Possible Macroscopic Effects of Single Lattice Defects

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(Received February 15, 1954)

A spiral dislocation with axis perpendicular to the lattice planes of a layer lattice converts the disconnected sheets to a connected helicoid. Crystal properties dependent on propagation effects and so strongly anisotropic in the layered crystal may approach isotropicity as intra-plane parameters can now dominate inter-plane propagation. A single defect may thereby have a macroscopic effect on semiconduction and photoduction, magnetic susceptibility, specific heat, and other properties. Substances in which such effects may exist are listed.

MOST effects of lattice defects are proportional to defect density, at least for small ratios of number of defects to number of lattice points. Color centers in alkali halides, structure-sensitive photoconductivity, and semiconductivity, provide such examples for vacancies, interstitials, and impurities, while work-hardening depends similarly on dislocation density. The screw or spiral dislocation, however, seems to be qualitatively different from these in that a single one might engender macroscopic change in a number of observable properties.

The role of dislocations in crystal growth has been discussed by Frank,[1] and supporting evidence for the theory put forth by Griffin,[2] Verma and Amelinckx,[3] Forty,[4] and Dawson and Vand.[5] The dislocations increase the rate of growth and produce growth contours visible in a microscope. The purpose of the present note is to call attention to the possibility of large effects on electric, magnetic, and other properties of fully grown layered crystals due to a single spiral dislocation. It seems probable that these dislocations are unique in this respect.

Consider, for purposes of illustration, a single crystal of graphite. Its pronounced anisotropicity is related to the large c/a ratio. The planar system of conjugated single and double bonds in lattice planes perpendicular to the c axis produces large electronic conductivity and diamagnetic susceptibility for electron flow parallel to these planes. Electron flow parallel to the c axis has a high activation energy and gives small susceptibility values. A screw dislocation whose axis lies parallel to the c axis converts the disconnected parallel sheets into a connected helicoid. A circuit about the dislocation, remaining on a sheet, then yields a translation parallel to the c axis from an initial to an adjacent lattice plane. Electron flow is then possible, within the system of conjugated bonds, without the necessity of surmounting the high interplanar activation energy.

TABLE I. Some layer lattices.

Type	Formula
CdI_2	Ag_2F, dibromides of Co, Fe, Mg, Mn, V, di-iodides of Ca, Cd, Co, Fe, Ge, Mg, Mn, Pb, Ti, V, Yb, dihydroxides of Ca, Cd, Co, Fe, Mg, Mn, Ni, disulfides of Pt, Sn, Ti, Zr, diselenides of Pt, Ti, Zr, ditellurides of Co, Ni, Pd, Pt, Ti, AlB_2, and Tl_2S (distorted CdI_2), $Co(OH)_{1.5}Br_{0.5}$, $Co(OH)_{1.5}Cl_{0.5}$, $Ni(OH)_{1.5}Cl_{0.5}$
$CdCl_2$	dibromides of Cd, Ni, dichlorides of Cd, Co, Fe, Mg, Mn, Ni, Zn, NiI_2, $Cd(OH)_{1.25}Cl_{0.75}$
BiI_3	$FeCl_3$, $CrBr_3$, AsI_3, SbI_3, BiI_3
MoS_2	MoS_2, WS_2
Other	$CrCl_3$, LiOH, $Al(OH)_3$, H_3BO_3, BN, graphitic compounds, $HgCl_2$, $HgBr_2$, yellow HgI_2, mica, and other minerals

The dc conductivity and static magnetic susceptibility are thus expected to lose their anisotropicity to a considerable extent, with parameters in the base plane being now approximately applicable in directions perpendicular thereto. At optical frequencies or higher, one would, of course, expect the effect of a single dislocation to be small again. At intermediate frequencies, the transition between the approximately isotropic dc regime and the anisotropic optical regime could well be accompanied by dispersion effects. A classical treatment of the electromagnetic properties of a conducting helicoid might be of value in indicating the kind of cutoffs, stop and pass bands, etc., to be expected.

The specific heat at low temperatures might also be affected by a spiral dislocation. The crystal is "clamped" in the neighborhood of the dislocation axis, but vibrations perpendicular to the lattice planes formerly constituting running waves confined to a plane now can spiral through the crystal. This might be expected to shift the vibration spectrum toward lower frequencies (as well as changing its shape), and thus to modify the reststrahlen also. Particle size effects on specific heat and elastic constants should be larger for crystals with a spiral dislocation.

It may be difficult to realize a spiral dislocation in graphite,[6] but there are many other layered crystals which occur naturally or which can be grown, for which

[1] F. C. Frank, Discussions Faraday Soc. **5**, 48 (1949).
[2] L. J. Griffin, Phil. Mag. **41**, 196 (1951).
[3] A. R. Verma and S. Amelinckx, Nature **167**, 939 (1951).
[4] A. J. Forty, Phil. Mag. **42**, 670 (1951), **43**, 481 (1952).
[5] I. M. Dawson and V. Vand, Nature **167**, 476 (1951).

[6] Spiral dislocations of the type contemplated have been observed in some graphite crystals by F. H. Horn, Nature **170**, 581 (1952).

such effects could be sought.[7] Some of these are listed in Table I. For those which are semiconductors, one arrives at conclusions similar to the conclusions of the previous discussion. With others, one would expect an anisotropic photoconductivity or extrinsic semiconductivity to tend toward isotropicity in the presence of a spiral dislocation. This "short-circuiting" of the anisotropicity might also be observed for diffusion, ionic conduction, and the like.

Note added in proof.—Many spiral dislocations have large Burgers' vectors, corresponding to axial displacement of many lattice distances. For such dislocations one has a set of interleaved helicoids rather than a single one (like a screw with a multiple thread) and similar considerations apply.

[7] CdI_2 seems like a particularly favorable case to investigate, as dislocations of the type contemplated have been much studied, e.g., A. J. Forty, reference 4, and Phil. Mag. **43**, 72 and 377 (1952). Spiral dislocations in beryl and CdI_2 are reported by B. J. Applebe and H. F. Kay, Phil. Mag. **44**, 105 (1953). For a general survey (with much information on SiC) and many references see A. R. Verma, *Crystal Growth and Dislocations* (Academic Press, Inc., New York, 1953).

PHYSICAL REVIEW VOLUME 95, NUMBER 2 JULY 15, 1954

Comparison of Various Approximate Exchange Potentials

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(Received April 9, 1954)

A modification of Slater's simplification of the Hartree-Fock equations is proposed, in which an averaged exchange potential is defined for each set of states having a common angular momentum. For a germanium atom we have calculated the approximate exchange potentials according to Slater's averaging procedures and according to our own, and have compared these with the usual Hartree-Fock exchange potentials.

SLATER[1] has recently shown how the Hartree-Fock equations can be approximated by a set of Schrödinger-type equations each containing the same "averaged" exchange potential. The Hartree-Fock equations as modified by Slater are more easily solved than are the original Hartree-Fock equations. It is natural to ask: is it possible to obtain approximate exchange potentials for the individual states better than the one represented by Slater's single averaged exchange potential and at the same time retain most of the simplicity and convenience of Slater's formulation?

That the exchange potentials of the states having a common angular momentum should bear a greater resemblance to each other than to the exchange potentials corresponding to states having other l was suggested to the authors by Herring.[2] Accordingly, we have defined an averaged exchange potential for each set of electronic states having a common l. Each of these averaged exchange potentials is formed from the Hartree-Fock exchange potentials belonging to the occupied states having a particular value of l.

With a view to comparing the various approximate exchange potentials, we calculated the Hartree-Fock, the Slater averaged, the s, p, and d averaged, and the free-electron exchange potentials for a germanium atom. Each of these potentials was computed from an orthonormalized set of radial wave functions $Q_{nl}(r)$ derived from the self-consistent wave functions $P_{nl}(r)$ obtained by Hartree and Hartree for the $(4s)^2(4p)^2$ state of the germanium atom.[3]

We made no attempt to determine self-consistent eigensolutions or potentials using any of the various exchange potential approximations.[4] Each of the potentials we did evaluate may be regarded as the starting potential in the first cycle of a self-consistent iteration procedure. Although a comparison of the potentials corresponding to self-consistent solutions would be more significant, we feel that some insight on the relative merits and special features of the various approximate exchange potentials may be gained by placing our potentials side by side.

The exact Hartree-Fock and the Slater averaged exchange potentials appearing in the wave equation for

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[1] J. C. Slater, Phys. Rev. **81**, 385 (1951).

[2] C. Herring (private communication); see also H. B. Huntington, Phys. Rev. **61**, 325 (1942).

[3] W. Hartree and D. R. Hartree, Phys. Rev. **59**, 306 (1941). We will express the orthonormalized wave function corresponding to state nlm in the form $\psi_{nlm}(\mathbf{r})=r^{-1}Q_{nl}(r)Y_l^m(\theta,\phi)$, where $\mathbf{r}=r,\theta,\phi$, and the $Y_l^m(\theta,\phi)$ are normalized spherical harmonics.

[4] A self-consistent solution for the Cu^+ ion has been obtained by Pratt using the free-electron approximation for the exchange potential; see G. W. Pratt, Jr., Phys. Rev. **88**, 1217 (1952).