$ in. sq and $\frac{1}{2}$ in. long cleaved from a $\frac{1}{2}$-in.-thick block of lithium fluoride whose faces had been polished to interferometric specifications.[7] Measurements were made to 1/20 fringe (about $\frac{1}{2}$ μin.) and are reported as such.

Absorption measurements were made with a Cary Model 11 recording spectrophotometer and are reported as optical densities per mm of thickness [i.e., $(\log_{10}I_0/I)$ /mm]. In all cases, the optical density reported is that above background in the vicinity of the peak. Thin cleaved specimens of lithium fluoride for absorption measurements were irradiated with the end standards. In most cases these were taken from the same block of lithium fluoride from which the end standards were cleaved. For many of the irradiations, the *F* peak was off the scale of the spectrophotometer. In such cases the peak height was estimated from the width of the peak by the method used by Primak.[3] The precision in this case was estimated at about 20%. After the series of irradiations was performed, the end standards were cleaved thin enough for the *F* peak to be on scale, and the absorption spectrum was obtained. In these measurements the greatest error was from irregularity of the cleaved plates; the precision was 5–10%.

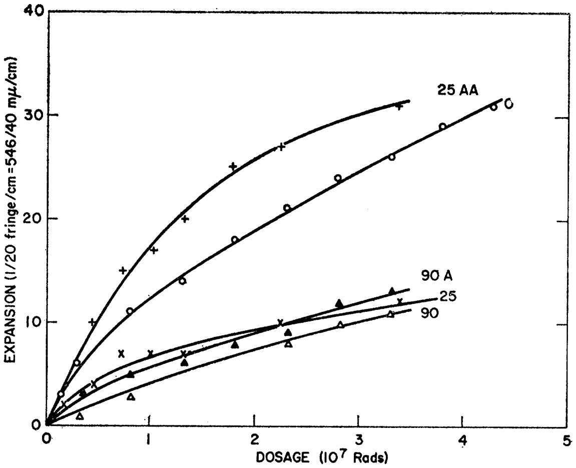

FIG. 1. The expansion of lithium fluoride end standards subjected to gamma-ray irradiation. The numbers on the graph are the temperatures (°C) of irradiation; *A* indicates the specimen was annealed, *AA*, twice annealed.

In addition to the peaks, there develops on irradiation a background absorption. In all cases, this background was sketched in assuming there was no detail beneath the peaks, and the peak heights were taken as the optical density above this background. The error introduced by this procedure is difficult to identify because the operation tends to be highly consistent.

RESULTS

Expansions observed for irradiations at three temperatures, 0, 25, and 90°C, are shown in Fig. 1. Expansion is smaller for irradiation at the higher temperatures. The annealed specimens showed a greater expansion rate. A set of data for an unannealed and an annealed specimen which had been observed after 4 progressive irradiations at 0°C extending to about 10^7 rad is not shown. The annealed specimen had expanded about 5% more than the unannealed specimen.

The behavior of the *F*-peak optical density per mm is shown in Fig. 2. The data were obtained with the specimens which were irradiated simultaneously with the end standards for the purpose of following the absorption during the course of progressive irradiations. The results obtained with the annealed absorption specimens are not shown. The one irradiated at 25°C gave a curve 6–12% higher than the one shown in Fig. 2, but in Table I it is seen that at the end of the

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[4] P. Pringsheim and P. H. Yuster, Phys. Rev. 78, 293 (1950).

[5] End standard is a technical term from optics and metrology for a length metric consisting of a bar whose metric is the distance between the end faces; in contrast to the usual length metric which is a ruled standard. The length of an end standard can be determined 1000 times more precisely than can the length of a ruled standard. See, e.g., C. Candler, *Modern Interferometers* (Hilger and Watts, Ltd., London, 1951), or a work on metrology. The lithium fluoride-end standards were used here uncoated; i.e., the reflection used for interferometry was from the dielectric surface of the crystal.

[6] This instrument was designed by the first author and constructed by J. Kwilos. The optics were made by E. W. Zacharias.

[7] We are indebted to E. W. Zacharias for fabricating these.

TABLE I. Measurements after final irradiation.

			Expansion specimen					Absorption specimen	
			Expansion		Optical absorption			Absorption	
Sample No.	Treatment[a] and irradiation temperature (°C)	Radiation dose (10^6 rad)	Measured (1/20 fringe/cm)[c]	Calculated[b] (1/20 fringe/cm)[c]	*F* peak $[\log_{10}(I_0/I)]$/mm	450 peak $[\log_{10}(I_0/I)]$/mm	*F*/450 ratio	*F* peak $[\log_{10}(I_0/I)]$/mm	450 peak $[\log_{10}(I_0/I)]$/mm
1034	0	43	24.5	16.1	19.2	3.28	5.85	18.8	3.35
1010*C*,*D*	25	54	15.9	10.8	12.8	3.95	3.24	11.7	3.36
979*F*	*AA*25	54	29.4	15.5	18.5	5.18	3.57		
1010*E*	90	33	8.7	5.7	6.75	0.54	12.5		
979*D*	90	33						7.7	0.60
1021*A*	*A*90	33	10.0	7.8	9.3	0.74	12.6	8.0	0.68
1038	*AA*25	38	26.6	13.7	16.3	3.61	4.51		
1039*A*	*A*25	22.5	17.5	7.1	8.4	1.84	4.56		
1039*B*	25	42	19.9	12.2	14.5	4.45	3.26		
1039*C*	25	134	55	26.1	31.0	11.9	2.60		

[a] Prefix *A*, annealed; prefix *AA*, doubly annealed.

[b] Assuming: (1) volume of an Li^+ and F^- is gram molecular weight ÷ (density × Avogadro's number), (2) this is the volume associated with the formation of an *F* center, (3) oscillator strength is unity, (4) Smakula's formula modified by Primak (Ref. 2).

[c] About 137 Å/cm.

irradiation, the *F*-peak height in cleaved sections of the end standard was $\frac{1}{3}$ higher than in the unannealed specimen.

The 450-mμ optical density per mm did not behave in a simple way paralleling the expansion and the *F*-peak optical density per mm. Accordingly, additional irradiations were made at other temperatures to learn the behavior. The results are given in Fig. 3.

From the results given in Figs. 2 and 3, the behavior of the ratio of the absorption coefficients were computed, and the results are shown in Fig. 4.

Expansions and optical density per mm data for the end standards (and some other specimens) are given in Table I. Included in this table are data for several specimens which were not studied progressively as shown in Fig. 1.

In an attempt to find the source of the enhanced effect in the annealed lithium fluoride specimens, specimens were annealed in vacuo, in air, and in a flowing anhydrous H_2F_2 atmosphere, and the *F*-peak heights were compared after about 2.5×10^6 rad irradiation (optical densities of the specimens were then about 2.5). The mean of 4 specimens was largest for the air annealed, smallest for the H_2F_2 annealed specimens, but the differences were less than the standard deviations. The differences tend to be small at these dosages. The results must be considered to be inconclusive except to indicate that these treatments do not produce large differences. No significant effects were found to be associated with polishing or straining specimens prior to the annealings.

The ratios of the widths (in wave numbers) at half-maximum height will be used to calculate the number of centers from dispersion theory. The *F*-peak $\frac{1}{2}$ width for 12 specimens was measured as 5990 cm^{-1}, standard deviation 160 cm^{-1}; for the 450 peak, mean width for 10 specimens 1535 cm^{-1}, standard deviation 29 cm^{-1}; ratio 3.90, standard deviation 0.20. On five of these

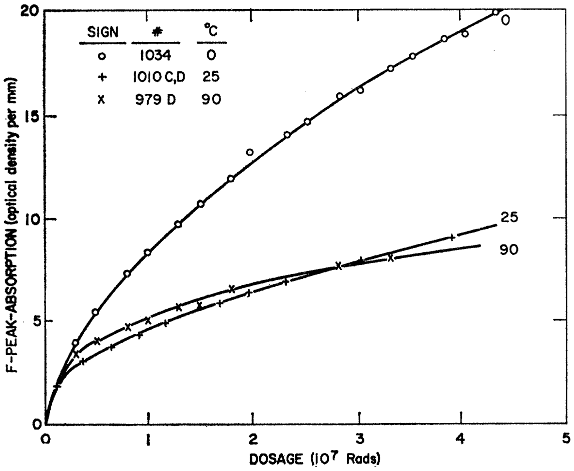

FIG. 2. The absorption coefficient of lithium fluoride at the peak of the *F*-center absorption band as a function of gamma-ray dosage.

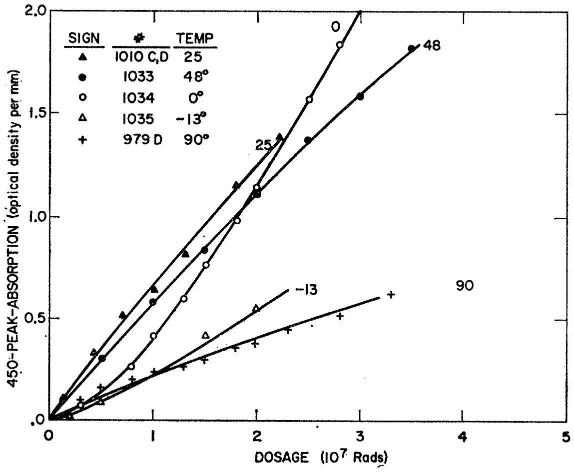

FIG. 3. The absorption coefficient of lithium fluoride at the peak of the 450-mμ absorption band as a function of gamma-ray dosage.

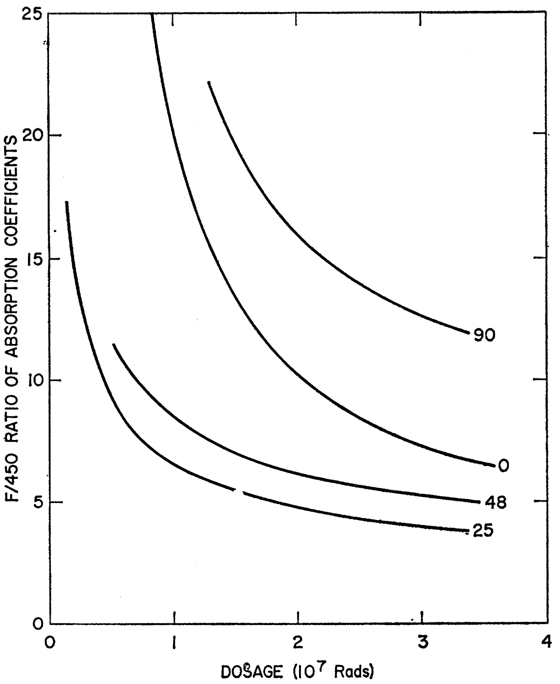

FIG. 4. The ratio of the absorption coefficients at the peaks of F center to that of the 450-mμ absorption bands as a function of gamma-ray dosage.

specimens both the F and the 450 peaks were measured; for these: Mean ratio of $\frac{1}{2}$ widths, 3.86, standard deviation 0.12. The standard deviations are probably an underestimation of the error since our estimates of background were surely more reproducible than reliable. The value 3.9 is considerably higher than some other reported results.[2,3]

DISCUSSION

From Figs. 1 and 2, it is evident that in this temperature range both the expansion rate and the rate of F-center formation decrease in a simple manner with increasing irradiation temperature. There is a large change between 0°C and room temperature, but the change between room temperature and 90°C is quite small. The effects of annealing specimens prior to irradiation have been discussed above. The rate of formation of the 450 center is seen from Fig. 3 to follow a much more complex behavior. It, too, at first decreases with increasing irradiation temperature; the rate becomes a minimum for specimens irradiated near room temperature; and the rate increases for higher temperatures. The ratio of the absorptions 450/F (this is the inverse of the quantity plotted in Fig. 4) increases with dosage in a manner similar to the F-center absorption and behaves with temperature much as the 450 absorption does.

From Table I, it is seen that although the expansion seems to parallel the F-center absorption in a general way, the data does not behave this way when examined in detail. The ratio of the expansion of F-center absorption varies by a factor of about 2 while the error for this ratio is estimated at 30%, and its reproducibility when determined by a single individual (as was done here) should be somewhat greater. The ratio of F/450 absorption varies by a factor of about 5. These conditions were the ones sought for the purpose of resolving the F- and 450-center expansions.

The expansion data given in Table I may be resolved among the two absorptions by the methods of the "small sample" statistics[8] and the results of such a treatment is given in Table II. The symbols are: $\hat{E}$ expectation value for the expansion, A_1 and A_2 respective absorptions of F and 450 centers, R multilinear correlation coefficient, s standard error of estimate, s_{b_1} and s_{b_2} standard deviations of the respective partial regression coefficients associated with A_1 and A_2. The first regression resolves the expansion among the two absorptions, the second associates it with the F-center absorption only. From a t test, the partial regression coefficient for the 450 absorption is significant at the 85% level, the one for the F-center absorption at the 95% level. The 95% confidence bands for the respective (partial) regression coefficients of the F-center absorptions for the two regressions do not overlap. Theoretical considerations (the constitution hypothesized for the 450 center should give an expansion if the F center does), statistical considerations (the values of R^2 and s^2) and physical considerations (the magnitude of the regression coefficient for the second regression leads to an excessive expansion per F center) all favor the first regression.

TABLE II. Analysis of variance.

	Regression (1) $\hat{E}=1.058A_1+1.764A_2$			Regression (2) $\hat{E}'=1.569A_1$		
	Degrees of freedom	Sum of squares	Mean square	Degrees of freedom	Sum of squares	Mean square
Due to regression	2	1460	730	1	1403	1403
Deviations from	6	84	14	7	141	20
Total	8	1544		8	1544	
Quantity		Value			Value	
R^2		0.946			0.909	
S^2		14.0			20.0	
S_{b_1}		0.53			0.21	
S_{b_2}		1.15			...	

The physical meaning of the partial regression coefficients is readily seen when they are converted to conventional units (E, b_1, b_2, A_1, A_2 refer to the units of Tables I and II and give convenient small numbers; the corresponding symbols for conventional units are δ

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[8] The nomenclature used here is that given by B. Ostle, *Statistics in Research* (Iowa State University Press, Ames, 1954).

volume/unit volume, B_1, B_2 regression coefficients in dilatation per absorption/cm,[9] α_1, α_2 absorption/cm).

$$B_1 = k_1 f_1^{-1} v_1; \quad B_2 = k_2 f_2^{-1} v_2,$$

where v_1 is the volume expansion associated with the formation of an F center, and v_2 that associated with the 450 center. The quantity k_1 is obtained from optical dispersion theory and is often written $N_1 f_1$, the product of the number of centers and their oscillator strength per unit absorption and unit volume. The value obtained depends on what assumptions are made about how the refractivity of the base material is affected by the introduction of the center (a small correction) and the shape of the absorption band (in quantum-mechanical formalism upon the energy levels involved and their transition probabilities). The value for k_1 used here, 0.9×10^{16}, taken from a previous paper,[3] is about that obtained from most conventional treatments. Then the volume increase associated with the formation of an F center is $2.1 \times 10^{-23} f_1$ cm^3 or $1.25 f_1$ molecules of LiF since the molecular volume is 1.67×10^{-23} cm^3 (reciprocal of the number of LiF per cm^3). If f_1 is about 0.8, a reasonable figure, the volume expansion corresponds to about one LiF volume per F center, in accord with previous observation.[2] The ratio k_1/k_2 is the ratio of the half-widths of the absorption peaks in wave numbers. In previous work,[3] it was reported as 3.2–3.8; here 3.9 was found. The volume expansion associated with the 450 center is then $12\text{–}13 \times 10^{-23} f_2$ cm^3, about $8 f_2$ LiF molecular volumes. If 2 molecular volumes of expansion are to be associated with the 450 center, then f_2 is about $\frac{1}{4}$, a reasonable oscillator strength for an unsymmetrical center.

Those unaccustomed to the use of the "small sample" statistics may find more physical meaning in considering the equation

$$\delta = k_1 v_1 \alpha_1 f_1^{-1} + k_2 v_2 \alpha_2 f_2^{-1},$$

regarding f_1^{-1} as a virtual independent variable and $k_2 v_2 \alpha_2 f_2^{-1}$ as a virtual dependent variable. The center of the population leads to a value of f_1 and for the group of constants $k_2 v_2 \alpha_2 f_2^{-1}$ which may be interpreted as above or in modified ways if particular hypotheses about the expansion are introduced.

The population of deviations $(E - \hat{E})$, where E is the observed value of the expansions and $\hat{E}$ is the expected value given by the first regression, shows a quite satisfactory random distribution. However, the results plotted in the figures indicate that measurements on a single specimen are more reproducible than among different specimens. Further, specimens annealed by us give consistently higher rates of permanent-center production than those used as obtained. No indication that the regression coefficients are affected was found in the data at hand, but the presence of systematic effects is suspected. From a comparison of (a) the deviations we estimate from the precision of the measurements with (b) the deviations actually found, we guess the contribution of systematic effects may perhaps be as much as half of the contribution of the 450 centers to the expansion of particular specimens.

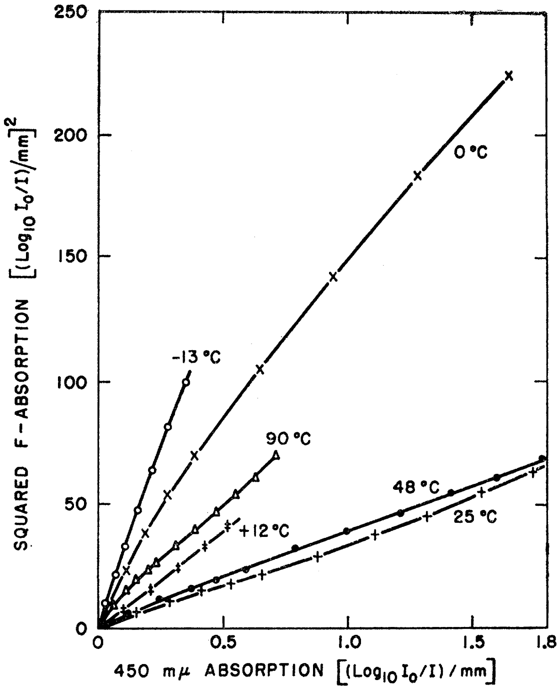

FIG. 5. The square of the absorption coefficient for the F peak plotted against the 450-mμ absorption coefficient for progressive irradiation of lithium fluoride at several temperatures indicated on the graph.

ADDENDUM

Since the conclusion of the above investigation, Faraday, Rabin, and Compton[10] have plotted the 450 absorption against the square of the F absorption for a specimen reported by Mador *et al.*,[11] and found the curve to be nearly a straight line. We reproduce similar curves from our work in Fig. 5 (with respect to Faraday *et al.*, our curves have axes reversed, and units which make the slope 23 times less). To be noted are: (1) As in the figure of Faraday *et al.*, there is a consistent departure from a straight line, the 450 absorption tending to increase relative to the square of the F absorption; and further, this deviation is temperature dependent; and (2) there is a large temperature dependence with a minimum slope (maximum in the figure of Faraday *et al.*) in the room-temperature region. The curve drawn by Faraday *et al.* corresponds to what we would have found at about 18 or 60°C rather than at

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[9] By absorption is meant $\ln(I_0/I)$, where I_0 and I are the incident and absorbed light intensities, respectively.

[10] B. J. Faraday, H. Rabin, and W. D. Compton, Phys. Rev. Letters 7, 57 (1961).

[11] I. L. Mador, R. F. Wallis, M. C. Williams, and R. C. Herman, Phys. Rev. 96, 617 (1954).

the 300°K given by Mador. The simple interpretation of a stability radius made by Faraday *et al.* seems inadequate to explain the complex behavior shown here. We propose kinetic effects involving labile forms, using lifetimes, capture probabilities, etc. Since the experimental data are inadequate for this problem, the subject is left to the interested reader.

Also, since the conclusion of this work, Wiegand[12] has reported that significant lattice parameter changes are associated with color center formation and the concomitant volume expansion. Such a result would indicate that the ratio of the expansion per color center to the molecular volume as reported here does not have the simple physical explanation offered earlier.[3] Wiegand did not observe a contribution of centers other than F centers to his volume expansions, a contribution which should have been significant since his lowest concentrations appear to be in the range of our highest ones. Additional work will be required to clarify these problems.

ACKNOWLEDGMENTS

We are indebted to Gladys Swope and her staff for assistance with the irradiations and for the calibrations of the gamma-ray flux in the Gamma Irradiation Facility. We are also indebted to E. J. Hart and his co-workers for the use of their cobalt sources. Charles Delbecq and Philip Yuster provided much helpful advice.

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[12] D. A. Wiegand, Phys. Rev. Letters **9**, 201 (1962).

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Heat Capacity of γ-CuZn Alloys below 4.2°K

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Low-temperature heat capacity measurements have been made on a series of high-purity specimens covering the entire γ phase of the Cu-Zn system. The electronic heat capacity decreases rapidly with increasing zinc concentration, thereby lending support to the hypothesis that the γ brasses are electron compounds. An excellent fit to the data may be obtained by assuming that the Fermi surface of these alloys is spherical and makes contact with the large Brillouin zone of the γ-brass structure. The Debye temperature of the alloys is 433°K and is approximately independent of zinc concentration.

I. INTRODUCTION

It was first pointed out by Hume-Rothery[1] that certain alloy structures, with narrow stability ranges, occur at a definite electron-atom ratio. The γ structure, which occurs at the ratio of 21/13, is perhaps the best known example of such an electron compound. Jones[2,3] has considered the so-called large Brillouin zone associated with the γ-brass structure. This zone is *not* the true zone containing two electrons/atom, but is the complex polyhedron formed by those planes having a large structure factor,[4] in this case $\{330\}$ and $\{411\}$. The large zone contains 90 states per unit cell or 1.73 states per atom, so that for an electron concentration of 21/13 (=1.615) it is almost completely full. On this basis, one would expect substantial contact between the associated Fermi surface and the zone faces. Furthermore, the density of states would decrease rapidly as a function of electron to atom ratio, thereby accounting for the narrow range of stability for the γ phase.[5]

Jones has calculated the expected form of the density-of-states curve for the γ-brass structure, assuming a spherical Fermi surface. He has also considered the possible effects resulting from the incompleteness of the large Brillouin zone, and also from the possibly different gaps across the different faces. It thus is of considerable interest to test these predictions experimentally. For this reason, the present measurements on the γ phase of the copper-zinc system were initiated. The results indicate that the coefficient of the electronic heat capacity, and hence the density of states, is indeed a rapidly decreasing function of electron concentration. It also appears that it is possible to obtain a very good fit to the data, assuming a spherical Fermi surface and an effective mass at the bottom of the band equal to the free-electron mass. The possible theoretical consequences of this fit are discussed.

II. EXPERIMENTAL

Heat capacity measurements were made from 1.4 to 4.2°K using the same calorimeter described previously.[6]

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[1] W. Hume-Rothery, *The Metallic State* (Oxford University Press, New York, 1931), p. 328.

[2] H. Jones, Proc. Roy. Soc. (London), **A144**, 225 (1934).

[3] H. Jones, *The Theory of Brillouin Zones and Electronic States in Crystals* (North-Holland Publishing Company, Amsterdam, 1960), p. 173.

[4] A. J. Bradley and J. Thewliss, Proc. Roy. Soc. (London), **A112**, 678 (1926).

[5] See for example, W. Hume-Rothery and G. V. Raynor, in *The Structure of Metals and Alloys* (Institute of Metals, London, 1954), p. 206.

[6] J. A. Rayne, Phys. Rev. **108**, 22 (1957).