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Pressure-induced changes in the reflectivity of SmSe and some comments on Nd-substituted SmSe

Benjamin Welber

IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

A. Jayaraman

Bell Laboratories, Murray Hill, New Jersey 07974

Pressure induced changes in the reflectivity of SmSe have been investigated up to 70 kbar hydrostatic pressure, using the gasketted diamond anvil high-pressure x-ray apparatus in conjunction with an optical microspectroscopic system. The effect of Nd substitution on the lattice parameter, resistivity, and color of SmSe has also been studied. Reflectivity data for GdSe at ambient pressure have been obtained for comparison with the metallic phase of SmSe. With increasing pressure the color of the sample (as observed in reflected light) goes through a sequence of changes, from black, steel-blue, deep purple, reddish purple, copperlike metallic color to bronze yellow at the highest pressure. From the reflectivity data, the static conductivity has been evaluated and is compared with the dc conductivity, previously measured on SmSe single crystals under hydrostatic pressure. Deviations from Drude theory indicate that the interband contribution to the dielectric constant plays an important role in determining the sequence of metallic colors observed in metallic rare-earth monochalcogenides.

INTRODUCTION

Samarium monochalcogenides undergo a pressure-induced change in the valence state of the rare-earth ion from divalent toward the trivalent state due to $4f$-electron delocalization. As a result, there is a transition from semiconducting to the metallic state.[1,2] Resistivity studies under hydrostatic pressures on single crystals have shown that the above transition in SmS is a first-order one, taking place at 6.5 kbar pressure[1] at ambient temperature, while in both SmSe and SmTe it takes place continuously in the 1–60 kbar range. Several interesting property changes accompanying this transition have been investigated both when it occurs under pressure as well as in systems where the transition can be induced by the substitution of a trivalent rare-earth ion.[2,3] The latter applies particularly to SmS-bases systems.

One of the most striking aspects of the $4f$-electron delocalization is the spectacular change in the optical reflectivity[4]; in SmS the color changes from black to a brilliant metallic gold color. Quantitative reflectivity measurements on metallic SmS[5] have shown that the plasma edge lies at about 2.5 eV and the characteristic golden color is due to an interband transition, which pulls the free-electron plasma edge into the visible region. In this connection the transition from the sulfur p band (valence band) to the $5d$ rare-earth band (conduction band) has been invoked.[4]

In SmSe, however, the $4f$-electron delocalization proceeds continuously with pressure[1] and it follows that a progressive shift in the plasma edge may be expected. Consequently, the color and hence the reflectivity spectrum should go through a sequence of changes with pressure. The present investigation was undertaken to establish the nature of the shift in the plasma edge with hydrostatic pressure in SmSe and to relate this to the dc conductivity change under pressure, as well as to the color changes that are observable in the SmSe-NdSe system. We have also studied the reflectivity of GdSe for comparison. The results of these studies will be presented and discussed in this paper.

EXPERIMENTS

The method of preparation of SmSe and its optical and electrical properties at atmospheric pressure have been described in earlier publications.[6] Briefly, SmSe crystallizes in the NaCl-type structure and is a semiconductor with a $4f$ to $5d$ conduction band energy gap of about 0.5 eV.[7] This gap dominates the optical and electrical properties of the material. When stoichiometric and pure, the dc resistivity can be several thousand Ω cm. Since the substance cleaves very easily, small rectangular shaped flat crystallites with almost perfect surfaces are obtainable for optical studies.

The high-pressure apparatus used consists of two diamond anvils with 0.6-m flat faces, the associated supporting steel backing blocks, and the spring-loaded lever arangement for applying the load. Hydrostatic pressure was a primary requirement for our studies and hence the metal gasket technique currently in use with the diamond anvil high-pressure apparatus was employed; a mixture of ethanol and methanol was used as the pressure medium. The optical microspectroscopic system used with the diamond anvil high-pressure cell was the same as the one described in earlier publications.[8,9] The pressure generated was determined using the shift of the ruby R line (ruby scale).[10]
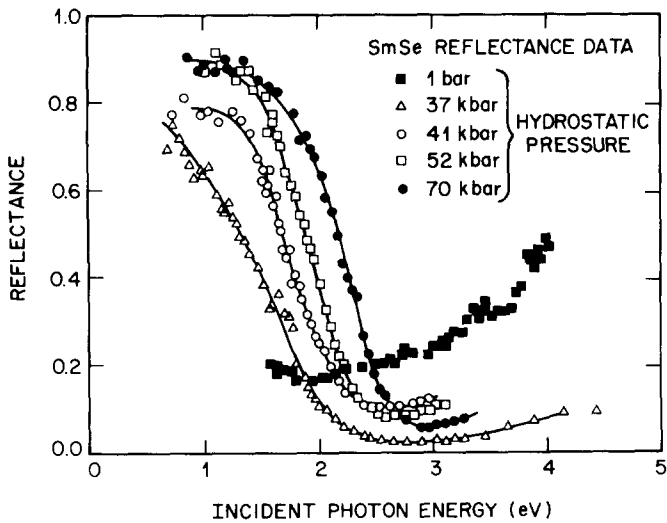
FIG. 1. Reflectance of SmSe under hydrostatic pressure. All the curves show a minimum in the reflectance. Y axis gives reflectance, nomalized with respect to Al.
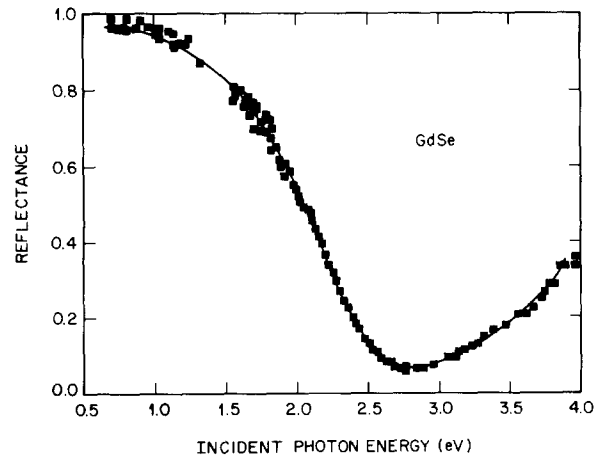

FIG. 2. Reflectance of GdSe at ambient pressure. The pronounced mimimum and rise in reflectance in the uv region is to be noted. Y axis gives reflectance, normalized with respect to Al.

RESULTS

The reflectivity data obtained for SmSe are presented in Fig. 1. The reflectance is measured with reference to an Al surface evaporated onto the lower diamond, and the data are then normalized, using accepted values for the variation of Al reflectance with wavelength.[11] In the semiconducting state the sample appears essentially black and the data taken at atmospheric pressure show the reflectance to be low (less than 25%) up to about 3 eV, exhibiting a pronounced tendency to rise in the near-uv range. With increasing pressure the reflectance increases, and the development of a plasma edge is obvious. With white light illumination and with increasing pressure, the following sequence of color changes is seen: steel-blue, deep purple, reddish purple, copper, bronze-yellow. The reflectivity data for pure GdSe are presented in Fig. 2 for comparison and the resemblance between the latter and that of SmSe at 70 kbar is striking. We also present the dc resistivity data in Fig. 3 which show progressive 4f-electron delocalization with increasing pressure.

DISCUSSION

It is well known that the high reflectivity of metallic systems is due to free electrons. The Drude theory accounts for the optical properties of simple metals.[12,13] Following Ehrenreich and Philipp,[14] the dielectric function for a metal can be written as

$$\epsilon(\omega) = \epsilon^{fe}(\omega) + \sum_j \epsilon_j^{ib}(\omega) \tag{1}$$

which separates explicitly the free-electron contribution (ϵ^{fe}) from that due to bound electrons (ϵ_j^{ib}) (interband terms). When the latter terms are present, the simple Drude model has to be modified by lumping the interband contributions into a single background dielectric constant ϵ_∞, assumed to be constant over the frequency range of optical reflectance in the metallic region. What results then is the well-known

three-parameter Drude expression for the complex dielectric function

$$\epsilon(\omega) = \epsilon_\infty - \frac{\omega_p^2}{\omega(\omega + i/\tau)} = \epsilon_1 + i\epsilon_2, \tag{2}$$

where the plasma frequency ω_p is given by

$$\omega_p^2 = 4\pi Ne^2/m^* \tag{3}$$

N being the number of free electrons per cm³ and m^* their effective mass. Combining Eq. (3) with the usual equation for the dc conductivity
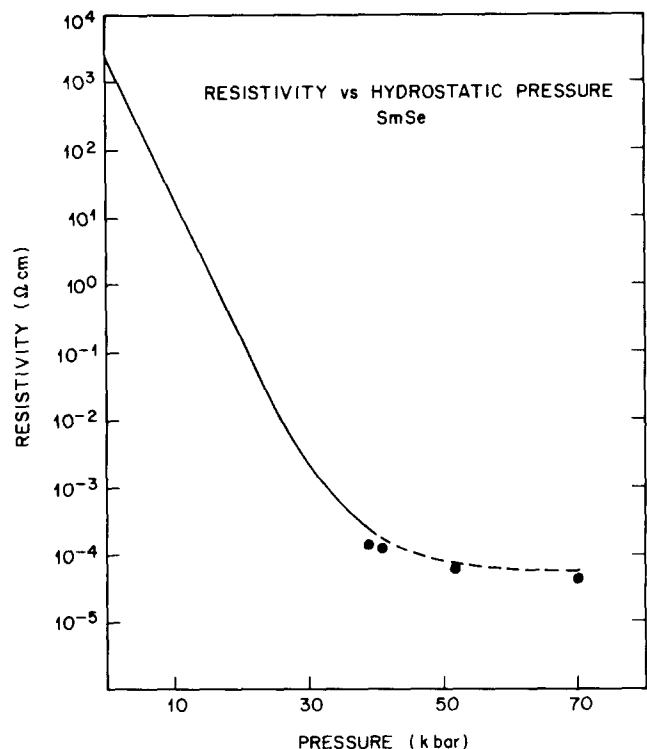

FIG. 3. Resistivity (dc) versus hydrostatic pressure data for SmSe single crystal. The filled circles at the higher pressure are the dc resistivity values extracted from the optical data, using Eq. (5) and after proper scaling to match.

TABLE I. dc conductivity extracted from the optical data of SmSe under high pressure.

P (kbar)± 1	$\sigma(0)$ $(\Omega\,cm)^{-1}$
37	$5.8\pm0.5\times10^3$
41	$8.7\pm0.5\times10^3$
52	$14.5\pm0.5\times10^3$
70	$16.2\pm0.5\times10^3$

$$\sigma(0)=Ne^2\tau/m^* \qquad (4)$$

yields the expression for the static conductivity

$$\sigma(0)=\omega_p^2\tau/4\pi \qquad (5)$$

where τ is a characteristic relaxation or collision time ($\sim 10^{-14}$ sec) of the electrons.

The reflectance R is related to the complex dielectric constant by

$$R=\frac{n_l^2+|\epsilon|-[2(|\epsilon|-\epsilon_1)]^{1/2}n_l}{n_l^2+|\epsilon|+[2(|\epsilon|+\epsilon_1)]^{1/2}n_l}, \qquad (6)$$

where n_l is the refractive index of the hydrostatic medium in which the reflectance is measured. For the ranges covered by these experiments, n_l is quite strongly dependent on the pressure and it is therefore important not to neglect this variation.

The experimental data, reflectance versus the incident photon energy, permit an evaluation of ω_p, τ, and finally $\sigma(0)$, through a fit to the three-parameter Drude expression. It should be noted however that the plasma frequency ω_p signifies a frequency located not at the reflectance edge, but displaced upward by the factor $(\epsilon_\infty)^{1/2}$. (For the metallic rare-earth monochalcogenides the unperturbed plasma frequency—evaluated purely from the electronic density and m^* values close to the free-electron mass—would place the plasma edge in the uv region; i.e., when ϵ_∞ is taken to be equal to unity in Eq. (2). Since interband contributions are
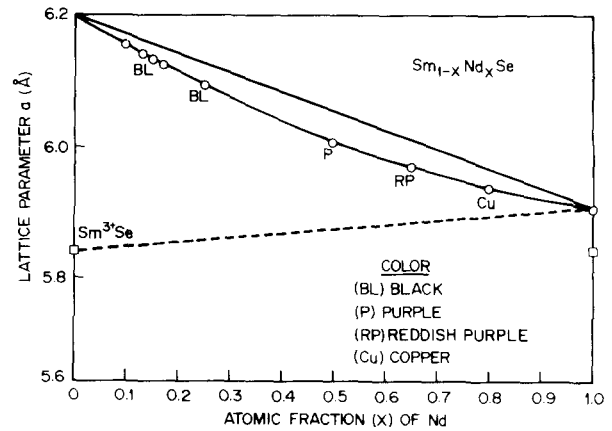

FIG. 4. Lattice parameter versus x for the $Sm_{1-x}Nd_xS$ system. The straight line (full line) represents the lattice parameter variation expected according to Vegard's law. Deviation must be due to a small change in the valence state of Sm ion. The observed color changes are shown in the figure.

important for the metallic rare-earth monochalcogenides, ϵ_∞ must be greater than unity. This would move the unperturbed plasma frequency into uv, while the edge remains in the visible.) The $\sigma(0)$ obtained from the optical data are shown in Table I and are plotted in Fig. 3. Regardless of the choice of ϵ_∞ between 2 and 8, the values of $\sigma(0)$ seem to scale very well with the trend of the dc resistivity, increasing by about a factor of ~3 when pressure is increased from 37 to 70 kbar. The values given in Table I were obtained for $\epsilon_\infty=5.0$. Beckenbaugh et al.[15] give values between 3 and 4 for ϵ_∞ in the case of LaS and the metallic Gd monochancogenides. It is also to be noted that the minimum in the reflectivity curves is a direct indication of substantial contribution to the reflectance from interband effects.

SOME OBSERVATIONS ON THE $Sm_{1-x}Nd_xSe$

We have studied the effect of Nd substitution in SmSe, over the full composition range, to find out if such substitution promotes the valence transition in SmSe and also to check how the reflectivity and resistivity correlate. The lat-

TABLE II. Some relevant data for the R^{3+} substituted $Sm_{1-x}R_x^{3+}Se$ compounds.

System	x	Lattice parameter a($\mathring{A}$)	ρ(298 K) $(\Omega\,cm)$	Color
$Sm_{1-x}Nd_xSe$	0.00	6.20	$\sim10^3$	Black
$Sm_{1-x}Nd_xSe$	0.15	6.13	13×10^{-4}	Black
$Sm_{1-x}Nd_xSe$	0.17	6.12	11×10^{-4}	Black
$Sm_{1-x}Nd_xSe$	0.25	6.09	4×10^{-4}	Black
$Sm_{1-x}Nd_xSe$	0.50	6.01	$\sim2\times10^{-4}$	Bluish purple
$Sm_{1-x}Nd_xSe$	0.65	5.97	$\sim2\times10^{-4}$	Reddish purple
$Sm_{1-x}Nd_xSe$	0.80	5.94	1×10^{-4}	Copper
$Sm_{1-x}Nd_xSe$	1.00	5.91	$\sim5\times10^{-5}$	Bronze
$Sm_{1-x}Gd_xSe$	0.5	5.95	NM^a	Deep purple
$Sm_{1-x}Y_xSe$	0.5	5.90	NM	Deep purple
$Pr_{1-x}Yb_xSe$	0.5	~5.94	NM	Deep purple

^{a}NM—not measured.

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Compound	a (Å)[a]	$n \times 10^{22}/cm^3$	$\dfrac{m^*}{m}$	Unperturbed plasma edge (eV)
LaS	5.854	2.0	1	5.2
LaSe	6.063	1.79	1	4.9
LaTe	6.422	1.51	1	4.5
GdS	5.563	2.32	1	5.6
GdSe	5.781	2.1	1	5.3
GdTe	6.139	1.73	1	4.8
LuS	~5.37	2.6	1	6.0
LuSe	~5.60	2.3		5.6
LuTe	~5.92	1.93	1	5.1

[a] Reference 19.

tice parameter data are reproduced in Fig. 4. In Table II the composition, measured resistivity values, and the observed colors are given. From the lattice parameter data (Fig. 4) it appears to us that in the above system the $4f^6$ electron of the Sm^{2+} ions are only partially delocalized. We find that high pressure is needed to effect complete delocalization in the compounds on the richer side of Sm; only then the black compounds change to metallic bronze color. With increasing Nd the resitivity decreases and the color as seen by reflected light goes through a similar sequence of changes as in SmSe under pressure. The color qualitatively scales with the resistivity. We have also observed in the $Pr_{1-x}Yb_xSe$ compounds the progression of colors and resistivity changes similar to that in the $Sm_{1-x}Nd_xSe$ system. In the former system Yb is definitely in the divalent state, and the electrons that contribute to the electrical conductivity as well as to the observed reflectivity are from the Pr ions.

Reid et al.[16] have claimed that in the $Sm_{1-x}Nd_xSe$ system near 17 at.% Nd, an abrupt drop in resistivity of several orders of magnitude is seen. In a more recent publication, Avignon and Dumas[17] have reported that their measurements on thin films (claimed to be polycrystalline) of $Sm_{1-x}Nd_xSe$ are in agreement with the data of Reid et al.[16] and they have attributed the effect to a semiconductor to metallic transition. Assuming the presence of Nd^{2+} and Nd^{3+} ions in the system, the latter authors[17] have presented a model to account for the transition; in this both localized and band states are introduced (Falicov-Kimball theory) with electron repulsion between the localized electrons on nearest-neighbor sites as an additional interaction. We observe that SmSe becomes degenerate even with small amounts of doping with Nd (even 1 at.% Nd). The results mentioned in Table II and the data obtained below 17 at.% Nd show that the dc resistivity scales with the number of Nd ions. No striking change either in the lattice parameter or in the resistivity is observed in the range 10–17 at.%. We do not understand the origin of the discrepancy between our results (obtained on single-crystal samples) and those of Reid et al.[16] and Avignon and Dumas.[17]

REFLECTIVITY OF GdSe

Stoichiometric GdSe has metallic bronze color. In the reflectivity curve there is a well-defined minimum at about 2.75 eV, and the reflectance dips down to less than 10% compared to Al. By 4.0 eV the reflectance has gone up to about 35%.

Earlier studies[15,18] on off-stoichiometric GdSe with NaCl-type structure have shown that the color and reflectivity is dependent upon the composition. The occurrence of a pronounced minimum in the reflectivity has also been noted. Holtzberg et al.[18] have shown with Hall-effect data that the electron concentration decreases with decreasing Gd content, and the color concomitantly changes from bronze copper, red gold, purple, bluish purple, and blue, starting from the Gd-rich side to the Se-rich side. They attributed these changes in color to the changes in electronic density, without invoking interband effects. However, our results and the study by Beckenbaugh et al. indicate that interband effects primarily determine the color.

COLORS OF METALLIC RARE-EARTH MONOCHALCOGENIDES

While the trivalent metallic rare-earth monochalcogenides exhibit a characteristic variation in color between the sulfides, selenides, and tellurides—bright gold, copper, and deep purple metallic colors, respectively—it is remarkable that these colors remain more or less the same in going from La to Lu, although the electronic density as evaluated from their lattice parameter appreciably changes (see Table III). That interband transitions must play an important role in determining the metallic colors is evident from the minimum in the reflectivity curves. Otherwise, the unperturbed plasma frequency evaluated purely from the electronic density and m^* values close to the free-electron mass would place the plasma edge in the near-uv region, in all these compounds, and they should all exhibit Al-like reflectivity. In earlier publications it has been suggested that the interband transition involved must be from the valence band to conduction band. If this is the transition that contributes, then the constancy of the color suggests that the interband energy separation does not appreciably change in going from La to Lu, for a particular series. This is hard to accept, in view of the large change in the lattice parameter (see Table III). We are thus faced with a puzzling problem and as a probable solution to

this situation we offer the following suggestion. There are two competing elements in these systems, namely, a decreasing interband separation and increasing electronic density at play, which compensate one for the other. While the interband separation decreases with the decrease in the lattice parameter, the electronic density will increase and keeps the Fermi energy E_f constant. Table III provides some relevant data on a few members in the series to illustrate our foregoing remarks. In the absence of quantitative studies on many members in these systems, it would be superfluous to make any further comments. The above discussion is mainly intended to draw attention to a series of compounds whose optical properties are of much interest.

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