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Electronic Hall Mobility in the Alkaline-Earth Fluorides[†]

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The electronic Hall mobility has been measured in additively colored samples of CaF_2, SrF_2, and BaF_2 over the temperature range 160–400 °K by a modified Redfield technique. In all cases the data show a temperature dependence which is much steeper than that predicted by the Feynman-Hellworth-Iddings-Platzman continuum polaron theory. It is suggested that a treatment of polaron transport which specifically considers the discreteness of the lattice may be necessary to fully understand transport in these intermediate-coupling materials.

I. INTRODUCTION

The alkaline-earth fluorides CaF_2, SrF_2, and BaF_2 have been of recent interest because of the photochromic behavior they exhibit when doped with rare-earth ions.[1,2] In addition, the simplicity of the fluorite structure has encouraged considerable theoretical work on their lattice dynamics[3,4] and dielectric properties.[5] The extensive body of measurements of the dielectric[6] and infrared optical properties[7,8] of these compounds permits reliable estimates to be made of many of the parameters crucial to any discussion of their electronic transport properties. The fact that all three fluorides can be made photoconducting by additive coloration[9,10] suggests that drift mobility and photo-Hall measurements might be utilized in an investigation of these transport properties. We present here a study of the temperature dependence of the electronic Hall mobility in all three alkaline-earth fluorides via a modified Redfield technique.

It is well known[11] that Hall-effect measurements have several advantages over other techniques in the study of the electronic properties of insulators. The first is that they are independent of shallow trapping effects; these effects often obscure the temperature dependence of the microscopic mobility in drift-mobility studies. The second is the availability of Hall techniques[12–14] which do not require the establishment of Ohmic contacts on wide-band-gap insulators, such as the alkaline-earth fluorides.

A glance at the similarity between the dielectric properties of the fluorides and those of the alkali halides[11] suggests that a discussion of their electronic-transport properties must proceed within the framework of polaron theory. In fact, the Fröhlich coupling constant, which describes the strength of the electron-phonon interaction in the continuum approximation, lies between 5 and 6 in the fluorides when the crystal band mass is equated to the free-electron value; these coupling constants are quite close to those computed for typical alkali halides.[11] It would, therefore, appear useful at this point to briefly review the polaron theories which have been applied to these materials with emphasis on their relevancy to experimental results on electronic-transport properties in the alkali halides.

II. THEORETICAL CONSIDERATIONS

In general, the polaron theories which have been applied to the alkali halides, and which at first glance would seem useful for the fluorides, have employed the continuum approximation. In this ansatz the electron-lattice interaction is treated as the interaction of an excess charged particle with a dielectric continuum. If the radius of the polaron is very large compared to the lattice constant of the material, such an approximation would appear to be reasonable.

Several polaron theories[15-17] using the continuum approximation have been developed which predict the temperature dependence of polaron mobility; these theories employ the assumption that LO-phonon scattering is the dominant mechanism limiting carrier motion. Calculations of the relative strength of acoustical- and optical-phonon scattering cross sections show that this is a good approximation in these ionic crystals,[11] except perhaps at very low temperatures where the optical modes are "frozen" out. All these theories with the exception of the Feynman-Hellworth-Iddings-Platzman (FHIP)[17] calculation are only valid at temperatures much lower than the LO-phonon temperature θ_{LO} ($\theta_{\text{LO}} = \hbar\omega_{\text{LO}}/k$, where ω_{LO} is the LO-phonon frequency and k the Boltzmann constant). A recent publication by Thornber and Feynman[18] contains an analytic expression for the FHIP polaron mobility which should be valid at temperatures around θ_{LO}.

Recently, Hall mobility measurements have been made on several alkali halides at temperatures near θ_{LO}.[14] These were compared with the predictions of the optical-scattering theory of Howarth and Sondheimer[19] (H + S), and (in a note added in proof) with the FHIP mobility expression given by Thornber and Feynman.[18] In all cases the experimental mobility values were shown to decrease much more rapidly with increasing temperature than the predictions of both the H + S and FHIP calculations. It was pointed out that this disagreement between theory and experiment is not totally unexpected; since values of polaron radii in the alkali halides have been estimated[20] within the continuum model to be roughly twice the lattice constant,[21] it is probable that application of the continuum approximation to these materials is not totally self-consistent.

Seager and Emin[14] have pointed out recently that polaron theories which specifically treat the discrete nature of the lattice[22,23] possess the feature that the polaron mass may be an increasing function of temperature, the increase becoming most pronounced above $T \sim \frac{1}{2}\theta_{\text{LO}}$. They concluded that this feature could explain the steep temperature dependence of μ_H in the alkali halides. Thus, it is possible that theoretical treatment of a larger than small polaron in a discrete lattice may be necessary to understand the transport properties of electrons in both the alkali halides and alkaline-earth fluorides.

In addition to these considerations, it is important in any discussion of transport in materials with low electronic mobility to determine the relevancy of the band picture in describing electronic motion. Fröhlich and Sewell[24] have emphasized a criterion which is relevant to consideration of carrier motion within any type of band scheme. They noted that the energy spread due to scattering, $\frac{3}{2} kT$, must be greater than $\hbar/\tau$, where τ is the scattering time. If this condition is violated it makes little sense to speak of band states and a more appropriate description must be found. In the case of the alkali halides and alkaline-earth fluorides, where the conduction bandwidth is probably much greater than kT, Fröhlich and Sewell's condition may be written as

$$\mu > 30\left(\frac{300}{T}\;\frac{m_e}{m^*}\right) , \tag{1}$$

where m^* is now the polaron mass, m_e is the free-electron mass, and T is the temperature in K. In the case of several of the alkali halides μ_H is less than 15 cm^2/V sec at room temperature which implies that we may be reaching the limits of validity of the band description for temperatures in this vicinity.

Holstein[22] has shown in the case of the small polaron that it is necessary to view the carrier motion within the framework of a localized-state (hopping) description at temperatures above the point where the band picture becomes inappropriate. Unfortunately, no such theoretical picture exists for the intermediate-size polarons which are probably present in both the alkali halides and the alkaline-earth fluorides. It should be pointed out, however, that if band narrowing is important, the polaron band may be narrowed enough at high temperatures to extend the validity of the band-state representation to temperatures where the mobilities are considerably less than 10 cm^2/V sec.

Finally, it is important in comparing the results of Hall-effect experiments with the predictions of polaron calculations to consider the relationship between the drift and Hall mobilities. This consideration has been for the most part neglected in the case of electronic-transport experiments on ionic crystals. In substances having weak electron-phonon coupling ($\alpha < 1$), the Hall and drift mobilities have been shown[25] to be related by a factor of order unity. On the other hand, in the small-polaron regime, in which a carrier can be described as moving in a small-polaron band or "hopping," the Hall and drift mobilities may depend on temperature in quite different ways[26-28] depending on lattice geometry and other factors. Although there exist no theories for these intermediate-coupling-strength materials which relate the Hall to the drift mobility, experimental results above 300 K in KCl by Hirth and Tödheide-Haupt[29] and Seager and Emin[14] appear to show that, at least in this material, they are very nearly equal, This remains as an important question to be clarified by future polaron studies which will hopefully consider the discreteness of the lattice directly or at least provide a criterion for application of the continuum approximation.

It is clear from the foregoing remarks that more theoretical and experimental work is needed to clarify the picture of polaron transport in the intermediate-coupling regime. Since the alkaline-earth fluorides are another example of compounds which lie within this regime, it is clear that measurements of electronic mobilities in these materials might be valuable; in particular they might provide a further test of the continuum approximation.

III. EXPERIMENTAL

A. Apparatus

The apparatus used to measure the Hall mobility in these materials is a modification of the Redfield[12] technique and has been described extensively elsewhere.[13,14] Therefore, only a description of a recent modification of the equipment will be given here.

Previously, calibration of the magnetic-field-induced charge response was accomplished by rotating the electric field via manually operated potentiometers before and after the magnetic field measurement. While these calibration runs rarely showed any disagreement which would indicate long-term changes in the photoresponse of the sample, it was felt that this procedure was inadequate in the case where many hours of continuous computer averaging were needed to improve the signal-to-noise ratio. Such was the case for BaF_2 which was only weakly photoconducting after additive coloration.

To remedy this situation a system was designed which turned the field-rotation potentiometers via servo motors in such a fashion as to implement a linearly increasing rotation of the electric field by a preset amount over the same time period required for the magnetic field cycle. The 5-min-duration computer sweep then consisted of a 1.5-min period during which the electric field was rotated through an angle which linearly increased up to some predetermined value and then rapidly decreased to zero, and a 1-min dead time which allowed the box car to come back to the zero-field signal level; this was followed by a linear increase of the magnetic field over a 1.5-min interval from 0 to ~15 kG and rapidly back to 0, and then another 1-min dead-time period. The next sweep is accomplished in the same fashion except that both the electric field rotation and magnetic field directions are reversed to cancel any small asymmetries present in the grid-wire network and to prevent the buildup of polarization in the Hall direction. With this modification it has been possible to run the apparatus for several hundred sweeps, thus increasing the signal-to-noise ratio by more than an order of magnitude.

B. Sample Preparation

Small blocks (typically 2 cm on a side) of all three alkaline-earth fluorides were purchased from the Harshaw Chemical Co. These blocks were cleaved into smaller (~ 1×1×1 cm) cubes and then electrolytically colored by standard techniques[30] in a resistance furnace. Coloration was achieved with a combination of point (negative polarity) and plane electrodes applied to the crystal at temperatures between 600 and 700 °C. By varying the interelectrode field between 10 and 225 V/cm the speed of coloration could be altered at any time during the process. After cleaving these cubes into several 1-mm-thick slices, the more heavily colored pieces were annealed for several minutes at 700 °C to bleach out some of the defects.

Optical-absorption spectra of samples of all three fluorides thus colored were taken on a Cary 14 recording spectrophotometer over the region 15 000–3500 Å. These agreed well with previously published spectra,[31,32] generally consisting of several broad peaks superimposed on a rather high-background-absorption level. Identification of the F-center absorption band has been established in the case of CaF_2 (~ 3700 Å) and SrF_2 (~ 4500 Å)[30] but appears to be still somewhat in doubt in the case of BaF_2.[31] Visually, samples of colored CaF_2 are deep blue, those of SrF_2 bright green, and those of BaF_2 bluish green.

Mobility measurements were made on lightly colored samples cleaved to a thickness of ~ 1 mm which were placed in thin polyethylene (0.003 cm) packets to guard against photoemission effects.

C. Experimental Procedure

After the sample had been inserted into the sample holder[14] the Dewar[14] was filled with either liquid N_2 or Freon 22. The heater power was then adjusted to bring the sample holder to the desired temperature and the apparatus was operated for a period long enough to achieve a reasonable signal-to-noise ratio in the computer-averaged print out. In BaF_2, up to 24 h of continuous signal averaging was required in some cases, while the magnitude of the photoresponse in CaF_2 and SrF_2 allowed data to be obtained over periods which rarely exceeded 2 h.

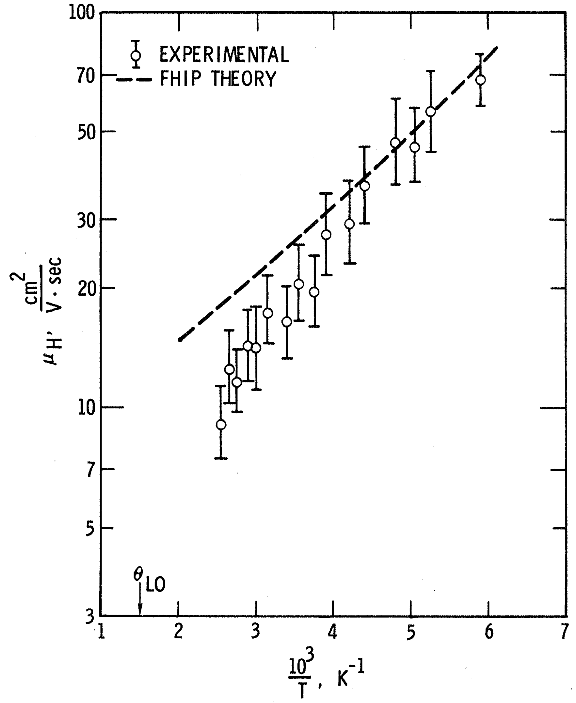

FIG. 1. Hall mobility in CaF_2.

It was noticed in the case of CaF_2 and BaF_2 that the photoresponse of the samples became slightly magnetic field dependent below ~ 200 K. This was eliminated in both by placing a Corning 4-72 filter in front of the xenon flash lamp which cut out the portion of the photo-excitation-spectrum lying above 6000 Å. It is possible that either magnetic-field-dependent trapping effects or the Zeeman splitting of the color center electronic levels could cause this phenomena, but no investigation into the nature of this effect was attempted.

Determination of the Hall mobility from the data is straightforward and is discussed in detail in Ref. 14. Briefly, it can be shown that

$$\mu_H(\text{in cgs units}) = -\frac{S_B}{S_c}\,\phi_c\,\frac{10^8}{B} \quad \text{for } \phi_c \ll 1 . \qquad (2)$$

Here S_B and S_c are the charge responses to the magnetic field and calibration procedures, respectively, ϕ_c is the maximum angle of rotation of the electric field during the calibration procedure, and B is the maximum magnetic field strength in gauss.

IV. RESULTS

The measured Hall mobilities for the three alkaline-earth fluorides are plotted versus reciprocal temperature in Figs. 1–3. In all cases the sign of the Hall effect was that of electrons. The error bars were determined by computing the maximum and minimum mobilities consistent with the noise spread of the computer-averaged x-y print out. Additional random errors are estimated to be less than 5% of the plotted values. Owing to possible uncertainties resulting from the long-time-averaging procedures necessary in the case of BaF_2, two samples were measured. Agreement between these two sets of data is quite satisfactory. Because of the freedom of Hall measurements from trapping effects, particularly in the case of materials with such short electronic mean free paths, one would expect these data to reflect the bulk properties of the samples.

Owing to lack of knowledge of the crystal band mass in the fluorides, comparison of these mobilities with polaron theories must be made on the basis of the predicted temperature dependence. Since the LO-phonon temperature is known for all three compounds,[7,8] this comparison is easily made. The dashed line in Figs. 1–3 is the computed temperature dependence of the FHIP theory normalized to the low-temperature data for ease of visual comparison. The FHIP calculation was performed on a computer using Eq. (24) of Ref. 18. The temperature dependence of the FHIP result appears to be essentially independent of coupling constant between $\alpha = 3$ and $\alpha = 7$ in the range of θ_{LO}/T of interest here. In general, all three materials exhibit sharper temperature dependence than those predicted by the FHIP calculation.

It is clear that the deviation from the FHIP result is larger as one goes in the direction of in-

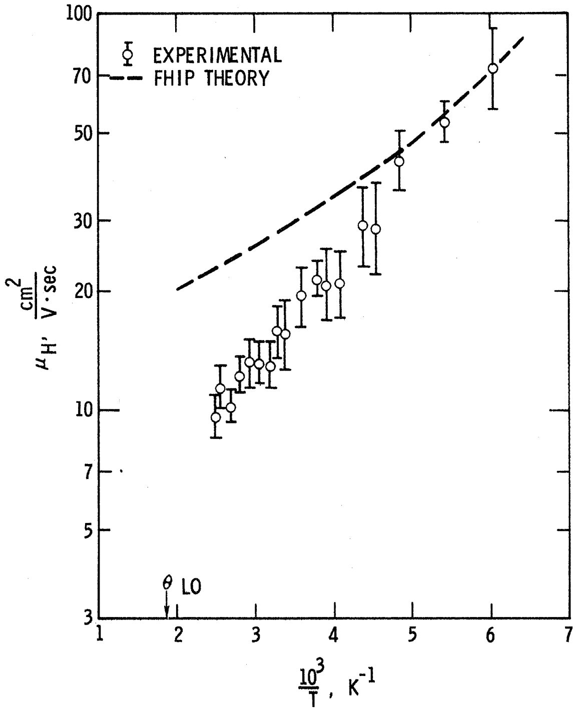

FIG. 2. Hall mobility in SrF_2.

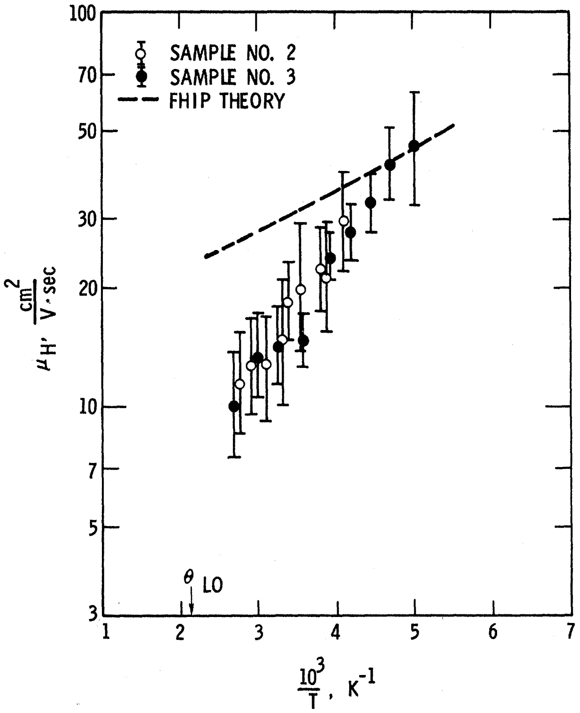

FIG. 3. Hall mobility in BaF_2.

creasing alkaline-earth atomic weight. It is perhaps significant in this regard that the lowest values of z ($z = \theta_{LO}/T$) covered during the measurements decrease from ~ 1.7 to nearly unity as one proceeds from CaF_2 to BaF_2. It was not possible to extend the range of measurements to the interesting regime where z is less than 1 because of apparatus limitations; although this range of z was accessible in measurements on the alkali halides, the LO-phonon frequencies[7,8] of the fluorides are typically two to three times higher than those found for the alkali halides. These higher phonon frequencies are a result of the presence of the divalent alkaline-earth ion in these structures.

As far as can be determined by the author, there exist no other measurements of μ_H in these materials which could be compared with the present data. Similarly there appear to be no values of the drift mobility with which comparisons might be made with the present results. As has been pointed out previously, there exist no theories valid for these intermediate-coupling materials which calculate the Hall mobility directly. Thus, the relationship of the Hall to the drift mobility is uncertain, so that a possible comparison of the two in these materials would be of great interest.

V. DISCUSSION

It is clear that in the alkaline-earth fluorides, as in the case of the alkali halides,[14] there is considerable disagreement between the experimental Hall mobilities and the predictions of continuum-polaron theory. These data reflect the trend evident from measurements on other ionic compounds since the previously reported alkali-halide data are also in substantial disagreement with the FHIP result. There is still some uncertainty as to why the low-temperature limit of the FHIP calculation fails to agree[18] with the results of other polaron theories[15,16] which are valid for $z \gg 1$. This is an unfortunate situation since this calculation is at present the only continuum-polaron theory which can reasonably be expected to be valid at temperatures around θ_{LO}.

One possible reason for the discrepancy between theory and experiment is the presence of polaron band narrowing. This phenomena arises from treating the discreteness of the lattice explicitly[22,23] and becomes most pronounced for values of $z \lesssim 1$. The trend of the alkaline-earth fluoride data toward larger discrepancies from continuum-polaron theory as z approaches unity indicates that this idea may have some validity. If band narrowing is important, the treatment of a larger than small polaron in a discrete lattice will be necessary to understand the mobility results in these ionic crystals.

Finally it should be emphasized that perhaps the band description itself may be inadequate in the treatment of polaron transport in these compounds above room temperature where the mobilities measured are typically less than 10 cm^2/V sec. The application of Fröhlich and Sewell's[24] condition [Eq. (1)] in this case requires that the polaron mass must be greater than 3 times the free-electron mass for the bandlike description of states to be a meaningful one. Rigid-lattice band-structure calculations for the alkali halides[33] indicate conduction bandwidths of a few eV; within the framework of continuum-polaron theory these widths are not generally consistent with such large polaron masses. It should be emphasized, however, that these rigid-lattice calculations ignore the electron-phonon interaction, a procedure which is questionable when applied to transport in these highly polar materials.

VI. CONCLUSIONS

The electronic Hall mobility has been measured in additively colored samples of CaF_2, SrF_2, and BaF_2 over the temperature range 160–400 K by a modified Redfield technique. As in the case of the alkali halides, the data are in substantial disagreement with the temperature dependence predicted by continuum-polaron theory. Generally they show a temperature dependence which is much steeper at high temperatures than that predicted by the FHIP polaron theory. It is suggested that a treatment of polaron transport which specifically considers the discreteness of the lattice may be necessary to fully understand transport in these intermediate-coupling materials.

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