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Electron Distribution about an Edge Dislocation in a Metal

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The self-consistent electrostatic potential and charge density associated with a straight edge dislocation in a free-electron metal are calculated to the first order in perturbation theory, the positive-ion background being replaced by a continuum of positive charge which is assumed to deform according to the equations of isotropic elasticity. The potential obtained is identical with the deformation potential outside the core of the dislocation, but approaches zero on the dislocation line. In contrast to the deformation-potential approach, the screening by the conduction electrons of the positive charge shift is incomplete, with the result that the total charge density behaves as $r^{-5/2}\sin(2k_f r+\frac{1}{4}\pi)$ outside the core of the dislocation. The effects of the core region, which is not well described by the model, are briefly considered, and the effects of the periodic lattice are obtained in the nearly-free-electron approximation.

I. INTRODUCTION

THE relative freedom of the valence electrons to move through the crystal is the fundamental characteristic distinguishing metals from nonmetals; thus it is not surprising that properties typical of metals in general are quite well explained by the familiar "free-electron" model. If we examine such properties more closely, seeking the effect of the individual structure of the crystal of each metallic element while at the same time emphasizing the characteristic freedom of the valence electrons, we are led in a natural way to the so-called "nearly-free-electron" model. Results of such studies have indicated the effect of the periodic lattice structure to be surprisingly small; this has been discussed by Cohen,[1] following the work of Phillips and Kleinman,[2,3] who attributes the smallness of the lattice effect to the partial screening of the ion-core potentials by the conduction electrons.

Since certain broad properties of perfect metal crystals can be understood in term of the free-electron model, it seems desirable to apply a similar treatment to the study of those properties of defect crystals which do not depend critically on the individual lattice structure, and likewise to estimate the effect of this structure by use of the nearly-free-electron model. In this paper we apply these ideas to the calculation of the electrostatic potential and charge distribution about an isolated, straight, edge dislocation in a metal. In addition to the intrinsic interest of the problem, these quantities are of interest for the study of properties such as nuclear-magnetic-resonance line broadening, residual electrical resistance in cold-worked crystals, and the electrical interaction of dislocations with solute atoms and other dislocations; however, such applications will not be considered here.

II. DESCRIPTION OF THE METHOD

We start with the unperturbed metal consisting of a lattice of positive ions and conduction electrons, the latter being described either by free-electron or nearly-free-electron wave functions. On introducing the defect we then consider the positive ion background to undergo displacements given by the equations of isotropic elasticity, and then let the electrons move so that the resulting potential is self-consistent in the Hartree sense. In the interest of simplicity, and in the same spirit as similar calculations for the case of point defects,[4–6] the calculation is carried out to first order in perturbation theory; such a procedure may be expected to be satisfactory provided the perturbed wave functions and eigenvalues differ only slightly from the unperturbed ones—in particular this precludes the formation of bound states on the dislocation. Fortunately the potential and charge density derived from this treatment are of a magnitude consistent with the use of first-order theory. Section V deals with this point in more detail.

The procedure outlined above assumes that the positions taken by the ions in the defect crystal are not influenced by the conduction electrons. This idea has been used by several authors,[7,8] in calculating atomic displacements about defects in close-packed metals, where the effects of the Born-Mayer closed-shell repulsion between neighboring ions are shown to dominate both conduction-electron effects and those of electrostatic interactions between the ions. The approximation is presumably not so good for body-centered cubic metals, but even here we can suppose any further relaxation of the ions, due to the calculated conduction-electron redistribution, to be of secondary importance, since, as is shown in Sec. V, the extra strain due to the motion of the ions in the electrostatic field of the dislocation is considerably smaller than the initial elastic strain, at

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[1] M. H. Cohen, in *The Fermi Surface*, edited by W. A. Harrison and M. B. Webb (John Wiley & Sons, Inc., New York, 1960), p. 318.

[2] J. C. Phillips, and L. Kleinman, Phys. Rev. **116**, 287 (1959).

[3] L. Kleinman and J. C. Phillips, Phys. Rev. **118**, 1153 (1960).

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[5] A. Blandin, J. Phys. Radium **22**, 507 (1961).

[6] J. S. Langer and S. H. Vosko, J. Phys. Chem. Solids **12**, 196 (1960).

[7] H. B. Huntington, Phys. Rev. **91**, 1092 (1953).

[8] L. Tewordt, Phys. Rev. **109**, 61 (1958).

least outside a small core region surrounding the dislocation.

Since the method uses the elastic expressions for the lattice dilatation, it is obviously incapable of treating the core region properly. We return to this point in Sec. V.

III. FREE-ELECTRON TREATMENT

Describing the unperturbed crystal by the free-electron model, we apply the treatment outlined in Sec. II to the case of an isolated, straight edge dislocation of Burgers vector **b**. We denote the perturbed charge density and self-consistent potential by $\rho(\mathbf{r})$, $V(\mathbf{r})$, respectively, define the Fourier transform over the crystal of volume Ω by

$$\bar{f}(\mathbf{q})\equiv\Omega^{-1}\int_{\Omega} e^{-i\mathbf{q}\cdot\mathbf{r}}f(\mathbf{r})d\mathbf{r}, \tag{3.1}$$

and obtain by a procedure similar to that of Ziman,[9] (see Appendix A),

$$\bar{V}(\mathbf{q})=\bar{\rho}_{+}(\mathbf{q})[\epsilon_0 q^2 K(q)]^{-1}$$

and (3.2)

$$\bar{\rho}_{-}(\mathbf{q})=\bar{\rho}_{+}(\mathbf{q})[1-1/K(q)].$$

Rationalized mksa units are used throughout. The charge density transforms $\bar{\rho}_{+}$ and $\bar{\rho}_{-}$ refer to the contributions to the charge shift from the positive ion background and the conduction electrons, respectively, while $K(q)$, the static dielectric constant of the electron gas, is given in this self-consistent-field (SCF) approximation by

$$K(q)=1+\frac{k_f m e^2}{2\pi^2\hbar^2\epsilon_0 q^2}\left[1+\frac{4k_f^2-q^2}{4k_f q}\ln\frac{2k_f+q}{2k_f-q}\right], \tag{3.3}$$

k_f being the wave vector at the free-electron Fermi surface.

We take our crystal to be a cylinder of large length L and radius R, with the dislocation line as axis. The theory of isotropic elasticity[10] then gives

$$\rho_{+}(\mathbf{r})=en_0 B r^{-1}\sin\phi, \quad B=\frac{Zb}{2\pi}\left(\frac{1-2\nu}{1-\nu}\right), \tag{3.4}$$

for a crystal with Poisson's ratio ν and an unperturbed density of n_0 ions per unit volume, each of charge Ze.

We introduce the right-handed orthonormal vectors $(\mathbf{i},\mathbf{j},\mathbf{d})$, with $\mathbf{d}$ along the dislocation axis, $\mathbf{i}$ in the slip plane, and $\mathbf{j}$ directed into the compressed half of the crystal, and write

$$\mathbf{q}=\mathbf{i}\xi\cos\eta+\mathbf{j}\xi\sin\eta+\mathbf{d}\chi,$$

to obtain, on using (3.4) in (3.1),

$$\bar{\rho}_{+}(\mathbf{q})=-(4\pi e n_0 B i\Omega^{-1})\xi^{-1}\delta(\chi)\sin\eta, \tag{3.5}$$

which on substitution in (3.2) and carrying out the inverse Fourier transforms yields finally

$$V(\mathbf{r})=en_0 B\epsilon_0^{-1}\sin\phi\int_0^\infty J_1(r\xi)[\xi^2K(\xi)]^{-1}d\xi,$$

(3.6)

$$\rho_{-}(\mathbf{r})=-en_0 B\sin\phi\int_0^\infty J_1(r\xi)[1-1/K(\xi)]d\xi,$$

where J_1 is the Bessel function of the first kind and first order. With

$$V(\mathbf{r})=F_v(r)\sin\phi, \quad \rho_{-}(\mathbf{r})=F_\rho(r)\sin\phi, \tag{3.7}$$

we show the form of F_v and F_ρ in Figs. 1 and 2 using constants typical of copper.

Analysis of the integrals of Eqs. (3.6) shows that as $r\rightarrow 0$,

$$V(\mathbf{r})\rightarrow-(en_0B/2\epsilon_0)\sin\phi[r\ln r+O(r)],$$

$$\rho_{-}(\mathbf{r})\rightarrow(n_0Bk_f^3me^3/24\pi^2\hbar^2\epsilon_0) \tag{3.8}$$

$$\times\sin\phi[r^3\ln r+O(r^3)],$$

while, as $r\rightarrow\infty$ (see Appendix B),

$$V(\mathbf{r})\sim\frac{n_0B\pi^2\hbar^2}{k_f me}$$

$$\times\sin\phi\left[\frac{1}{r}+C\frac{\sin(2k_fr+\frac{1}{4}\pi)}{(2k_fr)^{5/2}}+o(r^{-5/2})\right], \tag{3.9}$$

and

$$\rho_{-}(\mathbf{r})\sim-en_0B$$

$$\times\sin\phi\left[\frac{1}{r}-D\frac{\sin(2k_fr+\frac{1}{4}\pi)}{(2k_fr)^{5/2}}+o(r^{-5/2})\right]. \tag{3.10}$$

Here,

$$C=\frac{k_fm^2e^4(2/\pi)^{1/2}}{\pi^3\epsilon_0{}^2\hbar^4}\left[4k_f+\frac{me^2}{2\pi^2\epsilon_0\hbar^2}\right]^{-2},$$

and

$$D=\frac{4\pi^2\epsilon_0\hbar^2k_f}{me^2}C.$$

Figures 1 and 2 show the leading terms in Eqs. (3.9) and (3.10) to be excellent approximations up to less than a lattice constant from the dislocation line.

The total charge density at large distances from the dislocation line is obtained by adding Eq. (3.4) to Eq. (3.10) and oscillates according to

$$\rho(\mathbf{r})\sim en_0BD\sin\phi\times(2k_fr)^{-5/2}\sin(2k_fr+\tfrac{1}{4}\pi). \tag{3.11}$$

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[9] J. M. Ziman, *Principles of the Theory of Solids* (Cambridge University Press, Cambridge, England, 1964), Chap. 5.

[10] A. H. Cottrell, *Dislocations and Plastic Flow in Crystals* (Oxford University Press, London, 1953), p. 40.

IV. NEARLY-FREE-ELECTRON TREATMENT

We carry through the same procedure as that used to obtain Eqs. (3.6) except that we use nearly-free-electron wave functions and obtain for the SCF potential,

$$V(\mathbf{r})=V_0(\mathbf{r})+V_F(\mathbf{r})+\sum_{\mathbf{n}}{}' U_{\mathbf{n}}(\mathbf{r}), \qquad (4.1)$$

where $V_0(\mathbf{r})$ is the unperturbed periodic lattice potential, $V_F(\mathbf{r})$ is the free-electron contribution given by the first of Eqs. (3.6), and

$$U_{\mathbf{n}}(\mathbf{r})=\sum_{\mathbf{q}} e^{i\mathbf{q}\cdot\mathbf{r}}C(\mathbf{q})C(\mathbf{n}+\mathbf{q})B_{\mathbf{n}}(\mathbf{q})\bar{\rho}_+(\mathbf{n}+\mathbf{q}). \qquad (4.2)$$

The sum in Eq. (4.1) is over all nonzero reciprocal lattice vectors $\mathbf{n}$; that in Eq. (4.2) is over all wave vectors $\mathbf{q}$. The functions $C(\mathbf{q})$ and $B_{\mathbf{n}}(\mathbf{q})$ are defined by

$$\begin{aligned}C(\mathbf{q})&=[\epsilon_0 q^2K(q)]^{-1},\\ B_{\mathbf{n}}(\mathbf{q})&=-(16m^2e^3/\hbar^4\Omega)\bar{V}_0(\mathbf{n})\textstyle\sum_{\mathbf{k}} \{(1-\delta_{\mathbf{q},0})[(|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2)(|\mathbf{k}+\mathbf{q}|^2-|\mathbf{k}+\mathbf{q}+\mathbf{n}|^2)]^{-1}\\ &\quad+(1-\delta_{\mathbf{q},0})[(|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}|^2)(|\mathbf{k}|^2-|\mathbf{k}-\mathbf{n}|^2)]^{-1}+(1-\delta_{\mathbf{q},-\mathbf{n}})[(|\mathbf{k}|^2-|\mathbf{k}+\mathbf{n}|^2)(|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}+\mathbf{n}|^2)]^{-1}\\ &\quad+(1-\delta_{\mathbf{q},-\mathbf{n}})[(|\mathbf{k}+\mathbf{q}+\mathbf{n}|^2-|\mathbf{k}+\mathbf{q}|^2)(|\mathbf{k}|^2-|\mathbf{k}+\mathbf{q}+\mathbf{n}|^2)]^{-1}\}.\end{aligned}$$

Lengthy calculations show that for *monovalent* metals we obtain from Eq. (4.1):

$$V(\mathbf{r})\simeq V_0(\mathbf{r})+V_F(\mathbf{r})+\left(\frac{n_0Bme^2}{\epsilon_0\hbar^2k_f}\right)\frac{\sin\phi}{r}\left\{\sum_{\mu\neq0}\frac{\nu^2}{\mu}\frac{\bar{V}_0(\mathbf{n})\cos\mathbf{n}\cdot\mathbf{r}}{(\mu^2+\nu^2/2)n^2K(n)}\ln\left(\frac{n^2-2\mu k_f}{n^2+2\mu k_f}\right)+O(r^{-1})\right\}, \qquad (4.3)$$

where $\mathbf{n}\equiv\nu\mathbf{a}+\mu\mathbf{d}$, the unit vectors $\mathbf{a}$ and $\mathbf{d}$ being, respectively, perpendicular to and parallel to the dislocation line.

V. DISCUSSION

Although drawn for the case of copper, the general shape of the graphs in Figs. 1 and 2 is the same for all metals. We see from these graphs that

$$|\rho_-(\mathbf{r})/en_0|<0.13, \quad |V(\mathbf{r})|<0.77\text{ V}. \qquad (5.1)$$

Both these results are consistent with the use of first-order perturbation theory. The first suggests that the average change in the magnitude of an electron's wave function is less than 1/20 of its unperturbed value. The second shows the perturbation potential to be rather less than the average lattice potential for copper which the results of Ziman[11] indicate is greater than 3.5 eV. Thus our use of first-order perturbation theory is justified to at least the same extent as our adoption of the nearly-free-electron model which treats the lattice potential as a first-order perturbation. We further note that the perturbation (5.1) is also considerably less than the free-electron Fermi energy of 7.1 eV for copper.

Using Eq. (3.9) we see that the electrostatic force on an ion due to the dislocation falls off as r^{-2} and hence causes additional strains which are negligible compared to the original elastic strains outside a core region whose size depends on the nature of the inter-ionic forces,[7,12] and is calculated to be about three lattice constants in copper and about ten in sodium. It is probably within core-regions of similar size that the elastic continuum picture becomes inadequate anyway, so we may again regard our results as being consistent with the model originally proposed.

The first term in Eq. (3.9) is identical with the deformation potential of Dexter,[13] but unlike the latter we do not require perfect screening of the positive charge shift, and in fact obtain a resultant charge density which

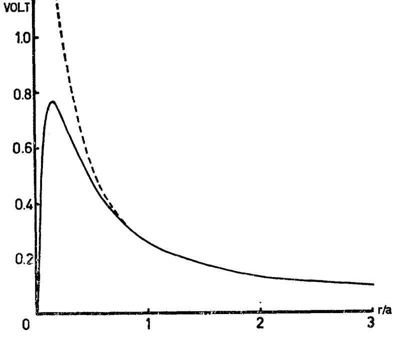

FIG. 1. —— Potential from Eq. (3.6); ----- asymptotic form.

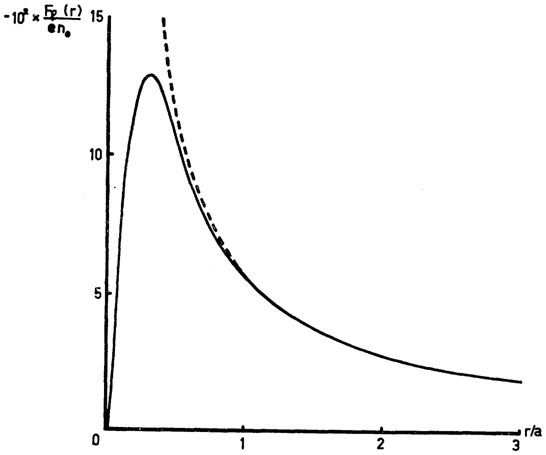

FIG. 2. —— Electronic charge density from Eq. (3.6); ---- asymptotic form.

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[13] D. L. Dexter, Phys. Rev. **86**, 770 (1952).

oscillates at large distances from the dislocation according to Eq. (3.11). Similar oscillations in charge density have been obtained by Flynn,[14] who considers the scattering of electrons from an axially symmetric singularity, and by several authors[4–6] for the case of a point singularity.

The second-order terms of Eqs. (3.9) and (3.10) are readily seen to arise from the singularity (infinite gradient) at $q=2k_f$ of the dielectric constant $K(q)$. This together with Flynn's result, indicates that these oscillations are characteristic of the structure of the electron gas and do not depend essentially on the nature of the perturbing influence, provided this be some sort of line defect. On the other hand the first-order terms are clearly a result of the extended nature of the positive charge shift.

These ideas assume some importance when we consider the core of the dislocation. Clearly the model cannot hope to describe the state within this core region, so we will be concerned only with the effect of the core on the region outside it. It is readily verified that the leading terms of Eqs. (3.9) and (3.10) are unchanged by the fact that the form (3.4) for the dilatation is valid only up to an inner radius which we denote by r_0; also the discussion of the previous paragraph indicates that any further perturbation on that already treated, being confined as it is to a cylinder of radius r_0, leads to effects of order $r^{-5/2}$ at large distances from the core. We may therefore suppose the dominant terms in the potential and electronic charge density of Eqs. (3.9) and (3.10) to be unchanged by any core effects, although the total charge density of Eq. (3.11) will be affected.

With regard to the nearly-free-electron corrections to the potential, we find from Eq. (4.3) that these are of order 1% of the free-electron potential, which is about ten times the correction found by Gousseland,[15] who considers the scattering of nearly free electrons by a localized point potential.

APPENDIX A

Apart from those assumptions necessary for the use of the SCF approximation at any time, Ziman[9] further assumes that each Fourier component of the perturbation can be treated independently. Defining the contribution $V_-(\mathbf{r})$ of the electron redistribution to the total (SCF) potential $V(\mathbf{r})$ by Poisson's equation, $\epsilon_0\nabla^2V_-(\mathbf{r})=-\rho_-(\mathbf{r})$, this latter assumption leads to

$$\epsilon_0 q^2\bar{V}_-(q)=\bar{\rho}_-(q)\,, \qquad \text{(A1)}$$

which is essentially Ziman's Eq. (5.8).

It is easy to show from the results of Sec. III that Eq. (A1) is not satisfied. Fortunately however one can obtain Eqs. (3.2) without making the above-mentioned assumption, but by replacing it with another which proves to be justified in the light of the final result. Specifically one integrates Poisson's equation connecting the charge density and potential to obtain, using Green's theorem,

$$\int_\Omega e^{-i\mathbf{q}\cdot\mathbf{r}}[q^2V(\mathbf{r})-\epsilon_0^{-1}\rho(\mathbf{r})]\,d\mathbf{r} = \int_S [e^{-i\mathbf{q}\cdot\mathbf{r}}\nabla V(\mathbf{r})-V(\mathbf{r})\nabla e^{-i\mathbf{q}\cdot\mathbf{r}}]\cdot d\mathbf{S}\,, \qquad \text{(A2)}$$

the integral on the right being over the surface S of the crystal.

In general, the function $V(\mathbf{r})$ will not satisfy everywhere the continuity and differentiability conditions required for Green's theorem, and one must assume that any such singularities do not alter Eq. (A2). Further we assume $V(\mathbf{r})$ approaches zero in such a way that the integral over the curved surface of our cylindrical crystal vanishes as the size of the crystal becomes infinite; periodic boundary conditions cause the integrals over the two ends to cancel and so we write

$$\epsilon_0 q^2\bar{V}(\mathbf{q})=\bar{\rho}(\mathbf{q})\,. \qquad \text{(A3)}$$

Equations (3.2) may be deduced from (A3) without using (A1), and on examining the resulting potential $V(\mathbf{r})$ it is found to be consistent with the assumptions of the previous paragraph and so with Eq. (A3), but the potential $V_-(\mathbf{r})$ is found to be inconsistent with (A1).

APPENDIX B

We briefly outline the derivation of the asymptotic expression (3.9) for $V(\mathbf{r})$. Introducing the lattice constant a, and changing to dimensionless variables, $\rho=ra^{-1}$, $u=\xi a$, the calculation of V from Eq. (3.6) reduces essentially to the calculation of

$$I(\rho)=\int_0^\infty G(u)J_1(\rho u)\,du; \qquad \text{(B1)}$$

where $G(u)=[u^2K(a^{-1}u)]^{-1}$. Integrating Eq. (B1) by parts, we have

$$I(\rho)=\rho^{-1}G(0)+\rho^{-1}\int_0^\infty J_0(\rho u)G'(u)\,du\,. \qquad \text{(B2)}$$

The first term of Eq. (B2) becomes the first term in Eq. (3.9). The integral in (B2) behaves asymptotically as the second term of (3.9); this is best seen by writing it as a double Fourier transform using the theorem[16]

$$\int_0^\infty uf(u)J_0(\rho u)\,du=(2\pi)^{-1}\times\iint_{-\infty}^{\infty} f[(x^2+y^2)^{1/2}]\exp[i(\xi x+\eta y)]\,dx\,dy\,,$$

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[15] G. Gousseland, J. Phys. Radium **23**, 928 (1962).

[16] I. N. Sneddon, *Fourier Transforms* (McGraw-Hill Book Company, Inc., New York, 1951).

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

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

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

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[17] M. J. Lighthill, *Introduction to Fourier Analysis and Generalised Functions* (Cambridge University Press, Cambridge, England, 1959).

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Properties of *F* Centers in NaF

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A weak intensity emission, centered at 785 mμ, 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 $\Delta E_1=0.12$ 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.[1,2]

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.[3]

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 ($\sim7\times7\times1$ mm^3) 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 mμ with an EMI photomultiplier type 9558 QA, and between 500 and 1100 mμ with a Philips 150 CVP with the photocathode cooled to liquid nitrogen temperature (LNT). In this way the dark current decreases from 6 μA to 2-3$\times10^{-9}$ 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[4]: 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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