PHYSICAL REVIEW B

CONDENSED MATTER

THIRD SERIES, VOLUME 24, NUMBER 9 1 NOVEMBER 1981

Optical transitions in $NaCrS_2$

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(Received 4 May 1981)

A Kramers-Kronig analysis of the reflectivity data, over a wide photon-energy range, at room temperature, from the basal plane $(\vec{E}\perp\hat{c})$ of single crystals of the layer-type compound, $NaCrS_2$, has been performed to obtain those optical functions such as $\epsilon_1(E)$, $\epsilon_2(E)$, $n_{\mathrm{eff}}(E)$, and $J(E)$ which are pertinent to the study of the electronic band structure of a material. The results are presented and discussed. Strong and sharp excitonlike peaks have been observed on the $\epsilon_2(E)$ spectrum and these peaks have been attributed to the presence of ligand-to-metal charge-transfer transitions in $NaCrS_2$. The Cr^{3+} d orbitals are envisaged as discrete and localized levels (*not Bloch states*) within the electronic bonding of $NaCrS_2$. The results of this Kramers-Kronig analysis of the $NaCrS_2$ reflectivity data support the rigid-ionic model, for this material, proposed previously by Khumalo and Hughes [Phys. Rev. B 22, 4066 (1980)].

I. INTRODUCTION

$NaCrS_2$ is a layer-type material that belongs to an interesting class of compounds with the general chemical formula ABX_2—where A is either an alkali metal (such as Na, Li, etc.) or a transition metal (such as Cu); B is a tripositive Cr^{3+} ion whose unfilled d shell exists as localized and discrete levels with unpaired spins giving rise to magnetic moments which are strongly coupled so that magnetic ordering would be observed; and X is a chalcogen (S, Se, or O). $NaCrS_2$ layer-type materials have received burgeoning interest over the last decade because they provide a chance to study correlations between physical properties and chemical constitution in a given structurally complex crystal, similar to other well-known cases such as spinels or perovskites.

The crystal structure of $NaCrS_2$ has been determined by many workers[1–7] and it is now known that this material crystallizes, in the space group $D_{3d}^5(R\bar{3}m)$, in a layer structure. This is also quite apparent from the $NaCrS_2$ crystals which are mica-like, shiny metallic-looking platelets which can be readily cleaved with adhesive tape or a pair of fine tweezers. Figure 1 shows the primitive rhombohedral cell (rock-salt-type) which contains one $NaCrS_2$ unit. Sulfur forms a cubic close packing while the chromium and sodium ions occupy the octahedral interstices in this packing, in alternate layers, so that CrS_2^- slabs can be distinguished and are *linked* by sodium ions. Clearly, CrS_2^- slabs are intercalated with Na^+ ions.

The transport properties of $NaCrS_2$, among other α-$NaFeO_2$ layer-structured compounds, have been

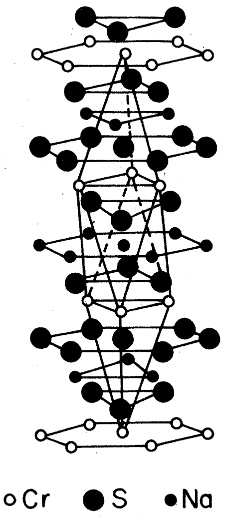

FIG. 1. $NaCrS_2$ structure. The lattice has been idealized by placing the S atoms midway between the Na and Cr atoms with light incident normal to the layer plane $(\vec{E}\perp\hat{c})$.

extensively studied[3–14] and are now fairly well understood. But, in sharp contrast very little optical data[10–16] is at hand about $NaCrS_2$ and thus a lot of fundamental data concerning the electronic properties of the material in relation to its band structure are still lacking. This paper deals with the results of a systematic optical study which has been undertaken in order to contribute to a further elucidation and understanding of the optical properties and electronic band structure of $NaCrS_2$, a prototype of α-$NaFeO_2$ layer-structured ternaries, whose structural complexity has so far precluded any theoretical band-structure calculations. Reflectivity data (in the photon energy range 1.5 to 30 eV) from basal planes (in the $\vec{E}\perp\hat{c}$ configuration) of single crystals of $NaCrS_2$ has been Kramers-Kronig (KK) analyzed to derive (among other optical functions) $\epsilon_2(E)$—an optical parameter whose spectral features are more closely related to, and also more highly illuminating about, the electronic band structure than the reflectivity or optical absorption spectrum of the material being investigated, in this case $NaCrS_2$.

II. EXPERIMENTAL ASPECTS

The reflectivity data used in our Kramers-Kronig analysis was obtained by the all too familiar sample-in (I) and sample-out (I_0) of the light path method and the normalized reflectance is then given by $R(E) = I/I_0$. The details of the experimental procedure used to obtain the reflectivity data of $NaCrS_2$, from the infrared to the vacuum ultraviolet, are similar to those described elsewhere.[15–18] The vacuum ultraviolet data used here has already been reported by Khumalo and Hughes,[16] where the energy range covered most of the low-energy electronic transitions. The reflectivity measurements were extended to far infrared energies by using the smooth curve $R=(n-1)/(n+1)^2$ with n the refractive index (of $NaCrS_2$) being regarded as a parameter. This smooth curve terminates in an energy-independent reflectance in the infrared region. Reflectivity measurements could not be taken in the infrared because $NaCrS_2$ (with a direct band gap ~ 2.3 eV, Ref. 10) transmits in that energy range and thus it would not be possible to obtain single surface reflectivity. All the reflectance data were obtained from freshly cleaved (using adhesive tape) basal planes of single crystals of $NaCrS_2$ at room temperature. The high-energy region of the reflectivity data was extrapolated to 10 000 eV by use of a power-law expression, $R(E) = [30/E(\text{eV})]R(30\ \text{eV})^{3.5}$ for $E \geqslant 30$ eV because after 30 eV, the reflectivity spectrum just tails off.

The low- and high-energy extrapolations enabled us to perform a Kramers-Kronig analysis of the reflectivity data and we obtained the following optical functions: the complex dielectric function $\hat{\epsilon} = \epsilon_1 + i\epsilon_2$ where $\epsilon_1(E)$ and $\epsilon_2(E)$ are the real and imaginary parts (respectively), of the dielectric function, the absorption coefficient $\alpha(E)$, the optical joint density-of-states function $J(E) \propto E^2\epsilon_2(E)$, the number of valence band electrons taking part in interband and intraband transitions, $n_{\text{eff}}(E)$ which is defined by $n_{\text{eff}}(E) = \int_0^E J(E)\,dE$, and the so-called electron energy-loss function $\text{Im}(-1/\epsilon) = \epsilon_2/(\epsilon_1^2+\epsilon_2^2)$. Among the optical functions, $\epsilon_1(E)$, $\epsilon_2(E)$, $\alpha(E)$, $n_{\text{eff}}(E)$, and $J(E)$ are probably the most pertinent to our present study of the optical transitions of $NaCrS_2$.

III. RESULTS AND DISCUSSIONS

The reflectivity spectrum, $R(E)$, used in our KK analysis is shown in Fig. 2 for room-temperature measurements. The reflectances taken at various photon energy ranges had more sample-to-sample differences than is usual due, mainly, to the differences in the number of cleavage steps on the basal surfaces (of the crystals) which produced scattered radiation. Spectra taken from different experimental energy ranges (infrared, visible, vuv, and soft x-ray regions) do not always agree with one another (even on the same layer crystal) in the region of overlap because of differences in numerical scaling and normalization procedures. We smoothed out the small differences, where they occurred, by averaging the two sets of data in the regions of overlap.

The optical parameters $\epsilon_1(E)$, $\epsilon_2(E)$, $\alpha(E)$, $\text{Im}(-1/\hat{\epsilon})$, and $J(E)$ derived by the KK analysis [of $R(E)$ data] are presented in Figs. 3–6. These optical parameters will be discussed in terms of the Khumalo and Hughes[16] rigid-ionic model of $NaCrS_2$ shown in Fig. 7. The derived parts of the dielectric function, $\epsilon_1(E)$ and $\epsilon_2(E)$, in Fig. 3, initially show strong dispersion and absorption (respectively), which can

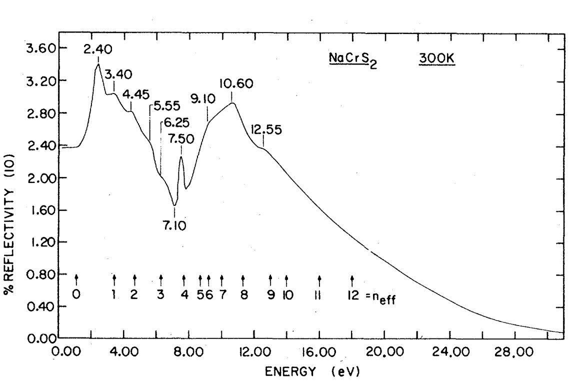

FIG. 2. Reflectivity spectrum of $NaCrS_2$, at room temperature. The prominent features on the spectrum are indicated by short vertical lines and the numbers above them are the photon energy positions. n_{eff} represents the number of valence-band electrons taking part in optical transitions.

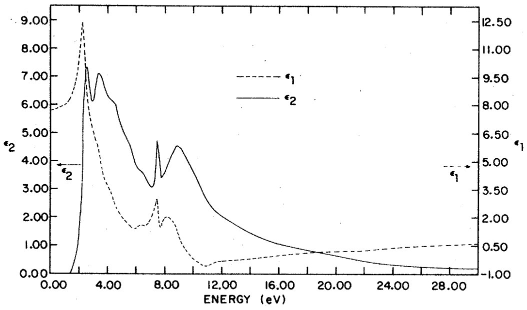

FIG. 3. Real (ϵ_1, – – –) and imaginary (ϵ_2; ——) parts of the dielectric function of NaCrS$_2$.

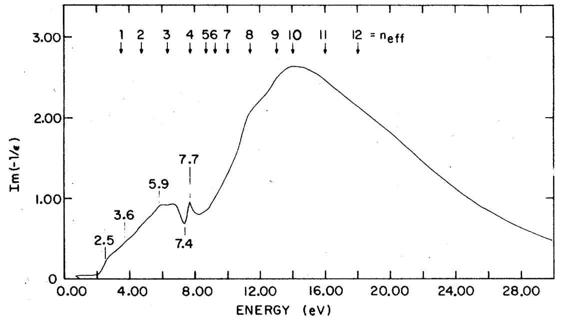

FIG. 5. Energy-loss function Im($-1/\tilde{\epsilon}$). The n_{eff} values are shown above the curve.

be attributed to the onset of the optical transitions from the full $p(S)$ valence band to the half-filled t_{2g} (non-Bloch) discrete level in Fig. 7. At their maxima, the values of ϵ_1 and ϵ_2 (Fig. 3) associated with the pronounced and sharp peak at 2.5 eV on the reflectivity spectrum (Fig. 2) are 12 and 7.3, respectively. The real part of the dielectric function extrapolates to the low positive value of $\epsilon_1(0) \sim 7.8$— a value consistent with the large band gap (~ 2.2 eV) of NaCrS$_2$. The $\epsilon_2(E)$ spectrum has two well-resolved excitonlike peaks at 2.5 and 3.40 eV—these two peaks are nearly equal in magnitude. It is worthwhile to discuss briefly the two sharp peaks, at 2.5 and 3.40 eV, on the $\epsilon_2(E)$ spectrum because they occur at the onset of optical transitions in NaCrS$_2$. In Sec. I, it was pointed out that, from the crystal structure (Fig. 1), NaCrS$_2$ can be viewed as a Na$^+$ intercalated chromium disulphide—a group-IVA dichalcogenide in the MoS$_2$ family of layered compounds. The electronic bonding in NaCrS$_2$ is essentially due to the sulfur *s*, *p* and chromium (III) *d* states from the CrS$_6$ octahedron, with Na$^+$ ions playing the role of stabilizing the otherwise unstable CrS$_2$ layer-type compound. It is worthwhile to note that Cr and Mo are in the same group (IVA) in the periodic table of elements. Also, we have observed that the reflectivity spectrum of Na intercalated CrS$_2$ (Fig. 2) and MoS$_2$ (from Ref. 19) are quite similar (see Fig. 8). If CrS$_2$ existed as a layered compound, would we expect it to exhibit optical properties similar to those of the much studied MoS$_2$? In overview, our qualitative comparison of the reflectivity spectra of the two materials (NaCrS$_2$ and MoS$_2$) in Fig. 8 could be interpreted as implying that the electronic structures (and *not* the optical transitions causing the observed spectral features) in these two materials are *probably* similar.[20] The electronic bonding of the *d* states in the two materials are quite different because in MoS$_2$, the metal d_{z^2} band sits just above the main $p(S)$ valence band and this leads to sharp excitonic peaks caused by the spin-orbit-split excitonic transitions associated with the main absorption edge (see Ref. 21), and yet in NaCrS$_2$, the octahedral ligand field split

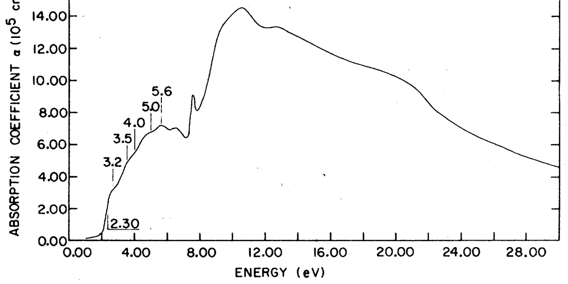

FIG. 4. Absorption coefficient, $\alpha(E)$, spectrum of NaCrS$_2$. The vertical arrows on the curve indicate the energy position of the features in the charge-transfer band-gap region.

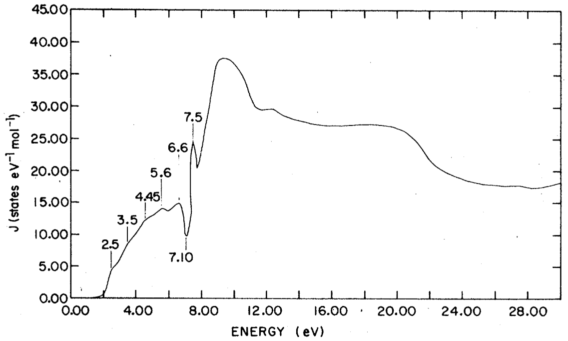

FIG. 6. Shows the optical joint density-of-states $J(E)$ curve which is proportional to $E^2\epsilon_2$.

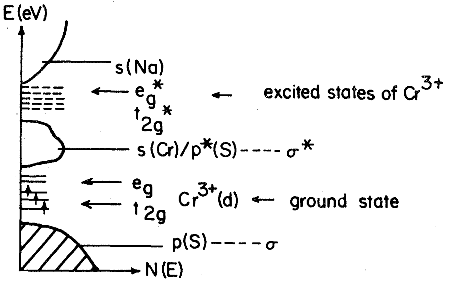

FIG. 7. Rigid-ionic-band model for $NaCrS_2$ by Khumalo and Hughes (Ref. 16).

Cr^{3+} d states [t_{2g}^3 (half-filled) and e_g (empty)] are envisaged[16] as discrete and localized levels (not bands as in MoS_2) which lie in the $\sigma\sigma^*$ gap (see Fig. 7). Thus, although in both $NaCrS_2$ and MoS_2, the optical transitions will start from the fully occupied $p(S)$ valence bands, the final states will be quite different because in the latter compound, the final state (in the absorption-edge energy range) will be a d_{z^2} band but in the former compound, the final state will be at t_{2g}^3 level with three electrons (spin parallel) as shown in Fig. 7. Therefore the two excitonlike peaks at 2.5 and 3.40 eV on the $\epsilon_2(E)$ spectrum of $NaCrS_2$ (Fig. 3) could not (as in MoS_2) be caused by the spin-orbit-split excitonic transitions [$p(S)$ valence $\rightarrow d$ (metal) conduction band]. Optical transitions in $NaCrS_2$ appear to be of a different nature from those of the usual layered transition-metal dichalcogenide. In agreement with Khumalo and Hughes,[16] we suggest that the excitonlike peaks at 2.50 and 3.40 eV are a result of a ligand-to-metal charge transfer optical transitions. The reflectivity spectrum, $R(E)$, of $NaCrS_2$, in Fig. 2, has a series of shoulders between 2.4 eV (a peak) and 7.1 eV (a distinct minimum). The $\epsilon_2(E)$ spectrum exhibits similar shoulders in the same photon energy range. As already mentioned earlier in this discussion, an optical transition originating from the $p(S)$ valence band (which is full) can end up in those *multiplet final states* of Cr^{2+} which can be reached by adding one electron to the $t_{2g}^3\, e_g^0$ configurations that make up the ground state of the Cr^{3+} ion. Such transitions would cause a series of shoulders observed on $R(E)$, $\epsilon_2(E)$ and on the joint density of states, $J(E)$ spectra in Figs. 2, 3, and 6, respectively.

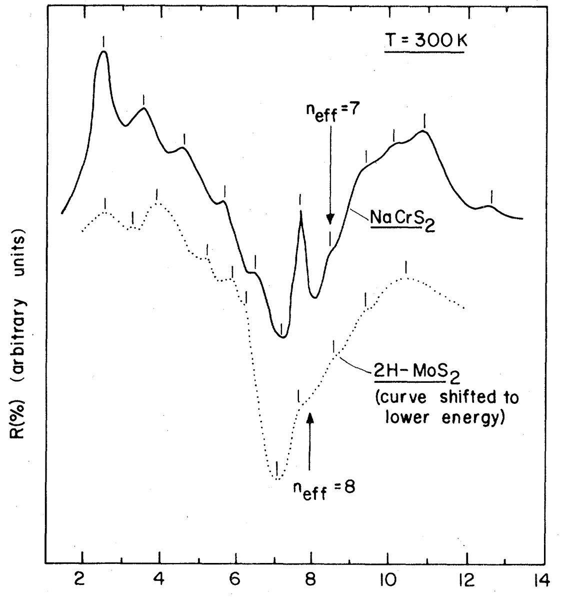

FIG. 8. Comparison of the reflectivity data of $NaCrS_2$ (from Ref. 16) and MoS_2 (from Ref. 19) where the photon energy range covers most of the low-energy electronic transitions. The MoS_2 spectrum has been shifted by ~2 eV to lower energies to superpose it with that of $NaCrS_2$.

A distinct minimum is present on the $R(E)$ spectrum at 7.10 eV (see Fig. 2). This distinct reflectivity minimum is related to the nonvanishing value of $\epsilon_2(E)$ at ~7.05 (in Fig. 3) and is indicative of the degree of overlap between the interband absorptions on either side of the window (at 7.10 eV) on the joint density of states, $J(E)$, shown in Fig. 6. Our results are in good agreement with the earlier predictions of Khumalo and Hughes[16] about the electronic structure of $NaCrS_2$. The minimum at ~7.10 eV on the $NaCrS_2$ reflectivity spectrum [$R(E)$], and at 7.05 eV on the $\epsilon_2(E)$ spectrum, therefore, marks the exhaustion of the $p(S) \rightarrow d$ (Cr^{3+}) transitions and the onset of $p(S) \rightarrow$ higher conduction band transitions.

We would now like to discuss, briefly, the existence of yet another sharp excitonlike peak at 7.5 eV on all the three spectra: $R(E)$, $\epsilon_2(E)$, and $J(E)$. This peak has been reported to sharpen considerably on cooling.[16] The sharpening of reflectivity features on cooling is reminiscent of excitons. Are we then observing a high-energy exciton on $NaCrS_2$ at 7.5 eV? We believe we are although this type of exciton is not of the Mott-Wannier-type[22] but a Frenkel-Peierls-type[23] exciton which is a result of a ligand-to-metal charge transfer transition, in this case, we are transferring charge from the sulfur p band to the (empty) sodium s level or excited e_g^* and t_{2g}^* levels up in the conduction band (see Fig. 7). This type of excitonic transition would be favored if Na is ionic within the electronic bonding of CrS_2— which is the case from the crystal structure in Fig. 1. In other words, our KK analysis results strongly suggest that the rigid-ionic model for $NaCrS_2$ proposed by Khumalo and Hughes[16] is appropriate.

In the derived electron-energy-loss spectrum of $NaCrS_2$, Fig. 5, there is a fairly distinct shoulder (at 2.5 eV) associated with the first charge transfer excitonlike peak (on Fig. 3). At high photon energies, after the exhaustion of the $p(S)$ valence band $\rightarrow d(\mathrm{Cr})$ discrete levels optical transitions, a well defined dip at 7.4 eV and a sharp peak at 7.7 eV are present. The latter structure is associated with a dip at the corresponding energy on the $\epsilon_2(E)$ spectrum. A striking feature of the energy loss function, Fig. 5, is the prominent broad peak in the region of 14 eV which is associated with a plasma excitation involving all the valence electrons in the material, $n_{\mathrm{eff}}=12$ in the case of $NaCrS_2$. This interpretation is justified by (i) the fact that $\epsilon_2(E)$ has a low value (~ 1.5) in this region and $\epsilon_1(E)$ crosses the zero axis from the negative side (at ~ 13.5 eV), a behavior consistent with such a plasmon and (ii) the fact that n_{eff} has a value approaching the "saturation" value of 12 valence electrons per formula unit on the high-energy side of this main plasmon (see Fig. 5).

The optical absorption spectrum of $NaCrS_2$, in Fig. 4, in the photon energy range $1.00 \rightarrow 2.4$ eV (where the charge-transfer band gap occurs) is in good agreement with the results of Blazey and Rohrer[10] who reported a direct band gap of ~ 2.298 eV for $NaCrS_2$. In our discussion of $\alpha(E)$ in Fig. 4, it is convenient to refer to the molecular orbital band scheme (proposed by Blazey and Rohrer[10]) for CrS_6 shown in Fig. 9. In this CrS_6 orbital scheme, all the orbitals are full up to and including the chromium $t_{2g}(\uparrow\uparrow\uparrow)$ orbitals and those of e_g are empty.[24] In Fig. 9, the allowed optical transitions are those from the sulfur bonding p orbitals to the e_g^0 Cr^{3+} orbitals. Such transitions would give rise to the series of shoulders we observe on the $NaCrS_2$ fundamental absorption edge between 2.00 and 4.8 eV. Below 2 eV our $\alpha(E)$ spectrum does not exhibit the $d \rightarrow d$ transitions that Blazey and Rohrer[10] have reported for $NaCrS_2$ at 5 K. This is not altogether surprising because our infrared reflectivity data were derived by use of the expression $R=[(n-1)/(n+1)]^2$ where n has been regarded as a parameter whereas Blazey and Rohrer's $\alpha(E)$ absorption data were measured experimentally. Finally, we would like to point that our KK analysis derived $\alpha(E)$ spectrum, in Fig. 4, is in excellent agreement with the optical density vs E(eV) spectrum for $NaCrS_2$ reported by Companion and Mackin.[14]

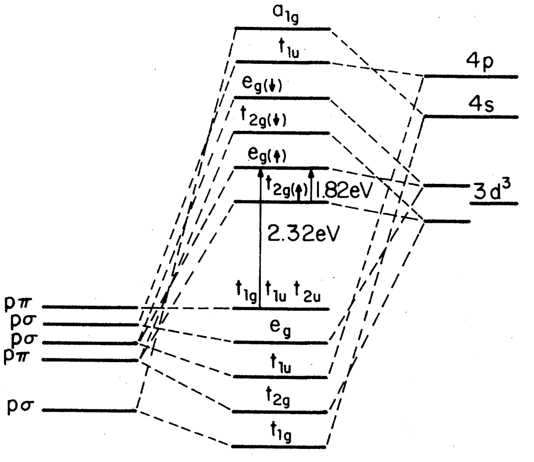

FIG. 9. Schematic molecular-orbital scheme for the CrS_6 octahedron (Ref. 10). The p orbitals originate from the sulfur atoms and the $3d$, $4s$, and $4p$ orbitals from the chromium atom. The arrows indicate the ${}^4A_2 \rightarrow {}^4T_2$ transitions at 1.82 eV and the optical gap at 2.32 eV.

IV. CONCLUDING REMARKS

A Kramers-Kronig analysis of the reflectivity data of $NaCrS_2$ measured over a wide photon energy range, and extrapolated at very low and very high photon energies, has been performed and the various optical functions pertinent to the optical study of the electronic band structure of $NaCrS_2$ have been obtained, presented, and discussed. From the $R(E)$, $\epsilon_1(E)$, $\epsilon_2(E)$, and $\alpha(E)$, it would appear that optical transitions in $NaCrS_2$ are predominantly of the *ligand-to-metal charge-transfer type,* which would explain why the $\epsilon_2(E)$ spectrum has several sharp excitonlike peaks. We believe that the d^3 shell on Cr^{3+} is perturbed and split (by the octahedral ligand field) into the t_{2g}^3 and e_g^0 localized and discrete levels *(not Bloch states)* which are situated in the $\sigma\sigma^*$ gap of $NaCrS_2$. The several excitonlike peaks on the $R(E)$ and $\alpha(E)$ (which we have attributed to charge-transfer transitions) strongly imply that there is a high degree of ionicity in $NaCrS_2$. For this reason, we suggest that the rigid-ionic model for $NaCrS_2$ which has been proposed by Khumalo and Hughes seems to be quite appropriate for this material. The ionicity of the Na–S, Cr–S, and Na–Cr bonds will be further investigated in the near future by carrying out x-ray photoemission studies on $NaCrS_2$.

ACKNOWLEDGMENTS

The Ames Laboratory is operated for the United States Department of Energy by Iowa State University under Contract No. W-7405-Eng-82. This research was supported by the Director for Energy Research, Office of Basic Energy Sciences, WPAS No. KC-02-02-02. Stimulating comments on the data were received from Professor Terakura of the Institute of Solid State Physics, Tokyo, Japan and Professor David Lynch of Ames Laboratory—the author benefitted greatly from cordial discussions with the above two colleagues. The author also extends sincerest thanks to Dr. Peter Narins of the Department of Biology, University of California at Los Angeles for his assistance on the retrieval of the reflectivity data from the computer floppy disks which had hardware errors on them.

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[20] If the CrS$_6$ octahedron *is regarded as a distorted trigonal prism* in Fig. 1, then the crystallographic structures of 2H-MoS$_2$ and NaCrS$_2$ can be viewed as being roughly similar to the optical spectra in Fig. 8. From the striking similarity of the reflectivity spectra of the two compounds, it is rather inviting to put forward the speculation that *perhaps* the electronic band structure of NaCrS$_2$ (as yet uncalculated) is similar to that of MoS$_2$ which is now known and well understood (see Ref. 19). The fact that the MoS$_2$ reflectivity spectrum was shifted by 2 eV to lower energies in order to superpose it with that of NaCrS$_2$ (in Fig. 8) implies that the MoS$_2$ conduction bands are ~ 2 eV higher with respect to the main valence band of NaCrS$_2$.

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[24] The schematic molecular orbital scheme for the CrS$_6$ octahedron proposed by Blazey and Rohrer (Ref. 10) is a *single-electron model* and thus is misleading in giving the energies of the final states which have their energies determined by many-body effects. Thus although both transitions ($^4A_2 \rightarrow {}^4T_2$ transitions at 1.82 and 2.32 eV) promote an electron into an $e_g(\uparrow)$ orbital, the final states will have different energies due to the different electron concentration on the chromium ions. Unfortunately the authors of Ref. 10 did not show this energy difference in their molecular scheme which is redrawn in Fig. 9.