Infrared Properties of CaF_2, SrF_2, and BaF_2

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Reflectivity and transmission measurements on CaF_2, SrF_2, and BaF_2 have been studied to obtain information on the lattice vibrations. The reflection band in each material has been analyzed with classical dispersion theory. In order to fit the data, it was necessary to use one strong and one weak resonance in each case. The strong resonance is identified as the transverse optical mode of vibration for zero wave vector and is at 38.9, 46.1, and 54.3 μ for CaF_2, SrF_2, and BaF_2, respectively. The long-wavelength value for the dielectric constant obtained from the optical measurements indicated a disagreement with the published value for SrF_2 obtained from capacity measurements. Capacity measurements were made and showed the previously accepted value for SrF_2 to be in error. The transverse optical-mode frequencies are shown to agree very well with the spacing of some of the satellite lines in the emission spectrum of Sm^{++} in these fluorides.

INTRODUCTION

THE fluorides CaF_2, SrF_2, and BaF_2 belong to the space group O_h^5 and are expected to have one infrared active transverse optical mode (*TO*) of vibration. At the present time the fundamental reststrahl frequency, *TO* at zero wave vector, has not been extablished with reasonable certainty. Although a number of measurements have been made in the infrared,[1–6] particularly on CaF_2, the data for the fundamental frequency are not consistent. The most recent measurements are those of Parodi[5] and of Heilmann.[6] Parodi measured the far infrared transmission of CaF_2, SrF_2, and BaF_2 powders and observed two absorption bands in each material. The bands in CaF_2 are at 31 and 51.5 μ, in SrF_2 at 40.6 and 69 μ, and in BaF_2 at 43 and 73 μ. The longer wavelength absorption band in each case was interpreted as the *TO* resonance and that at the shorter wavelength as a harmonic or combination band. Heilmann presents reflection data between 17 and 38 μ for CaF_2 measured with unpolarized radiation at normal incidence and with polarized radiation at an angle of incidence of 70°. From an analysis of these data and some transmission measurements on an evaporated film, he concluded that CaF_2 has a relatively weak resonance near 30 μ in agreement with Parodi and that the wavelength of the *TO* resonance is between 38 and 40 μ with a probable value of 38.4 μ. In a recent paper[7] some measurements of Yoshinaga, Mitsuishi, and Yamada were quoted as placing the CaF_2 fundamental resonance at ≈ 37 μ.

The fluorides CaF_2, SrF_2, and BaF_2 are receiving considerable attention since they are nearly ideal host lattices for paramagnetic ions. The ionic radii[8] of Ca^{++}(1.0 Å) and Sr^{++}(1.13 Å) are close to those of the ions of the rare-earth group and certain elements of the actinide group (e.g., U^{3+}). Alkaline earth fluorides doped with up to 1% of foreign ions can easily be prepared for optical and paramagnetic investigations.[9] The fluorescence of some of these ions shows clear evidence

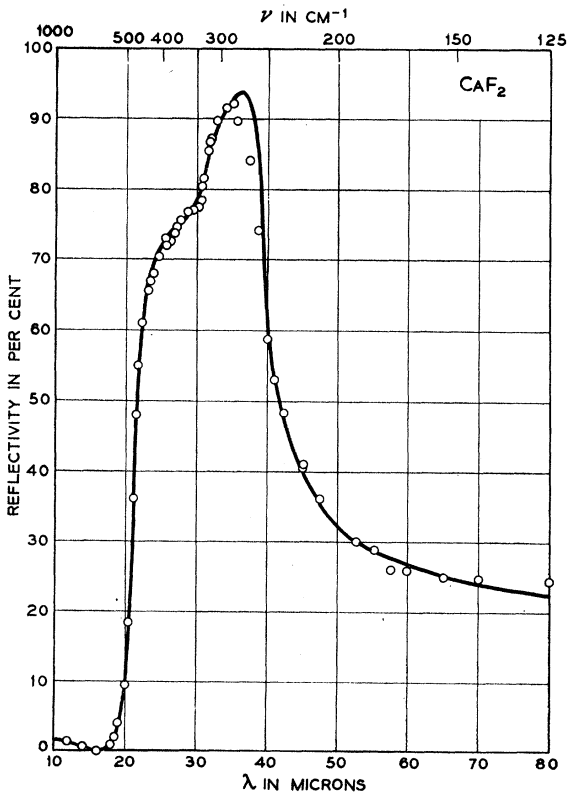

FIG. 1. Room temperature reflectivity of CaF_2. The data are indicated by the points. The curve is calculated from dispersion theory by using the parameters given in Table I.

[1] H. Rubens and G. Hertz, Akad. Wiss. Ber. Sitzenber. **14**, 268 (1912).
[2] L. Kellner, Z. Physik **56**, 215 (1929).
[3] O. Reinkober and M. Bluth, Ann. Physik **6**, 785 (1930).
[4] F. Matossi and H. Brix, Z. Physik **29**, 303 (1934).
[5] M. Parodi, Compt. rend. **206**, 1717 (1938).
[6] G. Heilmann, Z. Naturforsch. **16a**, 714 (1961).
[7] T. Shimanouchi, M. Tsuboi, and T. Miyazawa, J. Chem. Phys. **35**, 1597 (1961); also see A. Mitsuishi, Y. Yamada, and H. Yoshinaga, J. Opt. Soc. Am. **52**, 14 (1962).
[8] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, New York, 1960), 3rd ed., p. 514.
[9] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949); B. Bleaney, P. M. Llewellyn, and D. A. Jones, Proc. Phys. Soc. (London) **B69**, 858 (1956); and W. Low, *Advances in Quantum Electronics*, edited by J. P. Singer (Columbia University Press, New York, 1961), p. 138.

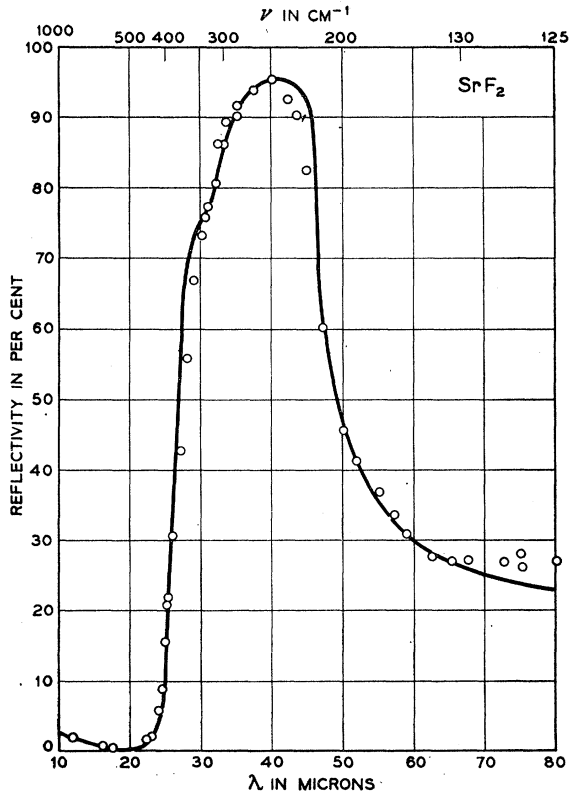

FIG. 2. Room temperature reflectivity of SrF_2. The data are indicated by the points. The curve is calculated from dispersion theory by using the parameters given in Table I.

of interactions between electronic transitions and lattice vibrations of the host crystal.[10] In the emission spectrum of Sm^{++}, for example, sharp emission lines ($4f \rightarrow 4f$ transitions) are followed by a distinct group of satellite lines which are the result of the interaction with lattice vibrations. It is, therefore, of importance to obtain information concerning the vibrational spectrum of the pure alkaline earth fluorides.

The transmission as a function of frequency and temperature has been measured on CaF_2, SrF_2, and BaF_2 single crystals on the high-frequency side of the reflectivity band. The reflectivity has been measured from 10 μ through the dispersion range to 80 μ. Applying classical dispersion analysis to the reflectivity data, the frequency and resonance strength of the *TO* mode are obtained and from a combination band the frequency of a phonon, assumed to be acoustical, could be estimated. The frequency of the *TO* phonon agrees very well with the observed separation of one of the satellite lines for Sm^{++} in each of the fluorides. From the transmission measurements and the dispersion analysis of the reflectivity, the optical constants are obtained between 10 and 80 μ (1000 and 125 cm^{-1} where frequency is given in units of cm^{-1}).

[10] D. L. Wood and W. Kaiser, Phys. Rev. **126**, 2079 (1962).

EXPERIMENTAL

Room temperature reflectivity measurements at near normal incidence have been made for each of the three fluorides. The equipment and experimental technique used in these measurements have been previously described in considerable detail.[11] Since the fluorides have cubic symmetry, the spectrometer beam was not polarized. One large area surface of each sample was polished by using standard metallographic polishing methods. The back surface was roughened so as to eliminate the contribution of multiple internal reflections to the reflectivity. The measured reflectivity of CaF_2, SrF_2, and BaF_2 is shown by the points in Figs. 1, 2, and 3, respectively.

At frequencies above the reflection band, the crystals are sufficiently transparent to allow direct transmission measurements. These measurements were made on a set of single crystals between ≈ 5 and 0.1 mm in thickness. Data were taken at 300, 77, 65, and in some cases 5°K. Similar to a number of other ionic crystals,[12] it was observed that below 77°K the transmission changed only very slightly with temperature. The absorption

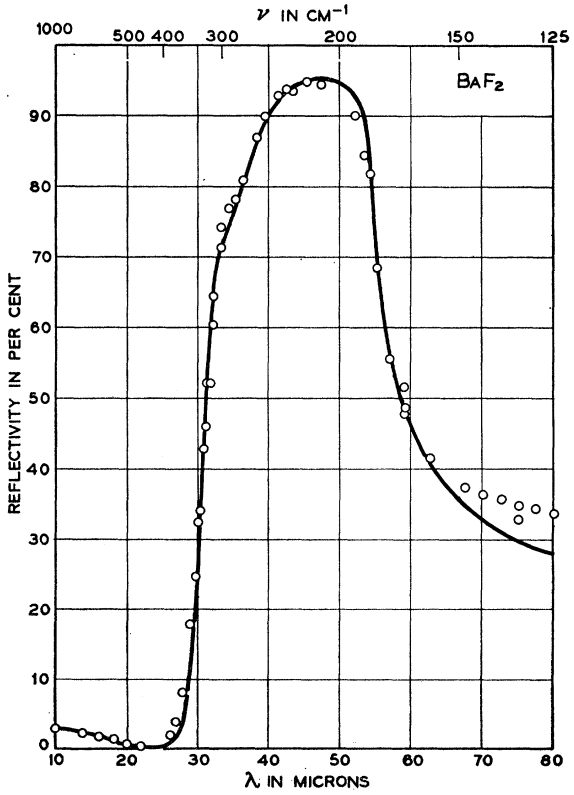

FIG. 3. Room temperature reflectivity of BaF_2. The data are indicated by the points. The curve is calculated from dispersion theory by using the parameters given in Table I.

[11] W. Spitzer, R. Miller, D. Kleinman, and L. Howarth, Phys. Rev. **126**, 1710 (1962).

[12] G. O. Jones, D. H. Martin, P. A. Mawer, and C. H. Perry, Proc. Roy. Soc. (London) **261**, 10 (1961).

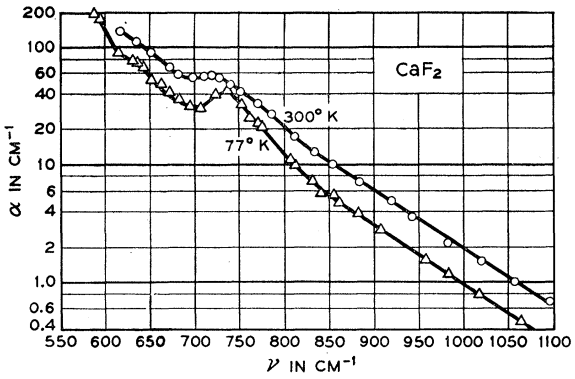

FIG. 4. Absorption coefficient of CaF_2 at 300 and 77°K.

coefficient α (cm^{-1}) was calculated from the transmission according to the equation

$$T=(1-R)^2e^{-\alpha x}/(1-R^2e^{-2\alpha x}),$$

where R is the reflectivity and x the sample thickness in cm. The room temperature and 77°K values of α for the fluorides are shown by the points in Figs. 4–6.

According to the literature, the value of the static dielectric constant ϵ_0 of SrF_2 [13] is larger than that for either CaF_2 or BaF_2.[14] From the results of the dispersion analysis of the reflectivity it was apparent that the large ϵ_0 for SrF_2 was not compatible with the present data. Therefore, the ϵ_0 for the three crystals was remeasured (at 10^3 and 10^6 cps) by using a conventional capacity bridge. The values of ϵ_0 measured on thin ($\approx$1 mm) single crystal plates are listed as ϵ_0(exp) in Table I. The measurements are estimated to have an accuracy of 5%. The value ϵ_0(exp)=6.6 for SrF_2 deviates substantially from the published value of 7.69. The ϵ_0(exp) values given here for CaF_2 and BaF_2 are in good agreement with previously published values given in Table I as ϵ_0 (literature).

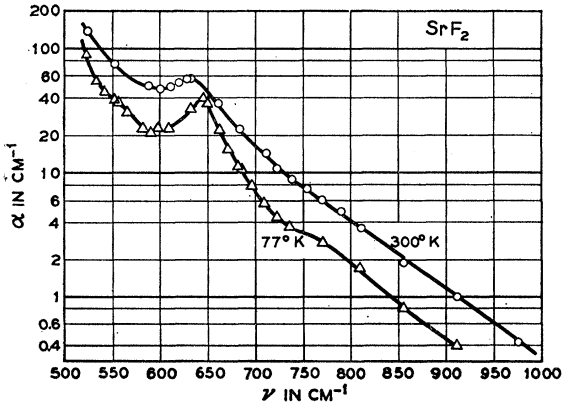

FIG. 5. Absorption coefficient of SrF_2 at 300 and 77°K.

[13] K. Hojendahl, Kgl. Danske Videnskab. Selskab, Mat.-fys. Medd. **16**, 2 (1938).

[14] *American Institute of Physics Handbook* (McGraw-Hill Book Company, Inc., New York, 1957), Vol. 5, p. 115.

DISCUSSION

In recent years it has been demonstrated for several materials that reflectivity data such as those of Figs. 1–3 can be accurately represented by classical dispersion theory.[15–18] Since the theory and technique of curve fitting have been discussed extensively in recent literature, no discussion of the method will be presented here. According to the theory, the real and imaginary parts of the complex dielectric constant, ϵ' and ϵ'', are given by

$$\epsilon'=n^2-k^2=\epsilon_\infty+\sum_j 4\pi\rho_j\nu_j^2\frac{\nu_j^2-\nu^2}{(\nu_j^2-\nu)^2+\gamma_j^2\nu^2\nu_j^2}$$

and

$$\epsilon''=2nk=\sum_j 4\pi\rho_j\nu_j^2\frac{\gamma_j\nu\nu_j}{(\nu_j^2-\nu^2)^2+\gamma_j^2\nu^2\nu_j^2},$$

where n is the refractive index, k the extinction coefficient, ϵ_∞ the high-frequency limiting value of the dielectric constant, $4\pi\rho_j$ the strength of the jth resonance, γ_j the width or damping constant for the jth resonance, and ν_j the resonance frequency. It was found that the reflectivity data could be quantitatively fitted throughout most of the measured spectral range with one strong and one weak resonance for each case. The curves of best fit obtained to date are given in Figs. 1–3, and the parameters used to obtain these curves are listed in Table I. The values of α listed in the table are the peak values of the absorption band. In all three cases a relatively poor fit is seen in a narrow spectral region on the long-wavelength side of the reflectivity peak. This discrepancy is not surprising since the sample surfaces

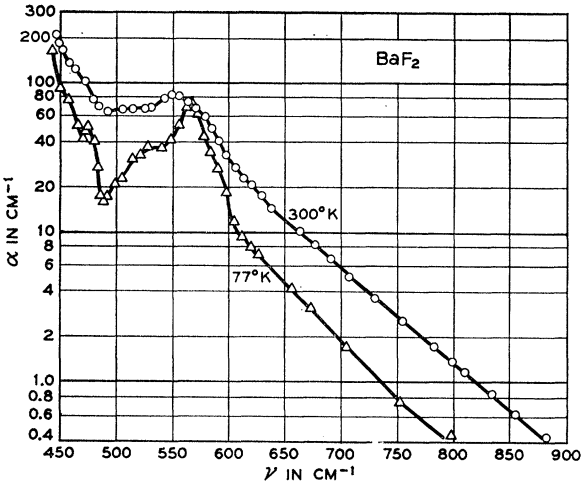

FIG. 6. Absorption coefficient of BaF_2 at 300 and 77°K.

[15] W. Spitzer, D. Kleinman, and D. Walsh, Phys. Rev. **113**, 127 (1959).

[16] W. Spitzer, D. Kleinman, and C. Frosch, Phys. Rev. **113**, 133 (1959).

[17] D. Kleinman and W. Spitzer, Phys. Rev. **118**, 110 (1960).

[18] W. Spitzer and D. Kleinman, Phys. Rev. **121**, 1324 (1961).

were mechanically polished. The same effect was observed on polished SiC surfaces[15] and shown to be the result of a thin ($\sim 1\ \mu$) damaged surface layer. It is also noted that particularly in the cases of SrF_2 and BaF_2, the calculated curve falls below the measured points at the longest wavelengths. This difference, which exceeds the experimental error in the measurements ($\pm 2\%$ reflectivity at $\lambda = 80\ \mu$) is also indicated by comparing the $\epsilon_\infty + \sum 4\pi\rho$ values with those of ϵ_0(exp) from capacity measurements as given in Table I. While the two values are in good agreement for CaF_2, the difference in the values for SrF_2 and for BaF_2 indicate the presence of some additional absorption at still lower frequency for these two materials. At present, the source of this additional absorption is not understood. The optical constants n and k deduced from the analysis of the reflectivity data are given in Figs. 7 and 8.

TABLE I. A list of the parameters used to calculate the dispersion curves of Figs. 1, 2, and 3. α_1 and α_2 are the peak values of the absorption coefficient due to the ν_1 and ν_2 resonances, respectively. Also listed are the frequencies of the longitudinal optical phonon, an acoustical phonon, and an absorption band observed in Figs. 4, 5, and 6. The values of the low-frequency dielectric constant as obtained from capacity measurements are given as ϵ_0(exp).

	CaF_2	SrF_2	BaF_2
$\nu_1(TO)$, cm^{-1}	257	217	184
λ_1, μ	38.9	46.1	54.3
γ_1	0.018	0.017	0.020
$4\pi\rho_1$	4.20	4.00	4.50
α_1 (peak value), cm^{-1}	3.9×10^4	3.3×10^4	2.8×10^4
ν_2, cm^{-1}	328	316	278
λ_2, μ	30.5	31.7	36.0
γ_2	0.35	0.25	0.30
$4\pi\rho_2$	0.40	0.07	0.07
α_2 (peak value), cm^{-1}	1.7×10^3	0.5×10^3	0.4×10^3
ϵ_∞	2.045	2.07	2.16
$\epsilon_0 = \epsilon_\infty + \Sigma 4\pi\rho$	6.65	6.14	6.73
ϵ_0(exp)	6.7	6.6	7.2
ϵ_0 (literature)[a]	6.8	7.69	7.33
ν_{LO}, cm^{-1}	463	374	326
ν_{ac}, cm^{-1}	71	99	94
ν_3, cm^{-1}	720	630	550
$\nu_1+\nu_{LO}$, cm^{-1}	720	591	510
$3\nu_1$, cm^{-1}	770	650	552

[a] See references 12 and 13.

The strong resonances (ν_1 of Table I) at 257, 217, and 184 cm^{-1} for CaF_2, SrF_2, and BaF_2, respectively, are identified as the optically active *TO* resonances. The *TO* frequency for CaF_2 is in reasonable agreement with the value given by Heilmann[6] and by Yoshinaga *et al.* The *TO* values for the three fluorides are not in agreement with those given by Parodi.[5] The frequency of the longitudinal optical phonon of zero wave vector can be estimated from the Lyddane, Sachs, Teller relation,[19]

$$\nu_{LO} = \nu_{TO}(\epsilon_0/\epsilon_\infty)^{\frac{1}{2}},$$

[19] R. Lyddane, R. Sachs, and E. Teller, Phys. Rev. **59**, 673 (1941). For a discussion concerning the applicability of this expression for CaF_2, see S. Ganisan and R. Srinivasan, Can. J. Phys. **40**, 74 (1962).

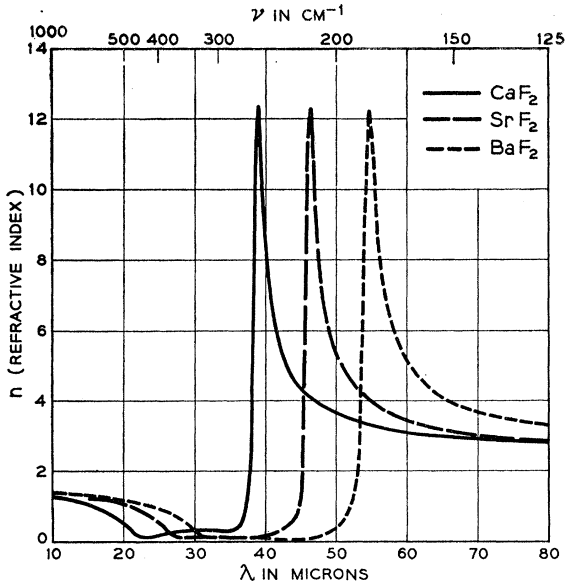

FIG. 7. Refractive index for each of the fluorides as obtained from the dispersion analysis of the reflectivity.

and the ν_{LO} for each material is also given in Table I. The second resonance used in each of the calculations (see ν_2 of Table I) is between one and two orders of magnitude weaker than the main resonance. If the ν_2 resonance is a two-phonon combination band involving the *TO* mode, then the frequency of the second phonon, probably acoustical, is given in Table I as ν_{ac}. The ν_2 frequency of CaF_2 is close to that given by Heilmann[6] and by Parodi.[5] However, the ν_2 frequencies for SrF_2 and BaF_2 do not agree with those given by Parodi. In the room temperature absorption curves for these

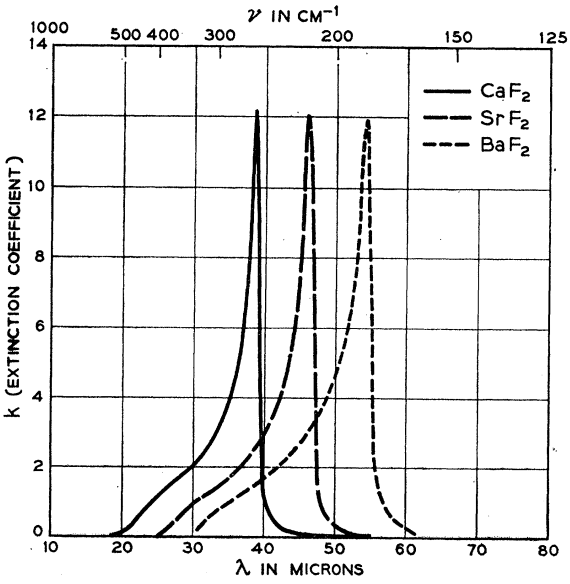

FIG. 8. Extinction coefficient for each of the fluorides as obtained from the dispersion analysis of the reflectivity.

crystals (Figs. 4–6) one weak absorption band is observed in each case. The frequency of this band, which is called ν_3 in Table I, is close to both $\nu_1(TO)+\nu_{LO}$ and $3\nu_1$. After subtracting out the background absorption, the strength of this band is approximately an order of magnitude less than the two phonon combination band at ν_2. Exact agreement is not expected between the values of $3\nu_1$ (or $\nu_1+\nu_{LO}$) and ν_3 since ν_1 is the *TO* frequency at zero wave vector which may differ considerably from the *TO* frequency in other parts of Brillouin zone. The question may be raised as to why the $2\nu_1$ was not observed for any of these materials. The frequency of this band places it beyond the spectral range of the transmission measurements, and it occurs very close to the minimum in the reflectivity curves. Assuming the strength of this band to be the same as that of the ν_2 band, calculations showed that it would be very difficult to observe in the reflectivity.

As previously indicated, several sharp emission lines of Sm^{++} in CaF_2, SrF_2, and BaF_2 were followed by a group of lines which were considered to be the result of interactions with the host lattice. One of the two strongest satellite lines in SrF_2 and BaF_2 is separated from the sharp electronic (magnetic dipole) transition by 216 and 186 cm^{-1}, respectively. These values agree very well with the measured *TO* frequencies of 217 cm^{-1} and 184 cm^{-1}, indicating that the fluorescence occurs to a vibrational level above the terminal electronic state. In SrF_2, a weak satellite line with a separation of ≈ 90 cm^{-1} is observed and a relation to the $\nu_{ac}=99$ cm^{-1} discussed above is likely. The fluorescence of Sm^{++} in CaF_2 is quite different from that in SrF_2 and BaF_2. The major emission line of Sm^{++} in CaF_2(14 118 cm^{-1}) corresponds to an electric dipole transition involving a lattice vibration. The vibrational structure following this intense line has several distinct maxima. One of these maxima is separated from the main fluorescent line by 250 cm^{-1} (at 77°K), which is close to the observed *TO* frequency of 257 cm^{-1}. Therefore, vibrational levels occur for Sm^{++} in all three fluorides which can be identified with the *TO* mode of vibration of the host lattice.

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Weak-Field Magnetoresistance of Impurity Conduction in *n*-Type Germanium*

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The coefficients B, C, and D of the weak-field magnetoresistance in n-type germanium are calculated in the phonon-induced hopping region at low temperatures. The shrinking of each donor wave function by a magnetic field decreases the transition probability of electrons from a donor site to an unoccupied one and gives rise to a magnetoresistive effect. The phase difference produced by the field between two neighboring donor wave functions contributes to the magnetoresistance to the same order of magnitude as the effect of the shrinking. The results show some characteristic properties of B, C, and D different from those of electrons in the conduction band: (1) The absolute magnitude of the coefficients is larger for specimens with smaller carrier mobility; (2) the magnitude is much larger than that expected from the usual transport theory of conduction electrons; (3) the isotropic part of the coefficients B is the largest; and (4) the coefficient D, which represents the anisotropy of the electronic motion, is the smallest among the three coefficients. These properties are in qualitative agreement with recent experiments in a slightly higher impurity concentration range in n-type germanium.

I. INTRODUCTION

THE theory of weak-field magnetoresistance was developed for conduction electrons in n-type germanium by Abeles and Meiboom[1] and Shibuya.[2] By introducing a many-valley model with an anisotropic effective mass in each valley, verified by cyclotron resonance experiments,[3] they could explain the large anisotropy of the magnetoresistance in n-type germanium.

A phenomenological relation[4] between the electric field $\mathbf{E}$ and the electric current $\mathbf{J}$ in a weak magnetic field $\mathbf{H}$,

$$\mathbf{E}=\rho_0[\mathbf{J}+A\mathbf{J}\times\mathbf{H}+BH^2\mathbf{J}+C\mathbf{H}(\mathbf{J}\cdot\mathbf{H})+D\mathbf{M}\mathbf{J}], \quad (1.1)$$

holds generally in cubic crystals such as germanium, where ρ_0 is the resistivity in zero magnetic field and

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† On leave of absence from the Electrotechnical Laboratory, Nagatacho, Tokyo, Japan, where this work was begun.
[1] B. Abeles and S. Meiboom, Phys. Rev. **95**, 31 (1954).
[2] M. Shibuya, Phys. Rev. **95**, 1385 (1954).
[3] G. Dresselhaus, A. F. Kip, and C. Kittel, Phys. Rev. **98**, 368 (1955).
[4] F. Seitz, Phys. Rev. **79**, 372 (1950).