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Infrared Absorption from L·S Splittings in Co^{2+} Salts

R. NEWMAN* AND R. M. CHRENKO
General Electric Research Laboratory, Schenectady, New York

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A line absorption spectrum has been observed at about 0.15 ev in CoO, $CoBr_2$, $CoCl_2$, and CoF_2 crystals. For the halides, the line has a complex structure. No absorption is observed in Cs_3CoCl_5 crystals. The absorption arises from transitions between various energy levels of the **L**·**S** fine structure multiplet. In CoF_2 some of the lines show changes in intensity on passing through the Néel temperature. Optical polarization effects are also observed in the CoF_2 spectrum.

INTRODUCTION

THE ground state of the free Co^{2+} ion is ^4F ($3d^7$). In a cubic crystal field, the sevenfold orbital degeneracy is lifted yielding an orbital triplet (Γ_4) as a ground state with another triplet (Γ_5) and singlet (Γ_2) lying at higher energies.[1] The degeneracy of the ground state will be further lifted by spin-orbit interaction.[2,3] The fine structure multiplet will consist of three levels. The over-all width of the multiplet will be 6λ, where λ is the spin-orbit coupling constant.[3] For a free Co^{2+}, λ is -180 cm^{-1}.[2] If, in a solid, λ is not appreciably changed, then one would expect the width of the fine structure multiplet to be ~ 1100 cm^{-1} or 0.135 ev. In a noncubic crystal field, further splittings will occur.[2] However, if the magnitude of the noncubic terms is small compared to the spin-orbit interaction, the over-all width of the multiplet will not change appreciably. In Fig. 1, the splitting of the ground state of the free ion by the different perturbations is shown schematically.

Optical transitions between different levels of a given configuration of a free ion (e.g., $3d^7$) are forbidden in electric dipole approximation for reasons of parity. This is also true for the ion in a crystal field which possesses a center of symmetry. However, the crystal field is the mechanism for coupling electron and phonon states. For such coupled states, the parity selection rules connecting the different electronic states are no longer rigorously obeyed. Exchange interaction between the ion and its neighbors is another effect through which the parity selection rule is invalidated. Both phonon and exchange effects may be important in any particular material.

In transition metal compounds, the failure of the parity selection rule is the general case. It is for this reason that line spectra in the near infrared, visible, and ultraviolet regions are usually observed in these materials.[4] Since selection rules probably would not be limiting, it was thought interesting to study various cobalt salts for evidence of transitions between different levels of the **L**·**S** fine structure multiplet. It was hoped that such studies would lead to a direct determination of the spin-orbit coupling constant, λ, in these solids. Estimation of the magnitude of noncubic effects might also be possible in cases where these would be expected. Thus it should be possible, in principle, to obtain information about a class of energy levels, determined in part by solid-state interactions, which are too widely separated to be seen directly by spin resonance techniques and too narrowly spaced to be readily seen by conventional spectroscopic methods (i.e., visible, ultraviolet). Accordingly, a study of the spectra of a number of anhydrous Co salts in the 0.25- to 0.08-ev (2000 to 650 cm^{-1}) range was undertaken.

Magnetic dipole transitions may occur between different levels of a configuration including those of the fine structure multiplet. For allowed transitions of this type, the transition probability will be $\sim 10^{-5}$ times that of an allowed electric dipole transition. It would seem that the electric dipole transition would have to be forbidden to a very high degree before it was overshadowed by the magnetic dipole process. However, to anticipate our results, the observed order of magnitude of the fine structure absorption (absorption coefficient $\sim 10^2$ cm^{-1}, line width $\sim 10^{-2}$ ev) is that which would be expected for a magnetic dipole transition. This complicates our understanding of some of the details of the spectra.

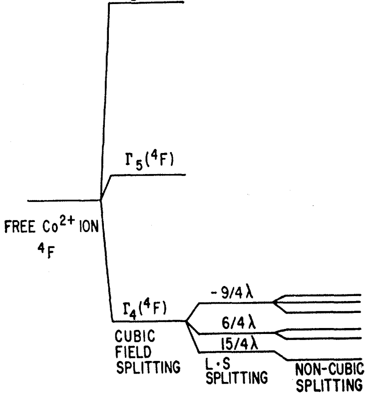

FIG. 1. Splitting of the degeneracy of a Co^{2+} ion ground state by various perturbations.

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* Present address: Materials Research Laboratory, Hughes Products, Newport Beach, California.

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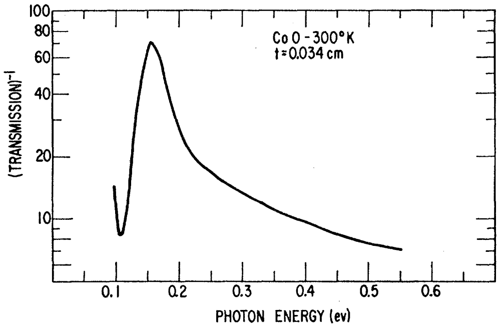

FIG. 2. Absorption spectrum of CoO.

EXPERIMENTAL

The following cobalt salts were studied: CoO, CoF_2, $CoCl_2$, $CoBr_2$, and Cs_3CoCl_5. Anhydrous salts with monatomic anions were selected for study to avoid the complication of absorption due to internal vibrations of the anions or of the waters of hydration. Single-crystal samples or polycrystalline samples containing a few large crystals were used for optical study. They were prepared in the following ways:

1. CoO—flame fusion[5] and halide decomposition.[6]
2. $CoBr_2$—growth from the melt or sublimation in in vacuum as (00.1) plates.
3. $CoCl_2$—growth from the melt or sublimation in vacuum as (00.1) plates.
4. CoF_2—growth from the melt under HF.[7]
5. Cs_3CoCl_5—growth from aqueous solution.[8]

The absorption spectra shown in the accompanying figures are plotted as reciprocal transmission. The sample thickness used is indicated in each figure.

RESULTS AND DISCUSSION

The general observation for all the cobalt salts studied, except Cs_3CoCl_5, was that there was an absorption band at about 0.15 ev possessing, in most cases, a complex structure. The existence of a band at approximately this energy in the Co^{2+} salts and its complete absence in the corresponding ismorphous Ni^{2+} and Mn^{2+} salts, which were studied under comparable experimental conditions, provides a positive identification of the band with a spin-orbit effect. With this main point established, it will be most convenient to discuss the details of each of the crystal spectra in turn.

1. CoO—Fig. 2 shows the portion of the absorption spectrum of interest. At room temperature there is a broad unsymmetrical line peaked at 0.156 ev (1250 cm^{-1}). At 77°K the line is substantially unchanged except that it is peaked at 0.165 ev. Above its Néel temperature (290°K)[9] CoO is a cubic crystal with the NaCl structure.[10] The fine structure multiplet in this case should consist of three levels with an over-all width of 6λ. Assuming that the peak of the absorption represents the energy of the transition from the ground state to the highest level of the multiplet, then $|\lambda_{300^\circ K}| = 0.026$ ev (210 cm^{-1}), $|\lambda_{77^\circ K}| = 0.027$ ev (220 cm^{-1}).

In CoO the antiferromagnetic interaction energy (which we take as $\sim kT_N = 0.025$ ev) is about 15% of the over-all width of the fine structure multiplet and about 50% of the separation between the ground state and the multiplet's first excited state. Further the optical phonon energy[11] is approximately equal to the latter separation (i.e., ~0.05 ev). Under these circumstances there is a question as to whether a simple atomic, or tight binding, approach to the fine structure multiplet is justified. The various perturbing effects (i.e., lattice vibrations, superexchange interaction) may be the cause of the considerable breadth of the line (~0.05 ev) and the asymmetry in its shape.

2. $CoBr_2$—This is a trigonal crystal, having the CdI_2 structure.[12] Each Co^{2+} is surrounded by six Br^- nearest neighbors in the form of a regular octahedron distorted along a trigonal axis. In other words, the crystal field at the Co^{2+} sites may be regarded as principally cubic with an admixture of higher order terms having trigonal symmetry. The fine structure spectrum is shown in Fig. 3. At room temperature it consists of a strong sharp line at 0.143 ev with a suggestion of a shoulder on the low-energy side. There is another much weaker sharp line at 0.0912 ev and a somewhat broader band peaked at about 0.105 ev. At 77°K the broad 0.105-ev line has disappeared completely whereas the other lines are unchanged except for some narrowing and slight decreases in their energy

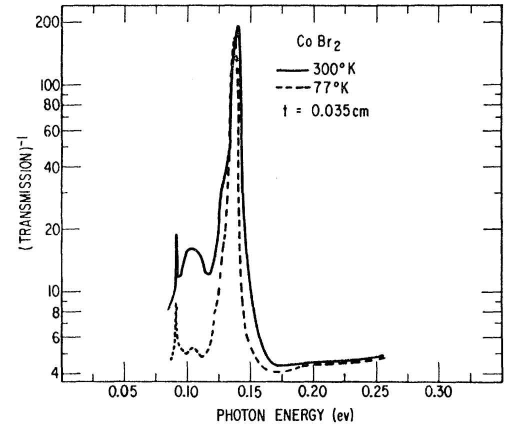

FIG. 3. Absorption spectrum of $CoBr_2$.

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[12] A. F. Wells, reference 10, p. 278.

with decreasing temperature. Studies at various temperatures in the range from 200°K to 500°K showed the intensity of the 0.105-ev band to be a continuously increasing function of increasing temperature, the other lines remaining unchanged except as previously noted. This difference in temperature dependence suggests that the 0.105-ev band arises from transitions involving a thermally excited initial state. The energy separation between the 0.105- and 0.143-ev bands is $\sim$0.04 ev. The temperature dependence of the absorption coefficient, α, of the 0.105-ev band can be empirically represented by the formula

$$\alpha \propto \frac{\exp(-0.04/kT)}{1+2\exp(-0.04/kT)},$$

in the 200°K to 500°K range. This is the statistical mechanical function representing the population of a thermally excited state 0.04 ev above the ground state, the excited state having twice the statistical weight of the ground state. For the case of a cubic crystal field, the first excited state (statistical weight=4) of the fine structure multiplet is $(9/4)\lambda$ above the ground state (statistical weight=2). If we take 0.143 ev as the over-all width of the multiplet and equate it to 6λ (cubic approx.), then $|\lambda_{\mathrm{CoBr_2}}|=0.0238$ ev (192 $\mathrm{cm^{-1}}$) and $(9/4)\lambda=0.054$ ev. The difference between the observed 0.04 ev and the calculated 0.054 ev seems larger than can be accounted for by experimental error and may reflect the inadequacy of the cubic approximation. Further, in this approximation there can be no explanation of the band at 0.0912 ev.

An attempt was made, using the method of Abragam and Pryce,[2] to fit the observed lines to a trigonal field splitting pattern using various combinations of the trigonal field parameters and various values of λ near that of the free ion. Rough calculations were made to find the conditions necessary for obtaining a set of levels $\sim$0.04, 0.09, and 0.14 ev above the ground state. This is a problem involving at least three parameters so that a unique solution is difficult to obtain. However, it would appear that some agreement with experiment could be had using a trigonal splitting energy,[2] $-\Delta$, in the range from 0.035 to 0.06 ev (300 to 500 $\mathrm{cm^{-1}}$).

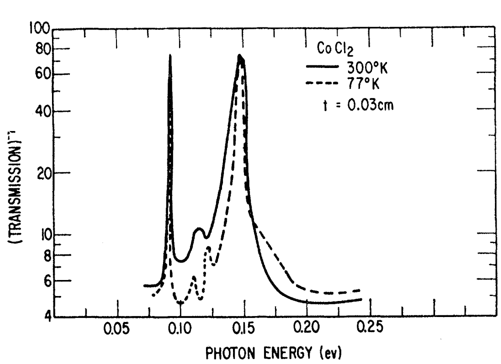

FIG. 4. Absorption spectrum of $CoCl_2$.

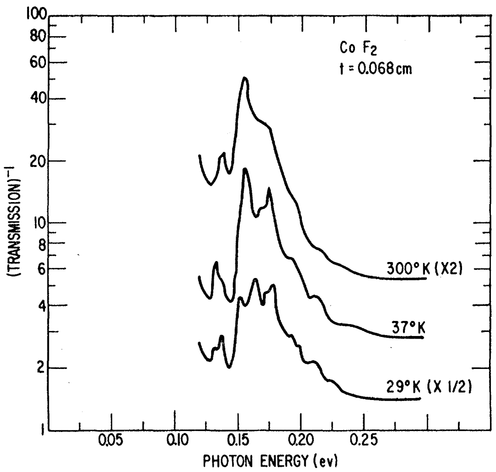

FIG. 5. Absorption spectrum of CoF_2. Different spectra are separated by the indicated factors for purposes of clarity.

3. $CoCl_2$—This is a trigonal crystal having the $CdCl_2$ structure.[12] Each Co ion has six nearest neighbor Cl ions arranged in a regular octahedron distorted along a trigonal axis ($r_{\mathrm{Co-Cl}}=2.42$ A). Figure 4 shows the fine structure spectrum. It is much like the spectrum of $CoBr_2$. The principle differences are the following: (a) The main absorption line occurs at 0.148 ev. (b) The line at 0.0912 is much stronger than that in the $CoBr_2$. (c) Additional lines at 0.112 and 0.122 ev become apparent at low temperatures. With respect to the strongest lines in the spectrum, an analysis of the $CoCl_2$ data could be made in a manner similar to that for the $CoBr_2$. However, the existence of the additional lines (item c) suggests that a more complex situation is being encountered. It does not appear possible to understand fully this spectrum on the basis of the Abragam and Pryce theory (see remarks on CoF_2 spectrum).

The observed width of the 0.0912-ev line at 20°K is $\sim 5\times10^{-4}$ ev. It would be a favorable case to test for a Zeeman effect, which, if observed, might clarify the interpretation of the spectrum.

4. Cs_3CoCl_5—This material was chosen for study to provide a comparison with the $CoCl_2$ spectrum. The crystal structure is complex but the pertinent factor is that each Co ion is surrounded tetrahedrally by four Cl ions in nearest neighbor positions ($r_{\mathrm{Co-Cl}}=2.34$ A).[8] For single crystals of this material we could observe no fine structure absorption. The experimental conditions were such that if the absorption cross section of the cobalt ion was as little as $\frac{1}{10}$ of that in the $CoCl_2$, an absorption could have been observed.

In a tetrahedral crystal field, the ordering of states should be inverted from that in the cubic (see Orgel, reference 4). That is, the lowest Co^{2+} state will be orbitally singlet with the two triplet states lying above it. Under these circumstances, there can be no splitting of the ground state by **L·S** coupling and hence no fine

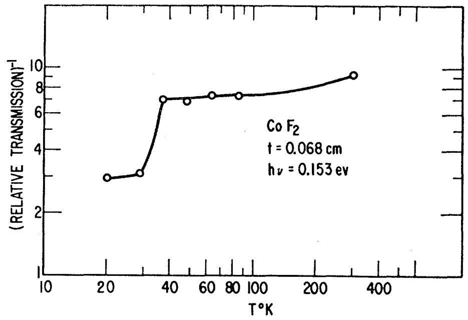

FIG. 6. Temperature dependence of the absorption intensity of the 0.153-ev line of CoF$_2$.

structure absorption would be expected in this salt. The comparison of the Cs$_3$CoCl$_5$ and CoCl$_2$ spectra seems a rather striking confirmation of this theoretical prediction.

5. CoF$_2$—This crystal is tetragonal and has the rutile structure.[13] Each Co ion is surrounded by 6 fluorine ions in octahedral positions. However, the point symmetry of the Co^{2+} sites is less than tetragonal.[14] This substance shows an antiferromagnetic transition at ~38°K.[9] Figure 5 shows the fine structure spectrum at several temperatures above and below the Néel temperature. The salient features of the spectrum are the following:

a. The main absorption occurs in the 0.15- to 0.20-ev range. That is somewhat higher than that for the other halides but roughly the same as that for the cobalt oxide.

b. The spectrum is a superposition of a number of lines which become better resolved from one another at lower temperatures.

c. On lowering the temperature through the Néel point, several of the lines show rather marked alterations of intensity, some lines increasing and others decreasing in intensity. Most prominent of those which show decreases is the line at 0.153 ev. Its behavior as a function of temperature is illustrated in Fig. 6. Another example is the doublet at ~0.13 ev where the two components appear to exchange intensity, one increases and the other decreases on passing through the Néel temperature.

d. The antiferromagnetic transition appears to produce very slight changes, of order 2×10^{-3} ev, in the energies of some of the absorption maxima. Since the width of the lines is also of this order the effect is on the borderline of detectability but it appeared reproducible.

e. The absorption lines are dichroic. In Fig. 7 are shown some polarized spectra at different temperatures. The lines at 0.153 ev and 0.135 ev show the largest effects. They show a perpendicular polarization behavior. For some of the other lines (e.g., 0.173 ev) the effects are smaller.

One is immediately faced with the impossibility of fitting the observed lines of the CoF$_2$ spectrum to a tetragonal field splitting pattern. For example, in the spectra taken at 37°K or higher there are at least 7 resolved or partially resolved lines in evidence. The theoretical prediction is that there should only be three lines in this spectral region for reasonable values of the noncubic splitting parameters and a maximum of five for any values of these parameters or any condition of symmetry. If one restricts one's attention to the three strongest lines at 0.173, ~0.165, and 0.153 ev, a rough fit to the Abragram and Pryce theory for the approximation of tetragonal symmetry may be made. This indicates a Δ of from +0.05 to 0.07 ev (400 to 550 cm^{-1}) depending on the value of λ chosen (210 to 180 cm^{-1}). However, the question still remains as to the origin of the remaining component lines, in particular that of the well defined doublet at about 0.13 ev. It seems clear that again the simple tight binding approach can not account for all the details of the spectrum and that other effects are involved (e.g., phonons).

The changes in the CoF$_2$ spectrum as it passes through the antiferromagnetic transition region are of two types, slight shifts in the energy of the peaks and

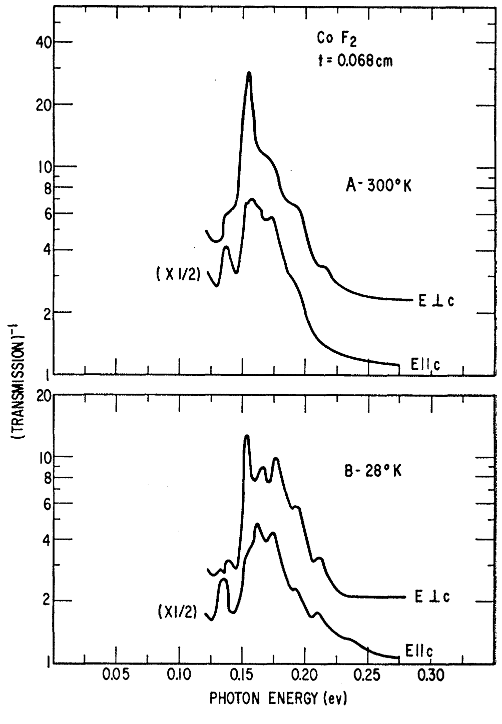

FIG. 7. Polarized spectrum of CoF$_2$. Different spectra are separated by the indicated factors for purposes of clarity. Spectra were taken with a crystal plate (*hk*0) containing the crystal *c* axis. The direction of polarization is referred to the direction of the electric vector of the radiation.

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[13] A. F. Wells, reference 10, p. 271.

[14] P. P. Ewald and C. Hermann, *Strukturbericht* (Becker and Erler, Leipzig, 1913–1926); Edward Brothers reprint, Ann Arbor, 1943), p. 156.

rather marked changes in their intensity. Small changes in energy are more readily understood. For example, one would expect that the spin doublet ground state could split in the antiferromagnetic state into two components separated by an energy of order $kT_N = 3\times10^{-3}$ ev. Higher energy states of the fine structure multiplet would split by energies of the same order of magnitude. Thus, changes in the positions of the absorption lines of order 3×10^{-3} ev might be expected and are observed.

The understanding of both the intensity and polarization effects is intimately connected with the precise mechanism of absorption, that is whether an electric or magnetic dipole transition is involved. We will assume first, that the transitions are electric dipole. For this case the fine structure transitions obtain intensity through either phonon or exchange interaction effects. It would seem unreasonable to assume that any phonon effects were appreciably changed on passing through the Néel point. Rather it is suggested that the rather abrupt changes in line intensity in the vicinity of T_N arise from the fact that the lines derive an important fraction of their intensity from exchange interactions. The latter are the cause of the magnetic ordering, and so some modification in the effects they produce on the spectrum would not be surprising.

For the electric dipole case, polarization effects will arise from transitions to levels which have spatial asymmetry associated with them. For example, in a fictitious system, one could suppose a totally symmetric ground state and excited states described by wave functions x, y, and z. In a tetragonal crystal field the spatial degeneracy would be partially lifted and the z level would be distinct. Only radiation with the E vector parallel to z could excite a transition to the z state. In the present case, the spin-orbit coupling mixes the basic orbital states so that to describe a definite direction to be associated with a given level would involve considerable calculational effort. Since to obtain any intensity of absorption, a higher approximation for the electronic states must be introduced, the utility of a simplified approach is questionable.

Magnetic dipole transitions between various levels of the fine structure multiplet are allowed. As was pointed out in the introduction, the order of magnitude of the observed absorption is consistent with a magnetic dipole mechanism.[15] The spin-orbit coupling provides a mechanism of interaction between the magnetic moment of the ion and the crystal field. Since the latter contains an exchange component, the possibility of effects related to antiferromagnetic ordering again arises.

Polarization phenomena could come from situations where the magnetic moment in different states was associated with specified spatial directions. As another fictitious example, if the crystal field had a 3- or 4-fold symmetry axis, then the magnetic moment would be quantized with respect to this axis and optical absorption would only result when the H radiation field was perpendicular to the unique direction. The situation in CoF_2 is certainly not this simple.

TABLE I.

Crystal	Photon energy (ev)	Dq (cm^{-1})
$CoBr_2$	0.74	700
$CoCl_2$	0.84	800
CoF_2	0.92	900
CoO	0.98	950

It was pointed out by E. O. Kane that a distinction between a magnetic dipole and an electric dipole process could be made using the optical polarization effect. Consider a crystal section with faces parallel to ($hk0$) and radiation at perpendicular incidence. Then the principal polarization conditions will be (a) $E\|c$ and $H\perp c$, or (b) $H\|c$, $E\perp c$. A spectrum is obtained and absorption is found for either case (a) or case (b). Now suppose that the spectrum of a (001) crystal plate is obtained. This is the condition $E\perp c$ and $H\perp c$.

If the spectrum of the (001) plate is identical with case (a), the magnetic dipole mechanism is operative; if it is identical with case (b), it would be an electric dipole process. Some preliminary measurements on the 0.153-ev line indicated that an electric dipole mechanism is important for this line. However, the measurements should be repeated with better samples than were available in this study.

An interpretation of the various aspects of the CoF_2 spectrum appears to involve considerable theoretical complexity. It is hoped that the experimental results presented here will have an heuristic value for further investigations.

6. A cursory study was made, in the various Co salts, of the absorption line in the near infrared which corresponds to the $\Gamma_4 \rightarrow \Gamma_5$ transition. The object was to see if any evidence for noncubic splittings could be found. The measurements at 300°K and 77°K showed only single structureless lines having line widths at the lower temperature of about 0.1 to 0.15 ev for the halides and 0.2 ev for CoO. The energies of the lines are given in Table I. The only conclusion that can be drawn is that the noncubic splittings in the Γ_5 state of the halides are probably less than 0.05 ev (400 cm^{-1}). By using Orgel's diagrams,[4] rough values for the cubic-field splitting parameters, Dq, can be obtained. These are also listed in the table.

SUMMARY

An absorption at ~0.15 ev has been observed in a number of Co^{2+} salts wherein the crystal field at the

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[15] The peak absorption coefficient for a magnetic dipole transition would be $\alpha \sim 8\pi^2 N\mu^2(\hbar\omega)n/\hbar c\Delta E$, where μ is the Bohr magneton, n the refractive index, N the density of absorbing centers, and ΔE the line width in energy units. For $\hbar\omega = 0.15$ ev and $\Delta E = 10^{-2}$ ev, $\alpha \sim 3\times10^2$ cm^{-1}.

Co^{2+} sites has, to first approximation, cubic symmetry. It was not observed in a salt where the crystal field had tetrahedral symmetry. The absorption is interpreted as resulting from transitions between energy levels of the $\mathbf{L}\cdot\mathbf{S}$ fine structure multiplet. These levels do not appear to be completely explicable in terms of a proposed crystal field theory.[2] The introduction of various solid state interaction mechanisms such as phonons or exchange may be required for quantitative understanding of both the basic absorption process, and of the finer details that are observed such as optical polarization and antiferromagnetic effects.

It should be pointed out that the fine structure absorption in Co salts offers the possibility of application in an infrared quantum detector of the type described by Bloembergen.[16]

ACKNOWLEDGMENTS

We are indebted to P. P. Friguletto who prepared many of the crystals used in this work. We should also like to express our thanks to E. O. Kane for both his general interest in this work and for his help in performing some of the calculations cited in the paper.

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Variational Approach to Deviations from Ohm's Law*

I. Adawi
RCA Laboratories, Princeton, New Jersey

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In a perturbation framework, Kohler's variational method has been extended to obtain deviations from Ohm's law for a nondegenerate electron gas. Solution for the distribution function reduces to solving sets of linear algebraic equations. It is shown that, to second order in the field strength, the "popular" Maxwellian distribution (with a new temperature) is only a first-order variational solution. The method becomes extremely simple if the diffusion approximation is introduced and a relaxation time can be defined. Under these conditions, the second-order term in the mobility is expressed as the ratio of two infinite determinants using the usual representation, in which the unknown function is expressed as an energy polynomial. This ratio can be expressed by an infinite series.

1. INTRODUCTION

FOR the past decade, Kohler's variational method[1-3] has been very useful in treating otherwise formidable problems in the theory of *linear* conductivity in solids. There is at the present considerable theoretical and experimental interest in the *nonlinear* part of the conductivity in semiconductors and insulators. One is usually interested in two regions of field strength. The first is the weak-field region in which the system does not deviate substantially from thermal equilibrium. The second is the high-field region in which the system departs considerably from its thermal behavior. It is with the weak-field region that this paper is concerned.[4]

We shall limit this treatment to a nondegenerate electron gas obeying classical statistics. For small departures from equilibrium, perturbation theory is valid and the distribution function is expanded in powers of the field. The Boltzmann equation is reduced to a set of linear equations in which the collision operator is symmetric and positive definite. Consequently, Kohler's variational method can be applied to solving these equations and thus obtaining deviations from Ohm's law. Although this method does not reduce the number of equations one has to solve to obtain corrections to Ohm's law, to a certain order in the field, yet for a given set of trial functions this method offers the best solution.

To obtain approximate solutions, the variational method offers a powerful practical tool. Its application leads to solving sets of linear algebraic equations whose number is not large in practice. This is a more general method than a numerical solution for the distribution function which is quite tedious. Needless to say, exact solutions are out of the question except in a limited number of cases.

In Sec. 3, two important applications of this variational method are discussed. The first application concerns the Maxwellian distribution (with a new temperature) which has become popular in discussing hot electron problems. To second order in the field, we shall show that under borad general conditions, a

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* This part covers the theoretical aspects of a paper presented at the 1959 Cambridge meeting of the American Physical Society. Part II of this work will deal with deviations from Ohm's law in nonpolar crystals. See I. Adawi, Bull. Am. Phys. Soc. **4**, 129 (1959).

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[2] E. H. Sondheimer, Proc. Roy. Soc. (London) **A203**, 75 (1950).

[3] See A. H. Wilson, *The Theory of Metals* (Cambridge University Press, Cambridge, 1954), Chap. X, second edition. Other references will be found there.

[4] Preliminary calculations for germanium at room temperature, for example, indicate that the theory is valid for fields below, say, 10^3 volts/cm.