

where  $\rho = (\xi^2 + \eta^2)^{1/2}$ . In particular, setting  $\xi = 0$  we have

$$\int_0^\infty u f(u) J_0(\rho u) du = (2\pi)^{-1} \times \int_{-\infty}^\infty \int_{-\infty}^\infty f[(x^2 + y^2)^{1/2}] \exp(i\rho y) dx dy. \quad (\text{B3})$$

We now substitute  $G'(u)$  for  $uf(u)$ , and evaluate the Fourier transform in Eq. (B3) asymptotically using the methods of Lighthill,<sup>17</sup> and then integrate with respect to  $x$  to obtain the result expressed in Eq. (3.9).

<sup>17</sup>M. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions* (Cambridge University Press, Cambridge, England, 1959).

## Properties of $F$ Centers in NaF

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A weak intensity emission, centered at 785  $m\mu$ , is identified as the  $F$  photoluminescence in NaF. The temperature dependence of photoionization and photoluminescence of  $F$  centers is investigated. Two thermal activation energies are found:  $\Delta E_L = 0.06$  eV for the photoluminescence, and  $\Delta E_I = 0.12$  eV for the photoionization efficiency. The nature of the quenching mechanism of the  $F$  luminescence is discussed.

### I. INTRODUCTION

IN the last few years many studies have been carried out on the emission and photoionization of the excited  $F$  centers in alkali halides. From the dependence of these phenomena on the photostimulation temperatures, information has been gained on the interaction of the  $F$  excited level with the crystal lattice. The results on KCl and KBr show that the temperature dependence of the luminescence yield corresponds to the same thermal activation energy as the photoconductivity intensity. This confirms that the temperature dependence of the two effects is controlled by the ionization process of the excited state of the  $F$  centers.<sup>1,2</sup>

Other alkali halides, however, do not show the same behavior. For instance, in LiF no  $F$  luminescence has been found, nor has a dependence of the  $F$  photoconductivity on the crystal temperature been detected.<sup>3</sup>

The aim of this research is to examine the behavior of the  $F$  center in NaF by studying the temperature dependence of the photoluminescence and photoionization of the center. In Sec. III the parameters of the  $F$  luminescence are briefly reported. In a following section the dependence of the emission and photoconductivity as a function of temperature is described and discussed.

### II. EXPERIMENTAL

NaF slices ( $\sim 7 \times 7 \times 1$  mm<sup>3</sup>) are cleaved from monocrystals supplied by Harshaw Chemical Company and

by Dr. Korth of Kiel. The samples are irradiated with an OEG 50 x-ray tube of Machlet; the x rays are filtered through a 0.5-mm target of NaF to ensure a uniform absorption. The crystals are photostimulated through a double monochromator with quartz prisms. Two lamps, both having 1 kW power, are used as light sources: a hot tungsten filament lamp for the visible range, and a Hanovia hydrogen discharge lamp with continuous spectrum for the ultraviolet.

The luminescence is analyzed with a Hilger and Watts monochromator having a glass prism and is then detected with photomultipliers; its intensity is automatically recorded on a paper recorder. Interference filters of Jena Glass-Werke are used when the whole emission is of interest. The emission intensity is measured in the spectral range between 200 and 700  $m\mu$  with an EMI photomultiplier type 9558 QA, and between 500 and 1100  $m\mu$  with a Philips 150 CVP with the photocathode cooled to liquid nitrogen temperature (LNT). In this way the dark current decreases from 6  $\mu\text{A}$  to  $2-3 \times 10^{-9}$  A without appreciable variation of the photomultiplier's average sensitivity. The absorption spectra are recorded with a Cary 14M spectrophotometer.

The relative ionization quantum yield is measured indirectly, from the intensity of glow peaks obtained by  $F$  photostimulation<sup>4</sup>: the NaF sample is irradiated at LNT, so that only  $F$  and  $V$  centers (no  $M$ ) are created; next, it is warmed to room temperature (RT) in order to evacuate the shallow electron traps. After these preliminary treatments, the crystal is photostimulated in the  $F$  absorption band (for 1 min) at

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<sup>1</sup>R. K. Swank and F. C. Brown, Phys. Rev. **130**, 34 (1963).

<sup>2</sup>G. Spinolo and F. C. Brown, Phys. Rev. **135**, A450 (1964).

<sup>3</sup>G. Spinolo (private communication).

<sup>4</sup>B. Bosacchi, R. Fieschi, and P. Scaramelli, Phys. Rev. **138**, A1760 (1965).

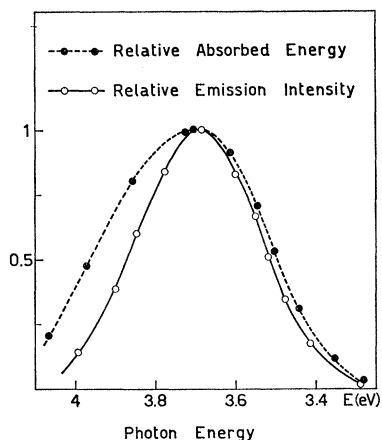


FIG. 1. Absorbed energy and total  $F$  emission intensity, in arbitrary units, as functions of the stimulation wavelength. The  $F$  luminescence is detected through an interference filter from Jena Glass-Werke. The absorbed energy is evaluated from the absorption spectrum of the same sample.

the desired temperature: part of the excited  $F$  centers are thermally ionized, and the electrons ejected into the conduction band are captured by traps present in the sample. Subsequent heating gives thermoluminescence glow bands whose intensity is proportional to the ionization quantum yield of the  $F$  excited state.

In Ref. 4 it is proved that the intensity of glow peaks—or, equivalently, the area of the glow peaks—is proportional to the number of photoelectrons ejected into the conduction band. Moreover it has been shown that this method is very sensitive and reliable.

### III. $F$ LUMINESCENCE

In a previous paper<sup>5</sup> we have observed that the  $x$  irradiation of NaF samples at LNT produces a weak luminescence whose band is centered on  $785\text{ m}\mu$ . The same emission band was detected by stimulating the sample in the  $F$  absorption band at low temperature ( $338\text{ m}\mu$  at LNT). We have therefore presumed that this emission is typical of  $F$  centers.

In order to obtain direct evidence of the nature of the  $785\text{-m}\mu$  emission, the present work describes the results of stimulating the sample with light at different wavelengths in the range of the  $F$  absorption bands; very narrow slits of the double monochromator, hence narrow bandwidths, were used. The total emission intensity, centered at  $785\text{ m}\mu$ , was correlated with the ratio of absorbed energy in the  $F$  band, at each stimulating wavelength in a spectral range  $250\text{--}420\text{ m}\mu$  wide. Figure 1 shows that there is satisfactory agreement between the absorption and the stimulation spectrum. The fact that the quantum yield drops when temperature increases (see Sec. IV) ensures that the emission

TABLE I. Optical properties of  $F$  centers in NaF.

	Room temperature		Liquid-nitrogen temperature	
Absorption	Max. 3.63 eV	$W=0.53\text{ eV}$	Max. 3.67 eV	$W=0.40\text{ eV}$
Luminescence	..	...	Max. 1.59 eV	$W=0.53\text{ eV}$

studied is not due to recombination of the photoelectrons with some unknown emitter.

The bandwidth of the  $F$  absorption band is  $0.40\text{ eV}$  at LNT and  $0.53\text{ eV}$  at RT; the width of the  $F$  emission band is  $0.53\text{ eV}$  at LNT and  $0.57\text{ eV}$  at  $123^\circ\text{K}$ . Table I summarizes the data we obtained.

### IV. ACTIVATION ENERGY OF LUMINESCENCE AND PHOTOCONDUCTIVITY

(a) The intensity of  $F$  luminescence is very sensitive to changes of temperature, even down to  $78^\circ\text{K}$ , i.e., the emission intensity  $I_F$  in NaF does not show the characteristic plateau at low temperature which is found in other alkali halides. From the plot of the luminescence efficiency versus  $1/T$ , the thermal activation energy of the  $F$  luminescence was evaluated in the high-temperature approximation;  $\Delta E_L = 0.06 \pm 0.003\text{ eV}$  (Fig. 2).

We point out that NaF shows a different behavior from other alkali halides such as KCl and KBr. In fact, while at RT the  $F$  band can be very easily bleached to form complex centers such as  $M$  and  $R$ , at temperatures between  $78$  and  $150^\circ\text{K}$  under intense and prolonged irradiation (2 h) with white light and with  $F$  light, no appreciable bleaching of the  $F$  band has been observed. On the other hand, at  $150^\circ\text{K}$ , as shown in Fig. 3,  $I_F$  is already very low.

These results show that the thermal activation energy  $\Delta E_L$  evaluated from the quantum yield of luminescence does not represent the energy gap between the excited state of the  $F$  centers and the bottom of the conduction

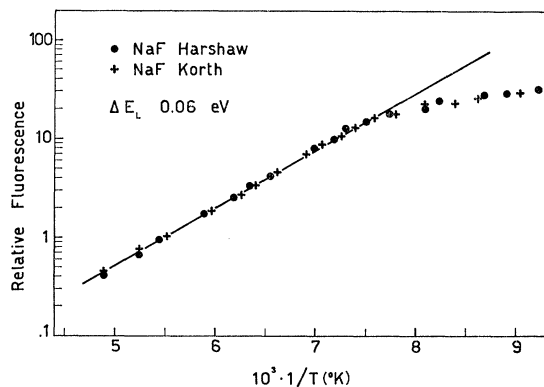


FIG. 2. Relative fluorescence of  $F$  centers in sodium fluoride. From the slope of the solid line the thermal activation energy of the  $F$  fluorescence has been evaluated in the high-temperature approximation.

<sup>5</sup> R. Fieschi, R. Oggioni, and P. Podini, Acta Phys. Polon. 26, 633 (1964).

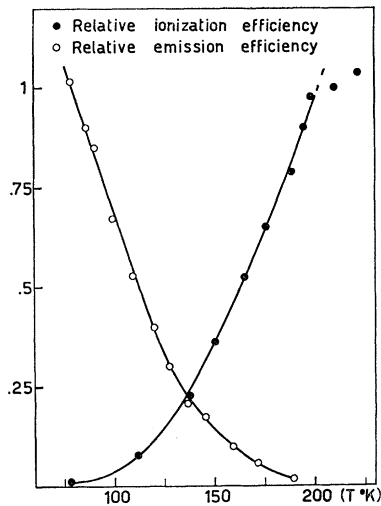


FIG. 3. Ionization efficiency of the excited  $F$  center and  $F$  emission intensity in arbitrary units. No  $M$  centers were present in the sample.

band, but is related to another electron process, as will be discussed later.

Let us observe, moreover, that at any temperature, even at RT, under the irradiation with  $F$  light, no growth of the  $F'$  band has been detected. One minute after the interruption of irradiation the whole spectral range between the  $M$  and  $F$  bands was investigated. Therefore we can conclude that in NaF the equilibrium concentration of  $F'$  centers under  $F$  light is much smaller than the concentration of  $F$  centers.

(b) Photoionization measurements on the  $F$  center support the above considerations. As explained in Sec. II, we assume that the intensity of the thermoluminescence glow peaks induced by photostimulation is proportional to the ionization quantum yield  $\eta_I$  of the excited  $F$  center.

Figure 4 shows three typical glow curves obtained after 1 min of  $F$ -light stimulation at three different

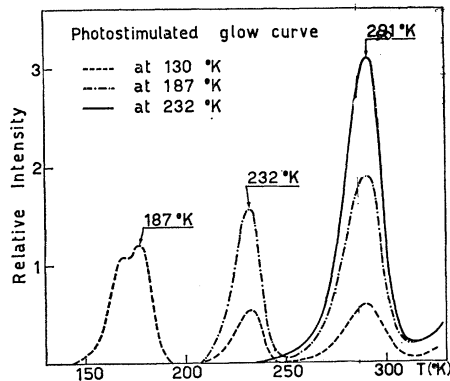


FIG. 4. Thermoluminescence glow curves after photostimulation, at three different temperatures. The glow peak at 291°K will be referred to as I.

temperatures. Three glow peaks have been detected at 187, 232, and 291°K.

The intensity of the glow peak at 291°K, which will be referred to as  $I$ , has been compared with the absorbed energy in the  $F$  band at each stimulating wavelength. All stimulations have been made at the same temperatures (232°K) and with the same photostimulation time; the peak intensity  $I$  was corrected for the lamp intensity. Figure 5 shows that there is a good agreement between the absorption and the peak intensity (which is proportional to the area under the glow band, as one expects). We shall therefore assume that the peak intensity  $I$  is proportional to the number of  $F$  photoelectrons ejected into the conduction band.

Figure 3 summarizes the temperature dependence of  $\eta_I$ ; for comparison, the behavior of photoluminescence is also plotted, in arbitrary units. One observes that at  $T=130^\circ\text{K}$ , the emission is already only 27% ( $\eta_F^*=0.27$ ) of its value at LNT, while the ionization is still very low—only 17% ( $\eta_I^*=0.17$ ) of the maximum value we measured at  $T=200^\circ\text{K}$ .

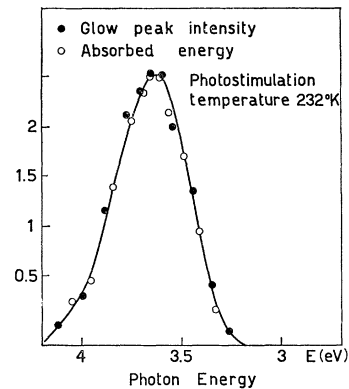


FIG. 5. Intensity of glow peak I after photostimulation at different wavelengths in the  $F$  absorption, compared with the absorbed energy at the same wavelengths. (Arbitrary units.) The absorbed energy is evaluated from the absorption spectrum on the same sample.

We do not know the maximum of either effect (our temperature range is not wide enough), but we can say that both maxima are certainly higher than the measured values. Therefore the real values of  $\eta_I$  and  $\eta_F$  at  $T=130^\circ\text{K}$  should be smaller than the obtained values; hence

$$\eta_F + \eta_I < \eta_F^* + \eta_I^* = 0.44 < 1.$$

## V. DISCUSSION

The results presented in the above section differ in many respects from those obtained on  $F$  centers in other alkali halides.

(1) The sum of the luminescence intensity and ionization value is smaller than one ( $\eta_F + \eta_I < 1$ ).

(2) No bleaching of  $F$  centers has been observed at

temperatures between 78 and 150°K. At this last temperature the  $F$  luminescence is already very low.

(3) After irradiation with  $F$  light at temperatures between 78 and 300°K, no  $F'$  centers have been detected.

First it should be considered whether a small concentration of  $F'$  centers could change the dependence of the  $F$  luminescence on temperature. It is known that the  $F'$  centers can be easily ionized. Therefore, as has been shown by Lüty,<sup>6</sup> if the free electron can be trapped by the vacancies with emission of  $F$  light, the luminescence intensity assumes the following form:

$$I_{\sigma\eta} = I_0 \eta_F \frac{1}{1 - \beta \eta_I} = \frac{I_0}{1 + (1 - \beta)(\tau_R/\tau_0) \exp[-(\Delta E/KT)]}$$

for  $[F'] \ll [F]$ , where  $\beta$  ( $0 < \beta < 1$ ) is a constant depending on the capture cross section of vacancies and  $F$  centers and on the light intensity, and  $\eta$  is the measured emission efficiency. Under these conditions one has  $\eta + \eta_I > 1$ . Since, on the contrary, we found  $\eta + \eta_I < 1$ , we can exclude this process.

Another possibility has to be considered. Let us assume that the free electrons can be trapped to form again a  $F$  center without emission. The emission intensity will be given by

$$I_{\sigma\eta} = [\mu_F/(\mu_F + \mu_{F'})] \eta_F I_0,$$

where  $\mu_F$  and  $\mu_{F'}$  are absorption coefficients of  $F$  and  $F'$  centers at the same wavelengths; but since  $\mu_{F'} \ll \mu_F$  we obtain  $\eta \approx \eta_F$ . In other words the change of  $\eta_F$  under this assumption would be too little to explain our experimental results.

Therefore we conclude that the influence of the  $F'$  centers cannot explain the behavior of  $F$  centers in NaF samples. It is necessary to assume that the electron in the excited state of the  $F$  center undergoes another process besides the radiative decay and the jump in the conduction band.

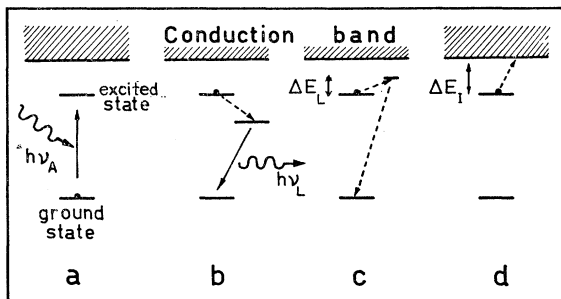


FIG. 6. (a) Optical absorption, (b) relaxation of the excited state, followed by a radiative decay, (c) radiationless decay with activation energy  $\Delta E_L$ , (d) thermal ionization, with activation energy  $\Delta E_I$ .

<sup>6</sup> F. Lüty, *Elektronenübergänge an Farbzentren-Halbleiterprobleme* (Verlag Frederick Vieweg und Sohn, Braunschweig, Germany, 1961), Vol. VI.

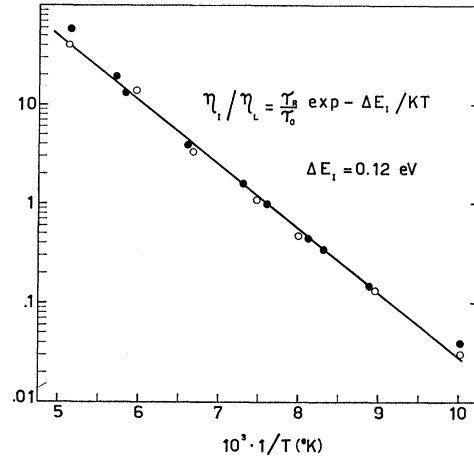


FIG. 7. Behavior of the ratio between the relative ionization efficiency and  $F$  luminescence efficiency. From the slope of the solid line the thermal activation energy of the ionization process has been evaluated.

As suggested by many authors,<sup>7,8</sup> this third process can be a nonradiative transition to the ground state with an activation energy  $\Delta E_L$  smaller than the activation energy of the ionization. Such a process has been sketched in Fig. 6 and is intuitively evident in the model of the configurational coordinates.

Let us denote by  $P_L$ ,  $P_I$ , and  $P_d$  the probability for the radiative decay, the thermal ionization, and the dissipative decay, respectively:

$$P_L = 1/\tau_R, \quad P_I = (1/\tau_0) \exp[-(\Delta E_I/KT)], \\ P_d = (1/\tau_0) \exp[-(\Delta E_L/KT)],$$

where  $\Delta E_L$  and  $\Delta E_I$  are the corresponding thermal activation energies.

The efficiencies for the three processes are:

$$\eta_L = P_L/(P_L + P_I + P_d), \quad \eta_I = P_I/(P_L + P_I + P_d), \\ \eta_d = P_d/(P_L + P_I + P_d).$$

From the ratio  $\eta_I/\eta_L$  we have directly:

$$\eta_I/\eta_L = (\tau_R/\tau_0) \exp(-\Delta E_I/KT); \\ \ln \eta_I/\eta_L = \ln(\tau_R/\tau_0) - \Delta E_I/KT.$$

Figure 7 shows the plot of  $\eta_I/\eta_L$  as a function of  $1/T$ . The value of the activation energy is found to be 0.12 eV.

From the above derivation it follows that the measured value is just the ionization energy of the  $F$ -center excited state. As expected, it turns out to be different from the activation energy for the temperature quenching of luminescence ( $\Delta E_L = 0.06$  eV).

<sup>7</sup> N. F. Mott and R. W. Gurney, *Electronic Processes in Ionic Crystals* (Clarendon Press, Oxford, England, 1948), pp. 218-224.

<sup>8</sup> D. L. Dexter, C. C. Klick, and D. A. Russel, *Phys. Rev.* **100** 603 (1955).

## VI. CONCLUSION

Our results on the temperature dependence of photoluminescence and photoionization yield of  $F$  centers in NaF support the following model: When an  $F$  center undergoes an absorption transition to the first excited state (Fig. 6a), the electron can either return to the ground state or be excited to the conduction band, according to the three processes sketched in Fig. 6 (b), (c), (d). The ionization energy obtained from the temperature dependence of the ratio  $\eta_I/\eta_L$  is  $\Delta E_I=0.12$  eV. The activation energy for a radiationless transition [Fig. 6(c)] is given by the thermal activation energy evaluated from the photoluminescence decay. In fact, in the temperature range where an exponential behavior of  $\eta_L$  has been observed (Fig. 2), i.e., between 130 and 200°K the factor  $\exp(-\Delta E_L/KT)$  with  $\Delta E_L=0.06$  eV assumes the following values:

$$\text{at } 130^\circ\text{K}, \approx 4.7 \times 10^{-3}; \quad \text{at } 200^\circ\text{K}, \approx 3.1 \times 10^{-2}.$$

On the other hand, for  $\exp(-\Delta E_I/KT)$ , with  $\Delta E_I=0.12$  eV, we found:

$$\text{at } 130^\circ\text{K}, \approx 0.022 \times 10^{-3}; \quad \text{at } 200^\circ\text{K}, \approx 0.81 \times 10^{-3}.$$

Since in this temperature range  $\exp(-\Delta E_L/KT) \gg \exp(-\Delta E_I/KT)$ , the ionization has little influence on the process and we conclude that 0.06 eV is effectively the activation energy of the  $F$  luminescence.

Our experimental results do not show what is the mechanism of the process of probability  $P_d$ . We can only suggest that its activation energy is 0.06 eV and that the electrons which undergo it finally return to the ground state of the  $F$  center.

## ACKNOWLEDGMENTS

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## Specific Heats of Copper, Silver, and Gold below 30°K

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The specific heats of pure copper, silver, and gold have been measured in the range 3 to 30°K. Gold has also been measured in the range 0.4 to 1.5°K. The  $\Theta_0^\circ$  and  $\gamma$  values are estimated as  $345.6 \pm 1.0^\circ\text{K}$  and  $166.3 \pm 1.3 \mu\text{cal } ^\circ\text{K}^{-2} (\text{g atom})^{-1}$  for copper,  $226.6 \pm 1.0^\circ\text{K}$  and  $154.4 \pm 1.0 \mu\text{cal } ^\circ\text{K}^{-2} (\text{g atom})^{-1}$  for silver, and  $162.4 \pm 2.0^\circ\text{K}$  and  $174.1 \pm 4.3 \mu\text{cal } ^\circ\text{K}^{-2} (\text{g atom})^{-1}$  for gold. The  $\Theta_0^\circ$  values are in good agreement with the most recent estimates for  $\Theta_0^{el}$ , the Debye temperature computed from the zero-temperature elastic constants. However, the lattice specific heat of gold is anomalous in that, on increasing the temperature from zero temperature, a maximum is first observed in the value of  $\Theta_0^\circ$ . The maximum is followed by the usual minimum on further increase of temperature. The results are discussed in terms of models due to Blackman and to Bhatia and Horton. The paper includes some remarks on thermometry below 30°K.

## INTRODUCTION

MEASUREMENTS on pure copper in the temperature range 3–30°K have been reported previously from this laboratory.<sup>1</sup> Since these measurements were made, the apparatus has been improved in a number of ways, resulting in increased precision at the lower temperatures. Very recently the original carbon secondary thermometers have been replaced by germanium thermometers. It was chiefly in order to check the performance of the altered apparatus that the present measurements on copper were made. However, they should also be of interest in relation to the proposal made at the 1964 Calorimetry Conference to consider the use of pure copper as a calorimetric standard substance in the temperature range below 20°K.

Measurements on gold were initially undertaken because of the significant discrepancy between the Debye temperature obtained from zero-temperature elastic constants ( $\Theta_0^{el}$ ) and the low-temperature limiting value obtained from specific-heat results ( $\Theta_0^\circ$ ). These measurements have been briefly reported<sup>2</sup> and it was shown that by making measurements at sufficiently low temperatures the discrepancy between the Debye temperatures was removed. However, the lattice specific heat of gold at higher temperatures was anomalous. As an independent check on these results, the measurements above 3°K have been repeated with the altered apparatus. The present results are in excellent agreement with the earlier results.<sup>2</sup>

The normal behavior of copper and the anomalous behavior of gold indicated that accurate measurements on silver, the intermediate metal in the periodic

<sup>1</sup> J. P. Franck, F. D. Manchester, and D. L. Martin, Proc. Roy. Soc. (London) **A263**, 494 (1961).

<sup>2</sup> D. L. Martin, Phys. Rev. Letters **12**, 723 (1964).